THERMODYNAMICS OF SOLUTION OF HAPTE NS AND CYCLODEXTRIN-HAP TEN COMPLEXES IN AQUEOUS AND NON-AQUEOUS MEDIA

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Doctor of Philosophy
of the University of Surrey, England

By

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Abstract

Thermodynamic parameters of solution ($\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$) of some haptens [ortho-, meta-, para-, 5-chloro-2-, 6-chloro-2-, 2-chloro-4- and 4-chloro-3-(parahydroxyphenylazo) sodium benzoate] and three cyclodextrins ($\alpha$, $\beta$ and $\gamma$) were carried out in different reaction media. Thermodynamic parameters for the transfer ($\Delta G^\circ$, $\Delta H^\circ$, $\Delta S^\circ$) of haptens and their anions from water to methanol and from water to N,N'-Dimethylformamide were derived. In addition, transfer free energy, enthalpy and entropy of cyclodextrins from water to N,N'-Dimethylformamide are reported. Thermodynamic parameters of complexation between haptenic anions and cyclodextrins were investigated in water and in N,N'-Dimethylformamide and their transfer quantities from water to N,N'-Dimethylformamide are also given.

It was found that the selected haptens (anions) are better solvated in methanol than in water than in N,N'-Dimethylformamide. The transfer enthalpies of the anions (data based on the Ph$_4$AsPh$_4$B convention) from water to methanol and from water to N,N'-Dimethylformamide [$\Delta H^\circ$ (X)] are largely compensated by their transfer entropies [$\Delta S^\circ$ (X)].

As far as solution thermodynamic data of cyclodextrins in water and N,N'-Dimethylformamide are concerned, it was noticed that a compensation effect between the $\Delta H^\circ$ and $\Delta S^\circ$ values is taking place in water and in N,N'-Dimethylformamide.

Only three anions complex with $\alpha$ and $\gamma$-cyclodextrins in water, whereas four haptens form complexes with $\alpha$, $\beta$ and $\gamma$-cyclodextrin in N,N'-Dimethylformamide. Again a compensation effect for cyclodextrin-anion complexes was observed in water and in N,N'-Dimethylformamide.

A cavity size effect was shown during the formation of cyclodextrin-hapten
complexes. Anion-cyclodextrin interaction becomes weaker with an increase in the cavity of cyclodextrin.

Inclusion complexes (axial) are found to take place in water and lid-type (equatorial) complexes are found between these haptenic anions and cyclodextrins in N,N'-Dimethylformamide.

The transfer parameters for the cyclodextrin-anion complexes were calculated using a thermodynamic cycle. This is the first set of data ever reported on the transfer of cyclodextrin adducts among solvents.
Acknowledgements

My thanks and gratitude to Dr A. F. Danil de Namor for her wonderful supervision, guidance, patience and support throughout the entire period of this study.

My thanks to Hariri Foundation whose without their help and financial support this study could not have been possible. I would sincerely like to take this opportunity to express my personal appreciation to the great person who established this academic institution, Mr Rafic Hariri. His help and financial support are gratefully acknowledged.

My thanks to Mrs Rosemary Walker, Mrs Nicola Walker and Mr Paul Greenwood for their help and assistance in the laboratory work. My colleagues whom I worked with at the Chemistry department, their pleasant company is greatly appreciated.

I also wish to thank my fellows, Marie Claude Ritt, Waleed Hindi, Mawieh Oulabi, Fadi Abou-Shakra and everybody else for a pleasant stay at the University of Surrey.

Finally, special thanks to Miss Alison Rodgers and Miss Cathy Rodgers for their support and help in typing this thesis.
To My
Loving Parents
Sisters and Brothers
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CHAPTER 1
INTRODUCTION
CHAPTER 1: INTRODUCTION

1.1 Generalities

Over the years, many investigations have been performed on both naturally occurring multidentate ligands, such as porphyrins and synthetic macrocycles. For instance, research into alkaline earth and alkali-metal cation complexes of the natural and synthetic macrocyclic ligands was stimulated by the discovery in 1964 of Moore and Pressman. It was found that the macrocyclic antibiotic valinomycin (Fig 1.1), was capable of selectively complexing potassium ions and therefore, it was suggested that this antibiotic was responsible for the transport of ions across membrane. Since then various other antibiotics and synthetic compounds were studied and reported to facilitate the passage of specific ions across biological membranes by selective complex formation.

In 1967, Pedersen reported the synthesis of a series of macrocyclic ligands; the "crown ethers" (Fig 1.2). Over fifty cyclic polyethers with varying size of macrocyclic ring, number of ethether oxygens, different types of substituent groups were produced. Initial studies showed a marked selectivity of these macrocyclic compounds towards alkali and alkali earth metal cations analogous to the behaviour of certain natural antibiotics.

Prompted by the use of ionophorous antibiotics as model systems for the elucidation of biological transport mechanisms, Lehn and co-workers shortly after introduced a class of polyoxadiamine macrobicyclic compounds containing three polyether strands joined by two bridgehead nitrogens. Studies on these three-dimensional synthetic compounds were found to form very stable complexes with suitable alkaline and alkaline earth metal ions in which the cation is contained in the intramolecular cavity or "crypt". These ligands were termed cryptands (Fig 1.4-1.5) and their inclusion complexes; cryptates.
Figure 1.1. Structures of some naturally occurring antibiotics.

a) Valinomycin

b) Monensin
Figure 1.2 Structures of some crown ethers
a) 15-Crown-5
b) 18-Crown-6
c) Dibenzo-18-Crown-6
Figure 1.3 Structures of some macrocyclic cryptands

| m = n = 0 | Cryptand 111 | [111] |
| m = n, n=1 | Cryptand 211 | [211] |
| m = n, n=0 | Cryptand 221 | [221] |
| m = n = 1 | Cryptand 222 | [222] |
| m = n, n=2 | Cryptand 322 | [322] |
| m = n, n=1 | Cryptand 332 | [332] |
| m = n = 2 | Cryptand 333 | [333] |
Figure 1.4 Structures of dibenzo cryptand 222 and cryptand 22C₈
Figure 1.5. Structure of a macrotricyclic cryptand
1.2 Cation Complexation

In an attempt to link chemical behaviour with biological phenomena, an enormous amount of effort has been devoted to obtain useful information regarding some of the principles underlying cation selectivity in biological systems.

Several articles and extensive reviews dealing with various aspects of crown ethers\textsuperscript{22-25} and cryptand\textsuperscript{26-29} chemistry, as well as a number of books\textsuperscript{1,2,39-52} have been published. As a result, macrocyclic and macrobicyclic-metal ion complexes have demonstrated their application in various areas of chemistry such as in solubilisation of metal cations in different solvents, the detection of cations in solution, and the separation of cations from mixtures. They were also used in organic synthesis, phase-transfer catalysis, anionic polymerisation, photochemical energy of conversion and isomers and isotopes separations. Of particular interest, is the potential application of macrobicyclic ligands in cryptatotherapy as well as in controlling industrial and environmental pollution problems\textsuperscript{33}.

Thermodynamic, kinetic and NMR studies on macrocyclic cation complexes were also carried out in different reaction media. Hundreds of papers have appeared on the complexation of the cations in group I and II, and thousands on complexes with other cations. An interesting review on the thermodynamic and kinetic cation-macroyclic interactions was presented by Christensen and Izatt\textsuperscript{34}.

1.3 Anion Complexation

Anions, or negatively charged ions play important roles in different areas. For instance, in biology anions are necessary partners of all positive centers (ammonium, guanidium and other cations). Their functions, transfer across membranes etc... are of the same importance as cations. Enzyme substrates\textsuperscript{35}, are more often anions than cations. Details of anion occurrence within the field of biology may be found in the literature\textsuperscript{36}. 
In chemistry, anions play many roles, for example as nucleophiles, as bases, as redox agents, and in phase transfer catalysis etc. Complexation of anions can bring about changes in chemical reactivity as does cation complexation.

Due to the lack of anion complexing agents, anion complexation has received very little attention and few publications is available in the literature.

Dietrich stated the different parameters for anion complexation. Compared to metal cations, the size of anions are very large. The small anion F$^-$ (1.36Å) is about the same size as potassium K$^+$ (1.33Å). Anions, compared to cations of the same size, have larger free energy of solvation, e.g. $\Delta G_{solv}(F^-) = 434.3$ kJ.mol$^{-1}$ while $\Delta G_{solv}(K^+) = 337.2$ kJ.mol$^{-1}$. As complexation is a competition with solvation this makes anions more difficult to complex. Finally, most of the anions exist only in a limited range of the normal pH scale; for example, above pH 5-6 for the carboxylates, above pH 7 for the CO$_3$H$^-$ ion.

The ligand has to take account of all the various anions peculiarities: size, geometry and pH dependence. The largest handicap for anion complexing ligands originates directly from the fact that no acceptor displaying the required characteristics for a ligand (no major synthetic difficulties, high chemical stability) is present in the periodic table. The alternative is to use either neutral ligands (binding sites are -OH, -SH etc) or positively charged ligands. Unfortunately, the charged ligands introduce a new difficulty; they are all more or less pH dependent. In short, anion complexation with charged ligands can occur when, over a certain range of pH, the anion exists and the ligand is in its protonated form.

The work presented in this thesis is related to the thermodynamics of anion-macrocyclic complexes in different reaction media. The selected ligands are α, β and γ-cyclodextrin. Therefore, a review of the literature on thermodynamics of anion-macrocyclic ligands and the chemistry of cyclodextrin would be relevant.
1.4 Cyclodextrins
1.4.1 Source and Nomenclature

Cyclodextrins or cycloamyloses are a homologous series of oligosaccharides produced by the action of Bacillus macerans amylase on starch.

Cyclodextrins were first isolated in 1891 by Villiers as degradation products of starch\(^9\) and they were characterised as oligosaccharides in 1904 by Schardinger\(^{40,41}\). It is for this reason that cyclodextrins (cycloamyloses) are described by some authors, especially in the older literature, as Schardinger dextrins.

Although, in retrospect, credit for the discovery of cyclodextrins must be given to Villiers, Franz Schardinger\(^{40,41}\) was the first to describe their preparation, isolation and properties in detail. The techniques developed by Schardinger have been extended and improved by French\(^9\), to whom much of our knowledge of the cyclodextrins can be attributed.

As the name implies, cyclodextrins are macrocyclic polymers of glucose (Fig 1.6). They contain a minimum of six D(+) glucopyranose units attached by \(\alpha\)-(1,4) linkages. Freudenberg et al.\(^43\) reported that cyclodextrins are constructed from \(\alpha\)(1,4)-linked glucose units. Although cyclodextrins containing as many as twelve glucose units have been identified\(^44,45\), only the first three members of the series have been studied in detail. These are designated as cyclohexaamylose (\(\alpha\)-cyclodextrin), cycloheptaamylose (\(\beta\)-cyclodextrin) and cyclooctaamylose (\(\gamma\)-cyclodextrin). They contain six, seven and eight glucose units, respectively. Unlike their straight chain analogs, the cyclodextrins have neither a reducing nor a non-reducing end-group. They are stable in alkaline medium and are somewhat resistant to acidic hydrolysis as well as to hydrolysis by \(\alpha\)- and \(\beta\)-amylase.
1.4.2 Structure

In 1965, Hybl et al. established the structure and stereochemistry of α-cyclodextrin from X-ray crystallographic studies. Hamilton et al. and Takeo and Kuge suggested that β and γ-cyclodextrin share the same structural features derived for α-cyclodextrin. Thus, cyclodextrins are doughnut-shaped molecules with all glucose units in substantially undistorted C1(D) (chair) conformations. As a result of this arrangement, the interior of the cavity (the hole of the doughnut) is lined by the glucosidic oxygen atoms, each of which is surrounded by four C-H groups (carbon 3 and 5 of each glucose group residue, Figure 1.6)

![Figure 1.6. Schematic diagram of two glucopyranose units of a cyclodextrin molecule illustrating details of the (1,4) glucosidic linkage and the numbering system employed to describe the glycopyranose rings.](image-url)

The open ends of the cavity are surrounded on one side by the primary hydroxyl groups situated at carbon 6 of the glucose rings, and on the other by the secondary hydroxyl groups of carbons 2 and 3. These secondary hydroxyl groups are related by means of hydrogen bonds involving the C-3 hydroxyl of one glucose residue and the C-2 oxygen of an adjacent residue. Details of this structural arrangement are presented schematically in Figure 1.6 and overall structure features are illustrated by the space-filling molecular models in Figures 1.7-1.9. Other properties of cyclodextrins, including dimensions of the cavities are listed in Table 1.1.
Table 1.1 Physical Properties of the Cyclodextrins

<table>
<thead>
<tr>
<th>Cyclodextrin</th>
<th>Number of glucose residue</th>
<th>Cavity Dimensions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diameter (Å)</td>
<td>Depth (Å)</td>
<td></td>
</tr>
<tr>
<td>α-cyclodextrin</td>
<td>6</td>
<td>4.5</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>β-cyclodextrin</td>
<td>7</td>
<td>7.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>γ-cyclodextrin</td>
<td>8</td>
<td>8.5</td>
<td>7.0</td>
<td></td>
</tr>
</tbody>
</table>

* From X-ray analysis, James et al.51

b Estimated from Courtaud molecular models, Thoma and Stewart52.

It has been suggested 53-59 that, because of the conformational restraints imposed on the cyclodextrins by their looped arrangement, the structural features derived for the crystalline state will be retained in solution. This has been confirmed53-59 by means of a variety of spectroscopic techniques. Nuclear magnetic resonance53-59 and optical rotatory dispersion studies60,61, for example, have conclusively demonstrated that all of the D-glucopyranose rings exist in C1 conformations in dimethyl sulfoxide as well as in deuterium oxide solution.
Figure 1.7 Molecular model of α-cyclodextrin as obtained by a molecular graphics computer package (COSMIC).

Figure 1.8 Molecular model of β-cyclodextrin as obtained by a molecular graphics computer package (COSMIC).
Figure 1.9 Molecular model of γ-cyclodextrin as obtained by a molecular graphics computer package (COSMIC).
Nuclear magnetic resonance and infrared spectra of the cyclodextrins in aprotic solvents such as dimethyl sulfoxide indicate that intramolecular hydrogen bonds are present in solution. The fact that they are retained in dimethyl sulfoxide, a solvent which usually competes effectively for intramolecular hydrogen bonds, suggests that these intramolecular bonds are strong in cyclodextrins aqueous solution and therefore, these bonds are retained in water. Figures 1.10-1.13 show schematic molecular structures of α and β-cyclodextrin crystalline and in solution with three centre of hydrogen bonds.

Figure 1.10 β-cyclodextrin, crystal, 120K. Schematic drawing of the crystal and solution structures of cyclodextrins with their three-center hydrogen bonds. Major(-) and minor(...) components are indicated, the arrows point from donor to acceptor atoms. OW denote water molecules.
Figure 1.11 β-cyclodextrin, crystal, 293K. For details see Figure 1.10 legend.

Figure 1.12 α-cyclodextrin, crystal, 293K. For details see Figure 1.10 legend.
Figure 1.13 α-cyclodextrin, crystal, 293K. For details see Figure 1.10 legend.
1.4.3 Synthesis of Cyclodextrins

Cyclodextrins can be obtained by enzymatic degradation of starch, a linear polysaccharide consisting of α-(1,4)-linked glucose units arranged into a left-threaded screw with six glucose units per turn. The amylase known as cyclodextrin glucosyl transferases can detach a turn from the starch helix and link the two ends of this fragment to give a cyclic molecule. There are many organisms which contain glycosyl transferase, but only those enzymes from Bacillus macerans, Bacillus megaterium, an alkaline Bacillus and Bacillus stereothermophilus have been examined. All of these glycosyl transferases act according to eqn. 1.1

\[
G_n \rightarrow G_{n+1} + \text{Cyclodextrin} \quad 1.1
\]

and can therefore be utilised for synthesizing interesting new oligo- and polysaccharides (G = glucose unit).

As the resulting enzymes never detach entirely specific lengths, the resulting cyclodextrins contain 6-12 glucose units per rings. However, the main fractions contain α, β and γ-cyclodextrin (with 6, 7 or 8 glucose units respectively). The relative quantities of these three groups depend on the type of enzyme employed and can be influenced by the addition of organic compounds.

1.4.4 Solubility of Cyclodextrins

Solubility data of α, β and γ-cyclodextrins in water and in a large number of non-aqueous solvents were reported by French et al. These data were obtained by measuring the specific rotation of the dextrin in the saturated solution in question. Table 1.2 contains the solubility data of cyclodextrins in different reaction media. The data refers to the room temperature (≈27°C).
Table 1.2 Solubility of Cyclodextrins in Different Solvents at Room Temperature\(^\circ\) (\(=27^\circ\)C)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\alpha)-CD (\text{g/100ml})</th>
<th>(\beta)-CD (\text{g/100ml})</th>
<th>(\gamma)-CD (\text{g/100ml})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>14.5</td>
<td>1.85</td>
<td>23.2</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral oil</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.15</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Decaline</td>
<td>0.08</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.90</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.90</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.90</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>3.30</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>p-Cymene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylidide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.80</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitromethane</td>
<td>over 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>0.08</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Ethylene Dichloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene Dibromide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.26</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>0.08</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td></td>
<td>0.70</td>
<td>0.004</td>
</tr>
<tr>
<td>Tetrabromothane</td>
<td>0.10</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Isomylidide</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>2.40</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>p-Chlorotoluene</td>
<td>0.02</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>o-Bromotoluene</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>p-Dichlorobenzene</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Bromonaphthalene</td>
<td></td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Benzyl Chloride</td>
<td>over 1</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>over 1</td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>Aniline</td>
<td>over 0.3</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Azobenzene</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butanol</td>
<td>over 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>over 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzyl alcohols</td>
<td>over 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>over 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\beta)-phenylethanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thymol</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It can be seen from the solubility data of cyclodextrins listed in Table 1.2 that, cyclodextrins are much more soluble in water than in non-aqueous solvents. Therefore, this may limit the determination of thermodynamic data of cyclodextrin-substrate complexes in these non-aqueous media.
1.4.5 Inclusion Complexes

The most interesting characteristic of the cyclodextrins is their ability to complex a variety of guest molecules in their cavities. This guest-host type of complexation is called "inclusion complexation". However, another type of complexation between organic molecules and cyclodextrins may exist, especially in non aqueous media\textsuperscript{64,65}.

Complex formation between cyclodextrins and their guest molecules has been the subject of a comprehensive literature. The number of publications dealing with cyclodextrin inclusion compounds alone amounts to more than 600. A great deal of interest has been shown in this phenomenon due to the fact that two components associate with each other without any specific interactions taking place and because parallels can be drawn with many biochemical processes. However, the ability of cyclodextrins to form insoluble crystalline complexes with relatively simple alcohols was recognised by Villiers\textsuperscript{39} and Schardinger\textsuperscript{64}. Also, Freudenberg et al. recognised that cyclodextrins could form inclusion compounds\textsuperscript{67}.

1.4.5.1 Thermodynamics and Kinetics of the Inclusion Process

The formation of a complex between cyclodextrin (CD) and guest (substrate, S) components may be described according to:

\[
\text{CD} + \text{S} \rightarrow \text{CDS} \quad 1.2
\]

The thermodynamic complexation constant of the process, \(K_e\), for 1:1 adduct formation may be defined as:

\[
K_e = \frac{a_{\text{CDS}}}{a_{\text{CD}}a_s} \quad 1.3
\]

Depending on the nature of the substrate, \(K_e\) can be determined by different
techniques. Among these are the spectroscopic, kinetic, potentiometric and calorimetric techniques. The most common studies are those which exploit light absorption; $K_c$ is obtained by plotting the absorption change of the substrate (at a constant wavelength) against the cyclodextrin concentration.

The kinetic technique involves the determination of the rate constants $\kappa_0$ for dissociation and $\kappa_\alpha$ for recombination of the cyclodextrin substrate complex. Thus, $K_c$ is given as:

$$K_c = \frac{\kappa_\alpha}{\kappa_0}$$

$K_0$ and $\kappa_\alpha$ can be obtained using the relaxation and mixing techniques.

The thermodynamic parameters enthalpy ($\Delta H^\circ_c$) and entropy ($\Delta S^\circ_c$) can be obtained from the temperature dependence of the complexation constant. However, better thermodynamic data can be obtained from direct calorimetric measurements.

Cramer, Saenger and Spatz, investigated the thermodynamics and kinetics for the interaction process which involves $\alpha$-cyclodextrin, nitrophenol and a series of azo-dyes. Measurements were carried out in aqueous solution using a spectrophotometric titration technique. The rate of recombination of the bimolecular reaction and the enthalpy of complexation ($\Delta H^\circ_c$) were reported. $\Delta H^\circ_c$ was derived from the complexation constant measured at different temperatures. It was found that $\alpha$-cyclodextrin forms 1:1 adduct with both, nitrophenol and the azo-dyes. The substitution of the dyes in the 4' and 3' positions has little influence on the equilibrium constant while the rate of the reaction is changed by seven orders of magnitude. Upon these results, it was suggested that the dyes are enclosed inside the cyclodextrin cavity.

Bender et al. reported complexation constants of complexes formed between $\alpha$, $\beta$ and $\gamma$-cyclodextrin and meta substituted phenyl acetates. The complexation
constants were determined by kinetic and spectrophotometric methods. Enthalpy of complexation was derived from measurements of complexation constants at temperatures between 15 and 55°C using the relationship:

\[ \frac{d[\ln(K)]}{d(1/T)} = -\frac{\Delta H^\circ}{R} \]

A remarkable stereoselective acceleration of the phenol release from substituted phenyl acetates in alkaline solutions was observed. Both, \( \alpha \) and \( \beta \)-cyclodextrin cause large, nonuniform effects. The rate of phenol release is greatly enhanced. The rate effects due to \( \gamma \)-cyclodextrin are also large but are much less stereoselective.

In another study, Bender et al.\textsuperscript{73}, investigated spectrophotometrically the release of phenol molecules from a number of phenyl benzoates in alkaline solution and in the presence of \( \alpha \) and \( \beta \)-cyclodextrin. The release of the \textit{meta}-substituted phenolic portion of the ester is considerably accelerated in the presence of 0.01 M cyclodextrin relative to the rate of alkaline hydrolysis at the same pH. Most importantly, a significant change in the overall reaction pathway in the presence of cyclodextrins was observed. The release of phenol occurs very rapidly, reaching completion in 30 seconds. It was concluded that, the large accelerations in the cleavage of \textit{meta}-substituted phenyl ester in alkaline solution are the result of a nucleophilic reaction of an alkoxide ion derived from either the C-2 or C-3 secondary hydroxyl groups of the cyclodextrins.

Calorimetric studies\textsuperscript{71} were carried out to determine the heat of complexation of cyclodextrins (\( \alpha \), \( \beta \) and \( \gamma \)) with triiodide ions and p-nitrophenolate anion in aqueous solution. It was found that the enthalpy of complexing (\( \Delta H^\circ \)) for each \( \alpha \), \( \beta \) and \( \gamma \)-cyclodextrin with the same guest molecule strikingly decreases with increasing cavity diameter of the cyclodextrins. Therefore, a definite size effect was observed, as the smaller the cavity size the more stable the complex.
A spectrophotometric study using circular dichroism for the above mentioned systems (iodine, triiodide, p-nitrophenolate and α, β and γ-cyclodextrin) has shown that the absorption spectra of I₂ solution shifted towards shorter wavelengths in the presence of cyclodextrins, indicating the binding of iodine with the cyclodextrins. The extent of the spectral shift decreased with increasing size of the cavity of the cyclodextrins. The largest shift was obtained with α-cyclodextrin and the smallest shift with γ-cyclodextrin. These results suggested that the binding between the guest molecule and α-cyclodextrin is stronger than that of β-cyclodextrin. The same phenomenon was observed for I₃⁻ and p-nitrophenolate anions.

In 1971, van Hooidonk and Breebaart-Hansen studied the kinetics and the thermodynamics of the alkaline hydrolysis reaction of diisopropyl phosphoro fluoride with α-cyclodextrin in aqueous alkaline medium. The temperature-dependency of the reaction rate, the complexation constant at various temperatures and the corresponding change in enthalpy and entropy were reported. It was suggested that polar interactions play a major role in the formation of an inclusion complex between the organophosphorus compound and the cyclodextrin. The inclusion is associated with a sizable enthalpy change (-30.54 kJ.mol⁻¹) and an unfavourable loss of entropy (-87.9 J.mol⁻¹K⁻¹). The enthalpy change was derived from measurements of the complexation constant at various temperatures using the van't Hoff isochore equation (eqn. 1.5).

Decarboxylation rate constants in aqueous solution were determined for ortho, meta and para substituted phenylcyanoacetate, 2-phenyl-2-cyanopropionate, and 6-nitrobenzisoxazole-3-carboxylate anions in the presence of β-cyclodextrin. Similar studies for para substituted phenylcyanoacetate anions were determined in methanol. In addition, 4-chlorophenylcyanoacetate decarboxylation was examined in methanol, 2-propanol, dioxane and aqueous 2-propanol. Decarboxylations of benzoylecetic acids in water were also carried out. The decarboxylation process of these compounds was followed spectrophotometrically by monitoring the decrease in
absorption as the reaction proceeded. It was stated that\textsuperscript{55}, β-cyclodextrin accelerated the decarboxylation rates of all the anions examined. In addition, it was concluded that the catalysis of decarboxylation by β-cyclodextrin is solely a result of a milieu change occurring on complex formation i.e., the micro-solvent effect and hydrogen bonding between β-cyclodextrin and the substrate was eliminated as a major contribution to complex stability and therefore, an inclusion complex was assumed to have taken place.

The thermodynamics of binding of guest molecules to α- and β-cyclodextrin were examined by Lewis and Hansen\textsuperscript{37} using titration calorimetry. These authors reported the thermodynamic parameters of complexing (ΔG°, ΔH°, and ΔS°) of cyclodextrins with several ions. It was found that:

a) the cyclodextrin-ClO\textsubscript{4}\textsuperscript{-} complex was able to bind cations.
b) α and β-cyclodextrin have similar equilibrium constants for binding the same guest molecule but, the enthalpy and entropy changes are quite different.
c) changes in ΔH° are largely compensated for by changes in ΔS°. It was suggested that this effect was due principally to the nature of the solvent, i.e. water.

Inclusion complexation of cinnamic acids\textsuperscript{59} and its derivatives with α and β-cyclodextrin in aqueous solution was studied by circular dichroism, ultra violet and nuclear magnetic resonance spectroscopies. 1:1 adducts were found in all cases. Complexation constants and thermodynamic parameters were also determined. The evidence obtained from the induced circular dichroism and NMR chemical shift led the authors to propose that phenyl moiety of cinnamic acid was fixed within the cavity of cyclodextrin.

Bender and Komiyama\textsuperscript{79} reported the importance of apolar binding in complex formation of cyclodextrins. As a result of their studies on the complexation of 1-adamantane carboxylate with α and β-cyclodextrin in water, enthalpy changes
were derived from the complexation constants.

The complexation of \( \alpha \)-cyclodextrin with 1-adamantane carboxylate exhibited a quite favourable \( \Delta S^\circ \), but only a small favourable \( \Delta H^\circ \); this is in contrast to a large favourable \( \Delta H^\circ \) reported for many inclusion complexes of cyclodextrins. The authors attributed the large favourable entropy (\( \Delta S^\circ > 70\% \) of the total stabilisation energy) to a transfer of the guest molecule from aqueous medium to more apolar medium such as the cavity of cyclodextrin. This transfer requires breakdown of structural water molecules around 1-adamantane carboxylate which results in a large favourable \( \Delta S^\circ \) and a small unfavourable \( \Delta H^\circ \). However, the complexation with \( \beta \)-cyclodextrin showed an opposite pattern to that observed with \( \alpha \)-cyclodextrin (large favourable \( \Delta H^\circ \) and a small unfavourable \( \Delta S^\circ \)). This was attributed to the deeper inclusion of the guest species accompanied by a loss of rotational freedom. The authors supported their arguments with similar results observed in the process of complexation of benzoic acid with \( \alpha \) and \( \beta \)-cyclodextrins in water.

Stability constants\(^{80}\) for complex formation between \( \alpha \)-cyclodextrin and some ortho- and para disubstituted benzenes were determined in aqueous solution by potentiometric, spectrophotometric, competitive spectrophotometric and solubility measurements in aqueous solution at 298.15 K. All systems were found to form 1:1 complexes, some para substrates form 1:2 complexes, but meta substrates do not form 1:2 complexes. Other substrates form weak complexes. Also, it was reported that the stability constants for meta and para disubstituted benzene were approximately equal. Predictions of stability constants for these systems from eqn. 1.6 were in good agreement with the experimental values.

\[
\log K = -0.636 \log S_\theta - 0.231 \mu + 0.524 \tag{1.6}
\]

where \( S_\theta \) and \( \mu \) are the solubility and polarity of the substrate; respectively. It was observed that an increase in the solubility leads to a decrease in the stability of the complex.
A compensation effect between $\Delta H^\circ$ and $\Delta S^\circ$, values for the 1:1 inclusion complexes of alcohols and cyclodextrins in water as observed by Takagi et al.\textsuperscript{91}. The enthalpy data were determined from direct microcalorimetric measurements. The data showed the enhancement of entropy as the main "driving force" of the inclusion of the alcohol molecules in these aqueous solutions. The two different enthalpy-entropy compensation effects observed were attributed to:

a) the formation of strong (stable) complexes ($\Delta G^\circ < -22$ kJ.mol\textsuperscript{-1}) and,

b) the formation of weak (less stable) complexes ($\Delta G^\circ > -20$ kJ.mol\textsuperscript{-1}).

The isoequilibrium temperatures (slope of $\Delta H^\circ$ vs $\Delta S^\circ$ plot) were (a) 339K and (b) 292K respectively. These results were explained in terms of hydrophobic hydration in the molecular inclusion phenomena.

Apparent complexation constants ($K_{pp}$)\textsuperscript{92} for $\beta$-cyclodextrin azo-dye (sodium $p$-(4-hydroxy-1-naphtylazo) benzene sulfonate) in water was determined by spectrophotometry in a phosphate buffer (pH 5.91) in the absence and in the presence of various inorganic salts. It was found that the azo-dye forms a 1:1 complex with a $K_{pp} = 410$ M in a 0.1 M phosphate buffer. $K_{pp}$ increases with an increase in the concentration of the phosphate buffer and with the addition of some inorganic salts ($\text{Li}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4$, $\text{K}_2\text{SO}_4$, $\text{LiIO}_3$, $\text{NaIO}_3$, $\text{KIO}_3$ and $\text{KF}$). These results were explained mainly in terms of the decrease in the activity of water, as a result of the formation of an inclusion complex, with an increase in the concentration of the inorganic salts. On the other hand, $K_{pp}$ decreases with the addition of salts such as $\text{KCl}$, $\text{KBr}$, $\text{KI}$, $\text{KNO}_3$, $\text{KSCN}$ and $\text{KClO}_4$. These results were attributed mainly to the formation of inclusion complexes of the cyclodextrins with the anions of these salts. These anions are assumed to compete with the azo-dye for the cyclodextrin binding site.

Formation of inclusion complexation between various barbituric and thiobarbituric acid derivatives with $\beta$-cyclodextrin\textsuperscript{83} in aqueous solution was studied
by UV, circular dichroism and nuclear magnetic resonance spectroscopies. The stability constants of these complexes at various pH were determined by UV methods. Enthalpy changes were calculated from stability constant data at various temperatures. It was stated that the induced circular dichroism observed for barbituric acids were substantially different from those for thiobarbituric acids. Chemical shift changes, $^1$H- and $^{13}$C-NMR spectra led the authors to suggest that not only meta-substituent but also heterocyclic moiety of barbiturate participated in inclusion complex formation. A compensation effect between $\Delta H^\circ$ and $\Delta S^\circ$ was observed. The isoequilibrium temperature was found to be 372K. From the thermodynamic data (favourable enthalpy $\Delta H^\circ < 0$ and unfavourable entropy $\Delta S^\circ < 0$) it was concluded that an inclusion complexation phenomenon is taking place and that hydrophobic interaction is not predominant for the inclusion of barbiturate ions in the $\beta$-cyclodextrin's cavity. The authors suggest that intermolecular forces such as hydrogen bonding and dipole-dipole interactions should be considered.

In a following publication, the potentiometric titration method was applied to determine the equilibrium constants of $\beta$-cyclodextrin-barbiturate complexes in water. The results obtained were in fair agreement with those obtained by UV, circular dichroism and solubility studies. The titration was carried out at various temperatures from which the thermodynamic parameters were derived.

Table 1.3-1.4 contain thermodynamic and kinetic data for cyclodextrin complexes in aqueous solution at 298.15 K.
Table 1.3 Thermodynamic Parameters of Some Cyclodextrin Inclusion Compounds in Aqueous Medium at 298.15K.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>K_a</th>
<th>ΔG°, kJ.mol⁻¹</th>
<th>ΔH°, kJ.mol⁻¹</th>
<th>ΔS°, J.mol⁻¹.K⁻¹</th>
<th>Method</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Nitrophenol(C₆)</td>
<td>385</td>
<td>-14.2</td>
<td>-17.6</td>
<td>-11.7</td>
<td>Sp</td>
<td>73</td>
</tr>
<tr>
<td>p-Nitrophenol(B₃)</td>
<td>1000</td>
<td>-17.7</td>
<td>-4.9</td>
<td>-87.9</td>
<td>Ca</td>
<td>73</td>
</tr>
<tr>
<td>p-Nitrophenol(C₆)</td>
<td>3720</td>
<td>-19.7</td>
<td>-30.1</td>
<td>-56.4</td>
<td>Sp</td>
<td>76</td>
</tr>
<tr>
<td>Perchloric acid(C₆)</td>
<td>2381</td>
<td>-19.2</td>
<td>-37.8</td>
<td>-42.6</td>
<td>Ca</td>
<td>82</td>
</tr>
<tr>
<td>Perchloric acid(B₃)</td>
<td>123</td>
<td>-12.1</td>
<td>-30.5</td>
<td>-62.8</td>
<td>Ca</td>
<td>82</td>
</tr>
<tr>
<td>Sodium perchlorate(C₆)</td>
<td>700</td>
<td>-17.2</td>
<td>-40.2</td>
<td>-75.3</td>
<td>Ca</td>
<td>82</td>
</tr>
<tr>
<td>Sodium perchlorate(B₃)</td>
<td>155</td>
<td>-12.1</td>
<td>-31.8</td>
<td>-66.9</td>
<td>Ca</td>
<td>82</td>
</tr>
<tr>
<td>Benzoic acid(C₆)</td>
<td>375</td>
<td>-15.9</td>
<td>-46.5</td>
<td>-108.8</td>
<td>Ca</td>
<td>82</td>
</tr>
<tr>
<td>Benzoic acid(B₃)</td>
<td>102</td>
<td>-28.5</td>
<td>-1.3</td>
<td>87.9</td>
<td>Ca</td>
<td>82</td>
</tr>
<tr>
<td>4-Aminobenzoic acid(C₆)</td>
<td>102</td>
<td>-11.3</td>
<td>-23.8</td>
<td>-56.0</td>
<td>Ki</td>
<td>81</td>
</tr>
<tr>
<td>4-Aminobenzoic acid(B₃)</td>
<td>1205</td>
<td>-17.6</td>
<td>-5.0</td>
<td>41.8</td>
<td>Sp</td>
<td>84</td>
</tr>
<tr>
<td>Dimethylphosphoroacetate(C₆)</td>
<td>256</td>
<td>-14.2</td>
<td>-4.2</td>
<td>33.5</td>
<td>Ki</td>
<td>75</td>
</tr>
<tr>
<td>m-Chlorobenzyl acetate(B₃)</td>
<td>475</td>
<td>-13.1</td>
<td>-19.2</td>
<td>-12.6</td>
<td>Ki</td>
<td>75</td>
</tr>
<tr>
<td>m-Fluorobenzyl acetate(B₃)</td>
<td>100</td>
<td>-11.3</td>
<td>-23.8</td>
<td>-56.0</td>
<td>Ki</td>
<td>81</td>
</tr>
<tr>
<td>1-Adamantane carboxylate(C₆)</td>
<td>1205</td>
<td>-17.6</td>
<td>-5.0</td>
<td>41.8</td>
<td>Sp</td>
<td>84</td>
</tr>
<tr>
<td>1-Adamantane carboxylate(B₃)</td>
<td>2000</td>
<td>-19.6</td>
<td>-19.7</td>
<td>-4.0</td>
<td>Sp</td>
<td>84</td>
</tr>
<tr>
<td>3,4,5 trimethoxybenzyl carboxylic acid(C₆)</td>
<td>159</td>
<td>-13.0</td>
<td>-10.5</td>
<td>-8.0</td>
<td>Ki</td>
<td>75</td>
</tr>
<tr>
<td>p-Methylbenzyl carboxylic acid(C₆)</td>
<td>535</td>
<td>-15.5</td>
<td>-27.6</td>
<td>-41.0</td>
<td>Ki</td>
<td>81</td>
</tr>
<tr>
<td>m-Chlorobenzyl carboxylic acid(C₆)</td>
<td>515</td>
<td>-14.2</td>
<td>-21.8</td>
<td>25.0</td>
<td>Ki</td>
<td>81</td>
</tr>
</tbody>
</table>

[a] Sp, Ca, Ki: signify spectroscopic, calorimetric and kinetic methods respectively. [b] At 14°C. [c] At 50°C.
Table 1.4 Thermodynamic and Kinetic Parameters for the Formation of Complexes between α-Cyclodextrin and p-Nitrophenol, p-Nitrophenolate or Azo Dyes of 4-(4-hydroxyphenylazo)-1-naphtalenesulfonate type according to Cramer et al.:

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_c$</th>
<th>$\Delta H^o_c$</th>
<th>$\kappa_R$</th>
<th>$\kappa_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2\text{N C}_6\text{H}_5\text{OH}$</td>
<td>385</td>
<td>-17.6</td>
<td>$&gt;4\times10^7$</td>
<td>$&gt;10^6$</td>
</tr>
<tr>
<td>$\text{O}_2\text{N C}_6\text{H}_5\text{O}^-$</td>
<td>3704</td>
<td>-30.1</td>
<td>$1.4\times10^6$</td>
<td>$3.1\times10^4$</td>
</tr>
<tr>
<td>$R^1$</td>
<td>$R^2$</td>
<td>$R^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}$</td>
<td>$\text{H}$</td>
<td>$\text{H}$</td>
<td>270</td>
<td>-29.3</td>
</tr>
<tr>
<td>$\text{H}$</td>
<td>-</td>
<td>$\text{H}$</td>
<td>645</td>
<td>-26.4</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>-</td>
<td>$\text{H}$</td>
<td>476</td>
<td>-24.3</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5$</td>
<td>-</td>
<td>$\text{H}$</td>
<td>286</td>
<td>-32.2</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>-</td>
<td>$\text{CH}_3$</td>
<td>no inclusion</td>
<td></td>
</tr>
</tbody>
</table>

The $K_c$ values for most of cyclodextrin inclusion complexes lie close to $10^3$ and are characteristic of weak intermolecular interactions. According to the authors, inclusion does not seem to depend primarily on the character of the guest, since no obvious correlation between the chemical properties (functional groups) of the guest molecules and the complexation constants was found.

In addition, cyclodextrins were found to complex with small molecules such as, $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$, $\text{SCN}^-$, $\text{NO}_2^-$ and $\text{ClO}_4^-$. Thermodynamic and kinetic data for the formation of complexes between $\beta$-cyclodextrin and several anions are listed in Table 1.5. Data are taken from the literature.
Table 1.5 Thermodynamic and Kinetic Parameters for the Formation of Complexes between β-Cyclodextrin and Several Anions.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_a$</th>
<th>$k_r$</th>
<th>$k_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>2.56</td>
<td>5.4x10⁷</td>
<td>2.1x10⁷</td>
</tr>
<tr>
<td>Br⁻</td>
<td>6.66</td>
<td>4.5x10⁷</td>
<td>6.9x10⁶</td>
</tr>
<tr>
<td>I⁻</td>
<td>18.18</td>
<td>6.5x10⁷</td>
<td>3.6x10⁶</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>10.00</td>
<td>4.4x10⁷</td>
<td>4.4x10⁶</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>5.55</td>
<td>4.5x10⁷</td>
<td>8.2x10⁵</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>27.03</td>
<td>2.0x10⁹</td>
<td>7.4x10⁷</td>
</tr>
</tbody>
</table>

It was concluded that the substrate molecules (Table 1.5) were so small as to cause no steric hindrance, and these complexes were therefore, formed more quickly than those of the azo dyes (Table 1.4).

1.4.5.2 Structure of the Cyclodextrin Inclusion Compounds

An interesting review involving the structure of cyclodextrin inclusion compounds has been given by Saenger.

The cyclodextrin molecules (empty molecules) and their adducts (inclusion complexes) have been crystallised from water and examined by X-ray crystallography. Depending on the size and ionic or molecular character of the substrate, "channel" or "cage" structures are formed in which the cyclodextrin molecules are stacked like coins in a roll or arranged in a herring-bone pattern.

α-Cyclodextrin complexes have been investigated in water, methanol and polyiodide. Figures 1.14-1.15 show results from X-ray structure analysis of "cage" and "channel" structures of α-cyclodextrin complexes. α-Cyclodextrin complexes
with iodine\textsuperscript{96}, krypton\textsuperscript{91}, n-propanol\textsuperscript{92}, p-iodoaniline\textsuperscript{93,94}, dimethyl sulfoxide and methanol\textsuperscript{95}, m-nitrophenol\textsuperscript{96}, methyl orange\textsuperscript{97} and potassium acetate\textsuperscript{98} have also been analysed.

In the case of β-cyclodextrin, the crystal structures of its inclusion complexes with water\textsuperscript{99}, n-propanol\textsuperscript{100}, p-iodophenol\textsuperscript{100}, 2,5 diiodobenzoic acid\textsuperscript{101} and p-nitroacetanilide\textsuperscript{102} have also been reported.

The structures of γ-cyclodextrin inclusion complexes with propanol/water\textsuperscript{103} and water\textsuperscript{104} have also been described.

Crystal structure analyses of the α, β and γ-cyclodextrin complexes revealed that\textsuperscript{85} the cyclodextrins always have a "round", slightly conical form whose narrower opening contains the O(6)H groups whereas the wider opening is occupied by the O(2)H and O(3)H groups. The glucose units always have a C1-chair conformation, the C(6)-O(6) bonds are preferentially directed away from the center of the ring (torsion angle O(5)-C(5)-C(6)-O(6) is (−)-gauche); these bonds can, however, turn "inwards" (torsion angle O(5)-C(5)-C(6)-O(6) (+)-gauche) after formation of hydrogen bonds between the O(6)H group and the guest molecule.
Figure 1.14. X-ray structure analyses of cage structures a) \(\alpha\)-cyclodextrin.6H\(_2\)O
b) \(\alpha\)-cyclodextrin.CH\(_3\)OH.4H\(_2\)O
Figure 1.15. A simplified side view of the channel structure of the complex (α-cyclodextrin)$_2$.LiI$_2.8$H$_2$O. ◊ = C, ◊ = O, ◆ = I and ◇ = disordered iodine.
The structure of α-cyclodextrin.6H₂O (Figure 1.14a) is unusual\textsuperscript{85}; when α-cyclodextrin is complexed with included methanol, krypton and n-propanol, the guest molecules are statistically disordered and occupy several positions; (empty) α-cyclodextrin has a "round" with a ring of hydrogen bonds between the O(2)H and O(3)H groups. When water is the guest molecule, however, α-cyclodextrin is somewhat collapsed; two of the O(3)H...O(2) bridges are opened and one glucose unit is rotated inwards to allow formation of a O(6)...H₂O hydrogen bonds. This rotation causes steric strain within the macrocycle\textsuperscript{87}; the α-cyclodextrin in this complex has a higher energy than in all other complexes.

NMR studies have revealed that in aqueous solution, aromatic guest molecules such as p-iodoaniline and p-nitrophenol interact with the H atoms at C(3) and C(5) inside the cyclodextrin\textsuperscript{105-107} to form a complex which has a structure similar to that found in the crystalline state\textsuperscript{93,94,95}. Nitrophenol enters the cavity from the O(2), O(3) side with its nitro group, this molecule can penetrate further into the cavity of β-cyclodextrin than into the cavity of α-cyclodextrin and is more strongly bonded by α-cyclodextrin.

It has been deduced from \(^2\)H and \(^13\)C-NMR data obtained with deuterated cinnamic acid derivatives that the mobility of the substrate within the complex is greater than that of the cyclodextrin and that the interaction between guest and host is only weak\textsuperscript{108}.

Inclusion complexes between electroactive molecules (acetophenone) and β-cyclodextrin were investigated in water and N,N’-Dimethylformamide using X-rays and \(^1\)H-NMR\textsuperscript{109}. It was found that inclusion complexation is important in water and becomes poor in N,N’-Dimethylformamide.

Lehn and Behr\textsuperscript{108} carried out a study on α-cyclodextrin with p-methylcinnamate, m-methylcinnamate and p-tert-butylphenate anions in water using \(^2\)H and \(^13\)C nuclear relaxation. The results show that, upon inclusion, the
reorientation times of the substrate increase by a factor of ca. 4, whereas for α-cyclodextrin the increase in overall tumbling motion depends on the substrate. The internal methyl group rotation of the substrates are hindered, showing that they are located inside or at least in contact with the macrocycle. Also, it was suggested that, a molecular complex should not be described only by its thermodynamic stability, its formation and dissociation kinetics, but also by its dynamic rigidity, defined by the coupling between the molecular motion of the two (or more) entities of which it is composed.

Kobayashi, using UV absorption, induced circular dichroism and NMR spectroscopy, investigated the complex formation between p-dimethyl aminobenzoic acid and 2,6-dimethyl-β-cyclodextrin in water and in chloroform. It was proposed that, an axial inclusion complex is taking place in water, and an equatorial or lid-type supramolecular complex in chloroform.

1.4.5.3 The Driving Force for Complex Formation

According to Cramer et al., complex formation can take place into several steps:

1) Approach of the substrate and cyclodextrin.
2) Elimination of water molecules from the cyclodextrin cavity and the immediate vicinity of the hydroxyphenyl group.
3) Assimilation of these water molecules by the surrounding water (gain in entropy).
4) Interaction of cyclodextrin and the substrate as a result of van der Waals forces and possibly formation of hydrogen bonds.
5) Reconstitution of the hydrated structure around the formed complex.

The intermolecular interactions responsible for complex formation have been discussed in the literature. Saenger, has discussed the different forces involved in the complex formation between cyclodextrins and guest molecule. It has
been shown that several forces act simultaneously. The extent to which each of them is involved is related to the substrate concerned.

The dependence of the binding constants on substrate polarisability indicates that, in general, van der Waals forces predominate; the formation of hydrogen bonds between the guest and (preferentially) the O(6)H groups of the substrate has been demonstrated crystallographically. Hydrophobic interactions are also involved - on inclusion within the cyclodextrin cavities the guest molecule must expel the water molecules already present and strip off its own hydration sphere. The liberated water molecules are taken up by the bulk water; they gain degrees of freedom and contribute to the stability of the complex owing to the resulting increase in entropy.
1.5 Application of Cyclodextrins

In recent years, the increasing number of patents has reflected the importance of the practical applications of cyclodextrins. Saenger\(^3\), has discussed in detail the various applications of cyclodextrins within the industries of pharmacy and agriculture. These include:

1.5.1 Micro-Encapsulation

Experiments have been performed with the aim of introducing micro-encapsulation by cyclodextrins into industries which manufacture drugs, foodstuffs, plant protective agents and toilet articles. The use of cyclodextrin complexes in industry has brought about the following improvements:\(^1\)\(^2\)\(^3\):

I- Stabilisation of light- or oxygen-sensitive substances.
II- Modification of the chemical activity of guest molecules:
   a) Reactive substances are protected by inclusion and can be mixed with other substances without any risk.
   b) Reaction can be made selective by inclusion of functional groups.
   c) Reactions can be promoted or suppressed.

III- Fixation of very volatile substances:
   a) Storage and handling are improved, especially in the case of toxic substances.
   b) The quality of the volatile substance required can be reduced since little or no vaporisation takes place.
   c) The quantities of aromatics and physiologically active substances can be better measured out.
IV- Modification of the physicochemical properties of guest molecules:

a) Substances which are sparingly soluble in water are made more soluble by the addition of cyclodextrins or they can be more easily emulsified.

b) Powdered, freeze-dried cyclodextrin complexes are finely dispersed and more soluble than uncomplexed guest molecules which are only sparingly soluble in water.

c) Pigments can be masked or the colour of substances can be altered as inclusion generally produce changes in the spectrum of the molecule.

d) Unpleasant tastes can be suppressed.

1.5.2 Cyclodextrin Polymers in Gel Inclusion Chromatography

The cyclodextrin polymers are preferred as filling materials for column chromatography (gel inclusion chromatography). Cyclodextrin polymers have the advantage that they strongly retard molecules of an appropriate size therefore, molecules with similar molecular weights or even isomers can be separated. For example, o- and p-nitrophenol, benzoic and o-chlorobenzoic acid; these substances can be well separated on cyclodextrin polymers but not on Sephadex. Similar separations have been achieved with amino acids particularly those with aromatic side groups. Chromatography of nucleosides and nucleotides on cyclodextrin polymers also produced successful results.

The polymer-linked cyclodextrin can be used to advantage for affinity chromatography of amylases which bind cyclodextrins as inhibitors but do not act upon them enzymatically. ß-amylases from potatoes, for example, is related to column filled with α-cyclodextrin-sepharose whilst the closely related α-amylase passes through the column without hindrance.
1.5.3 Racemate Resolution with Cyclodextrins

As cyclodextrins are optically active molecules they form a diastereomeric pair with each included racemate. The two components of the pair exhibit different physical properties.

\[
\begin{align*}
D(+) & \text{-Cyclodextrin (}) \text{-antipode} \\
D(+) & \text{-Cyclodextrin (} \text{-antipode} \\
\end{align*}
\]

Diastereomers

1.5.4 Cyclodextrins in Agriculture

As it was mentioned in section 1.5.1, cyclodextrins can be employed for the molecular encapsulation. This technique has been used for stabilisation of unstable or very volatile insecticides and herbicides.

Surprisingly\(^5\), if the grain is treated with aqueous \(\beta\)-cyclodextrin solution before being sworn, the harvest is increased by 20-45%.
1.6 Aims of the Present Work

From the literature survey presented in this thesis it is quite clear that most of the research on cyclodextrin-substrate complexation reactions in solution is mostly referred to water as the reaction medium. It may be correctly argued from the applications of cyclodextrins described under section 1.5, that water is the obvious reaction medium to select. However, it has been frequently claimed that studies in non-aqueous media, particularly in solvent systems for which some of the features of water are eliminated, have been most valuable in the interpretation of the behaviour of electrolytes and non electrolytes in water. A further corroboration of this statement is found in the work carried out by Danil de Namor and co-workers\textsuperscript{124-127}. Indeed, complexation data for macrocyclic ligands (cryptands) and metal ions in dipolar aprotic solvents proved to be very useful in the interpretation of these processes in water. In addition, this work has shown the important role played by the solvation of the cation and the ligand in complexation reactions involving macrocyclic ligands. Therefore, the approach taken in this thesis to study the binding properties of cyclodextrins towards substrates considers the solvation of the substrate and the ligand reflected in their transfer parameters from a reference solvent to another. The transfer properties such as free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) provide information about the changes in the interactions that electrolytes and non electrolytes undergo in their transfer from a reference medium (reference solvent) to another. These data reflect the medium effect changes much better than corresponding solvation data. (Readers interested to have further information on transfer parameters are referred to the several review articles written by workers\textsuperscript{128-132} as well as previous PhD dissertations from the Laboratory of Thermochemistry\textsuperscript{133,134}. This thesis covers aspects related to the calculation of transfer data in the appropriate chapter).

It must be emphasised that no previous studies on cyclodextrin-substrate complexation reactions have involved quantitative data on the transfer of the substrate and the ligand from one solvent to another. In fact, there is hardly any
information on the thermodynamics of complexation of cyclodextrins and substrates in non-aqueous media. Hence, the approach to be taken in this thesis is a novel approach in the study of the complexing abilities of cyclodextrins towards guest species.

An account on the aims of this thesis, the selection of substrates, ligands and reaction media is now given.

The main aim of this thesis is to obtain detailed understanding of the complexation reactions involving cyclodextrins and substrate species in water and in non-aqueous media by involving transfer data for the ligand and the substrate among these media.

Taking into account the suggestion made by Cramer\textsuperscript{68,135} that cyclodextrins can serve as models for antibody molecules, electrolytes containing anions known as antigenic determinants were selected for this study. These are:

- **ortho** (p-hydroxyphenylazo) benzoate \([o(p-OHPhN_2)B^-]\)
- **meta** (p-hydroxyphenylazo) benzoate \([m(p-OHPhN_2)B^-]\)
- **para** (p-hydroxyphenylazo) benzoate \([p(p-OHPhN_2)B^-]\)
- **5Cl-2** (p-hydroxyphenylazo) benzoate \([5Cl-2(p-OHPhN_2)B^-]\)
- **6Cl-2** (p-hydroxyphenylazo) benzoate \([6Cl-2(p-OHPhN_2)B^-]\)
- **2Cl-4** (p-hydroxyphenylazo) benzoate \([2Cl-4(p-OHPhN_2)B^-]\)
- **4Cl-3** (p-hydroxyphenylazo) benzoate \([4Cl-3(p-OHPhN_2)B^-]\)

The reaction media selected for complexation studies are water and N,N'-Dimethylformamide. Water is commonly used as reference solvent. In addition, if the biological implications of these results are to be explored at a later stage, data in water are required. N,N'-Dimethylformamide is a dipolar aprotic solvent. It is not as highly structured solvent as water. It is known to be a poor solvator for anions.
The present collection of data on the transfer parameters involve electrolytes containing anions other than azobenzoate anions. In fact, transfer data for anions from water to most solvents, including N,N'-Dimethylformamide are only limited to a few anions. Solution thermodynamic data for cyclodextrins in water and in non-aqueous media (hence, transfer data) have not been previously reported. Therefore, solution thermodynamic studies for both, electrolytes and ligands in water and N,N'-Dimethylformamide were carried out. In addition, solution studies, for these electrolytes are also carried out in methanol and their transfer parameters to methanol are evaluated. Methanol was selected because this solvent contains functional groups common to cyclodextrin molecules. Therefore, transfer data for these anions from a given reference solvent to methanol could be of relevance for the interpretation of the complexation process between these anions and cyclodextrins in different reaction media.

In order to assist the reader, a brief summary of the lay out of this thesis and the contents of each chapter is now given.

The different experimental procedures followed in this work is presented in chapter 2. These include the preparation and purification of the haptens in question; the potentiometric and conductimetric techniques; the experimental procedure of determination of solubility data and also the purification procedures of methanol and N,N'-Dimethylformamide.

Results and discussion of this work are presented in Chapters 3, 5 and 7. However, since solution and titration calorimetry techniques were most prominent in this research, they have been described separately in Chapters 4 and 6.

Since dissociation and ion pair formation constants are needed to evaluate free energy of solution of the dissociated haptens in the different reaction media considered, these data were presented first in chapter 3. A description of the different techniques that can be used to determine dissociation and ion pair
formation constants are included in this chapter. Hammett substituent constants of the acids in water were also determined and reported.

Solution and transfer thermodynamic parameters of the cyclodextrins and the haptens in different media were determined and reported in chapter 5.

In chapter 7, complexation thermodynamic data of haptens and cyclodextrins in water and N,N’-Dimethylformamide are given. In addition, complexation thermodynamic data for the transfer of cyclodextrin-substrate from water to N,N’-Dimethylformamide using a thermodynamic cycle were derived. The complexing thermodynamic data were determined using the titration calorimetric technique.
1.6.1 Abbreviations Used for Solvents

In this thesis, the following abbreviations are used:

1) Water \( H_2O \)
2) Methanol \( MeOH \)
3) N,N'-Dimethylformamide \( DMF \)

1.6.2 Physical Properties of Used Solvents

Physical properties of the solvents used in this work are given in Table 1.6. Included in this table are values calculated for the Debye-Huckel parameters (A and B) at 298.15K.

Table 1.6 Physical Properties of Different Solvents at 298.15K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Density</th>
<th>Dielectric Constant</th>
<th>Viscosity</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O )</td>
<td>0.9971</td>
<td>78.30</td>
<td>0.8903</td>
<td>0.5109</td>
<td>0.3290</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.7866</td>
<td>32.70</td>
<td>0.5445</td>
<td>1.9006</td>
<td>0.5098</td>
</tr>
<tr>
<td>DMF</td>
<td>0.9443</td>
<td>36.71</td>
<td>0.7960</td>
<td>1.5934</td>
<td>0.4807</td>
</tr>
</tbody>
</table>
CHAPTER 2: EXPERIMENTAL PROCEDURES

2.1 Reagents Used

The different chemical reagents used in this work include:-

**Macrocyclic Ligands**

Alpha Cyclodextrin (pfs), Shradinger α-Dextrin; Cyclohexamylose, Crystalline, anhydrous molecular weight 972.9, Sigma.
Beta Cyclodextrin (pfs), Shradinger β-Dextrin; Cycloheptaamylose, Crystalline, anhydrous molecular weight 1135, Sigma.
Gamma Cyclodextrin (pfs), Shradinger γ-Dextrin; Cyclooctaamylose, Crystalline, anhydrous molecular weight 1297.2, Sigma.

**Haptens - Starting Materials**

In order to prepare haptens containing parahydroxyphenylazo and Chloro substituted parahydroxyphenylazo benzoate anions, the following chemicals were used as starting materials. These include:-

*Ortho*-Aminobenzoic Acid (Aldrich, 98%)
*Meta*-Aminobenzoic Acid (Aldrich, 98%)
*Para*-Aminobenzoic Acid (Aldrich, 99%)
2-Amino-6-Chlorobenzoic Acid (Lancaster Synthesis, 98%)
2-Amino-5-Chlorobenzoic Acid (Aldrich, 98%)
4-Amino-2-Chlorobenzoic Acid (Aldrich, 97%)
3-Amino-4-Chlorobenzoic Acid (Aldrich, 98%)

Sodium bicarbonate, NaHCO₃ (BDH, AR) was used to prepare the sodium salt of the different haptens involved in this thesis.
Reagents Used For Standard Chemical Reactions

Tris (hydroxymethyl) aminomethane (THAM), (Sigma 99-99.5%)
Perchloric Acid, HClO₄ (BDH, 70-72%)
Sodium hydroxide, NaOH (C.V.S., 0.1M)

Solvents

The different solvents used in this work involved:

Deionized Water
Methanol (HPLC grade, 99.8%)
Methanol (BDH)
N,N’-Dimethylformamide (BDH, 99%)

Barium oxide anhydrous, BaO (BDH, 95%) was used as a pre-distillation drying agent for N,N’-Dimethylformamide.

2.2 Purification of Solvents
2.2.1 N,N’-Dimethylformamide

N,N’-Dimethylformamide (BDH, 98%) was left for 24 hours over barium oxide, BaO, in order to reduce the content of water in the solvent. The solvent was then further purified by fractional distillation under vacuum at temperatures of between 60-80°C. Only the middle fraction was collected and used immediately, or stored in 500 ml round flasks under nitrogen. The water content of the distilled solvent, as measured by the Karl Fisher titration method, was found to be less than 0.05%.
2.2.2 Methanol

Methanol (BDH) was distilled from water according to the technique described by Vogel\textsuperscript{137}. The procedure involves the following reactions:

\begin{align*}
2 \text{CH}_3\text{OH} + \text{Mg} &\rightarrow 2\text{H}_2\text{O} + \text{Mg} \text{(OCH}_3\text{)}_2 \quad (1) \\
\text{Mg} \text{(OCH}_3\text{)}_2 + 2\text{H}_2\text{O} &\rightarrow 2\text{CH}_3\text{OH} + \text{Mg} \text{(OH)}_2 \\
\end{align*}

Reaction (1) proceeds readily since the magnesium (Mg) is activated with iodine (I\textsubscript{2}) and the water content does not exceed 1%. Subsequent interaction between magnesium methoxide [Mg(OCH\textsubscript{3})\textsubscript{2}] and water gives the highly insoluble magnesium hydroxide [Mg(OH)\textsubscript{2}] and methanol (CH\textsubscript{3}OH) of high purity.

Magnesium (5g) and iodine (0.5g) were added to 50 ml of methanol, the mixture was then gently heated until all of the iodine had disappeared and, all of the magnesium had been converted into magnesium methoxide [Mg(OCH\textsubscript{3})\textsubscript{2}]. The new mixture was refluxed for 30 minutes. Following this, methanol was further purified by fractional distillation and only the middle fraction was collected and used. The water content of the distilled methanol was checked by gas chromatography and Karl Fisher titration techniques and was found to be less than 0.05%.

2.3 Purification of Tris(hydroxymethyl) Aminomethane (THAM)

Tris(hydroxymethyl) aminomethane (Sigma, 98%), known as TRIS or THAM, was used to perform the THAM standard chemical reaction, so allowing the reproducibility of the calorimeter to be checked. Further purification, as suggested by Fossom et al.\textsuperscript{138}, was carried out.

A hot concentrated aqueous solution was prepared by dissolving Tris (400g) in 300 ml of near-boiling water. To the hot solution, 1200 ml of pure methanol was added. The solution, with constant stirring, was left to cool at room temperature.
Then, the temperature of the solution was further reduced to about 3°C, at which crystals of THAM were obtained and filtered off. This procedure was repeated twice, using the same methanol to water ratio. Following this stage, the crystals were thoroughly washed with methanol. The product obtained was dried in air for 24 hours, then screened and finally dried under vacuum for three days.

2.4 Synthesis of Haptens
2.4.1 Parahydroxyphenylazo and chloro-Substituted parahydroxyphenylazo Benzoic Acids

The preparation of parahydroxyphenylazo benzoic acids and chloro-substituted parahydroxyphenylazo benzoic acids was carried out, as suggested by Vogel\(^{19}\), using the appropriate ortho, meta and para aminobenzoic acids and chloro-substituted ortho, meta and para aminobenzoic acids. This can be summarized as follows:-

1) Diazotisation of amino and chloroamino benzoic acids with sodium nitrite in acid medium and at temperatures between 3-5°C.
2) Coupling with phenol at pH 9 and a temperature less than 10°C.
3) The highly coloured azobenzoic acids were precipitated at pH 2 at room temperature.

The products were then further purified by recrystallization from water and ethanol mixtures. Purity was confirmed by determination of their melting points. Microanalysis on the samples was carried out at the University of Surrey. Table 2.1 contains the different microanalysis and melting points of the synthesised acids.

---

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Table 2.1. Melting Points and Microanalysis Data of parahydroxyphenylazo and chloro-Substituted parahydroxyphenylazo Benzoic Acids.

<table>
<thead>
<tr>
<th></th>
<th>Microanalysis</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
<td>Hydrogen</td>
</tr>
<tr>
<td></td>
<td>Calc. Found</td>
<td>Calc. Found</td>
</tr>
<tr>
<td>ortho (pOHPhN₂) B.A</td>
<td>64.40</td>
<td>64.54</td>
</tr>
<tr>
<td>meta (pOHPhN₂) B.A</td>
<td>64.40</td>
<td>64.33</td>
</tr>
<tr>
<td>para (pOHPhN₂) B.A</td>
<td>64.40</td>
<td>64.06</td>
</tr>
<tr>
<td>6-Chloro-2-(pOHPhN₂) B.A</td>
<td>56.42</td>
<td>56.52</td>
</tr>
<tr>
<td>4-Chloro-3-(pOHPhN₂) B.A</td>
<td>56.42</td>
<td>56.30</td>
</tr>
</tbody>
</table>

* Data reported by D. Pressman et al.¹⁴⁰

a) Reaction

![Chemical reaction diagram]

b) Experimental Procedure

Example: ortho (para-hydroxyphenylazo) benzoic acid

Reagents: ortho aminobenzoic acid (Aldrich, 98%)
- sodium nitrite (BDH, AR)
- hydrochloric acid conc, HCl
- sulphamic acid (BDH, AR)
- phenol (BDH, AR)

ortho Aminobenzoic acid or anthranilic acid (0.02 moles or 2.54 g) was dissolved in a solution of distilled water (20 ml) containing concentrated HCl (5 ml). Stirring was carried out until the anthranilic acid powder had dissolved. A solution of sodium nitrite (0.022 moles or 1.52 g) 2.2 M (10 ml) was prepared and added to the above solution at temperatures of between 3-5°C, using a dropping funnel. As a result of the formation of the diazonium salt, the solution changed colour from white to yellow. Excess of sodium nitrite was added to ensure complete diazotisation of the used amount of anthranilic acid. This was then removed by neutralizing the solution with sulphamic acid. Following this, the diazonium salt solution was pipetted into 100 ml of a solution which contained phenol (2.07g), NaOH (1g) and Na₂CO₃ (10g) (pH 9, T<10°C). The mixture was then left overnight, with constant stirring to ensure maximum yield. Finally, ortho
(parahydroxyphenylazo) benzoic acid was precipitated at pH 2 and purified, at least twice, by recrystallization from water and ethanol (96%).

The preparation of others was carried out in the same manner.

2.4.2 Parahydroxyphenylazo and Chloro Substituted parahydroxyphenylazo Sodium Benzoates

The synthesis of parahydroxyphenylazo and chloro substituted parahydroxy phenylazo sodium benzoate is based upon the following reaction:

$$R-\text{COOH} + \text{NaHCO}_3 \rightarrow R-\text{COONa} + \text{CO}_2 + \text{H}_2\text{O} \quad (3)$$

**Experimental Procedure**

One mole of the acid was dissolved in one mole of sodium bicarbonate solution. Then, it was heated and stirred until all of the acid had disappeared and left overnight. The solution was then filtered off and the sodium salt of the hapten in question was obtained by evaporating the water under vaccum. The purity was further improved by recrystalisation of the product, at least twice, from water and ethanol mixtures. Microanalysis results of these compounds are shown in Table 2.2.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ortho</strong> (pOHPhN₂) Na.B</td>
<td>59.09 58.40</td>
<td>3.41 3.46</td>
<td>10.61 10.43</td>
</tr>
<tr>
<td><strong>meta</strong> (pOHPhN₂) Na.B</td>
<td>59.09 58.71</td>
<td>3.41 3.38</td>
<td>10.61 10.69</td>
</tr>
<tr>
<td><strong>para</strong> (pOHPhN₂) Na.B</td>
<td>59.09 59.29</td>
<td>3.41 3.47</td>
<td>10.61 10.59</td>
</tr>
<tr>
<td><strong>5-Chloro-2-(pOHPhN₂) Na.B</strong></td>
<td>52.26 52.02</td>
<td>2.68 2.68</td>
<td>9.38 9.41</td>
</tr>
<tr>
<td><strong>6-Chloro-2-(pOHPhN₂) Na.B</strong></td>
<td>52.26 52.16</td>
<td>2.68 2.96</td>
<td>9.38 9.09</td>
</tr>
<tr>
<td><strong>2-Chloro-4-(pOHPhN₂) Na.B</strong></td>
<td>52.26 52.01</td>
<td>2.68 2.71</td>
<td>9.38 9.09</td>
</tr>
<tr>
<td><strong>4-Chloro-3-(pOHPhN₂) Na.B</strong></td>
<td>52.26 52.15</td>
<td>2.68 2.79</td>
<td>9.38 8.99</td>
</tr>
</tbody>
</table>

Table 2.2. Microanalysis Data of *para* hydroxyphenylazo and *chloro*-Substituted *para* hydroxyphenylazo Sodium Benzoates.
2.5 Conductivity Measurements - Experimental Procedure

The apparatus, used to measure conductivities of parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo sodium benzoates, comprises a Wheatstone bridge arrangement and a Tip-type glass conductivity cell with bright platinum electrodes. The bridge, used to measure the resistances of electrolyte solutions, was a Wayne-Kerr automatic conductivity bridge of the transformer ratio-arm type B642 with input voltages between 0.2-1.2 V. The cell was such that samples of the electrolyte could be injected through its side arm. Nitrogen was passed through in order to ensure uniform distribution of the ions in solution and to keep the solution free of CO₂. The conductivity measurements were carried out at a fixed frequency (1592 Hz) and at a temperature of 298.15 ± 0.01K. This was ensured by a thermostated water bath.

Conductivity measurements were performed as follows:-

The appropriate solvent (100 ml) was pipetted into the cell and left to reach thermal equilibrium, and its conductivity was measured before any addition of the electrolyte solution. Then, ten to fifteen samples (1ml) of the electrolyte stock solution were added using a glass syringe. In order to determine the exact amount injected into the cell, and therefore, the exact concentration at which the conductivity reading corresponded, the syringe was accurately weighed out to ± 0.0001g before and after each injection. The conductivity readings were taken after a stream of nitrogen was passed through for a period of time (2-5 mins). Then, a set of readings was taken. The molar conductance was calculated from mean conductivity readings. This procedure was repeated after each addition.

A computer program (see appendix A), written in the FORTRAN language, was devised to calculate the corresponding molar conductance after every addition of electrolyte.
In order to determine the conductivity cell constant, this was calibrated against standard potassium chloride solution using the Jones and Bradshaw method. KCl (BDH, AR) was recrystallised twice from deionised water and dried at 120°C for several days. Then, a stock solution of potassium chloride was prepared from accurately weighed amounts of KCl dissolved in a known volume of fresh deionised water. Weighings were made to ± 0.0001g.

2.6 Potentiometric Titration - Experimental Procedure

Sodium hydroxide (0.01M) was delivered from a radiometer autoburette ABU12 (capacity 2.5 ml), into an aqueous solution of para-hydroxyphenylazo or chloro-substituted para-hydroxyphenylazo benzoic acid contained in a double-walled vessel (capacity 50 ml), thermostated at 298.15 ± 0.01 K. The pH of the solution was measured using a radiometer pH meter 62 equipped with K4040 calomel reference electrode and a radiometer G20401 glass electrode. Before each titration the pH meter was calibrated using potassium hydrogenphthalate (0.05M, pH 4.008 at 298.15 K) and borax (0.01M, pH 9.18 at 298.15 K) buffers. The buffers used were ANALAR and solutions were made up with twice-distilled deionised water. The pH electrode system and reaction vessel were mounted on a radiometer titrations assembly TTA60, thus enabling the solutions to be stirred. The titrations were carried out under a flow of nitrogen. Experiments were carried out at least three times. In Figure 2.1 the equipment used for potentiometric titration is shown.
Figure 2.1 A schematic description of the potentiometer titrator system
2.7 Solubility Measurements

2.7.1 Experimental Procedure

Solubilities of para-hydroxyphenylazo benzoic acids, chloro-substituted para-hydroxyphenylazo benzoic acids and then corresponding sodium salts were determined at 298.15 ± 0.01 K in water, methanol and N,N'-Dimethylformamide using the saturation method. An excess of the solid was added to the solvent. The mixture was left to equilibrate for several days in a thermostatic water bath at 298.15 ± 0.01 K. Samples for analysis were taken at the equilibrium temperature and analysed spectrophotometrically as described below. Solvate formation was checked using the De Ligny method. No solvate formation was observed. Measurements were carried out in triplicate.

Solubilities of α, β and γ-cyclodextrins were also determined in N,N'-Dimethyl formamide at 298.15 ± 0.01 K. The same experimental procedure was followed and samples were analysed using the titration calorimetric technique.

2.7.2 Analytical Methods

a) Spectrophotometric Determination of Haptens in Water, Methanol and N,N'-Dimethylformamide at 298.15 K

To measure the solubilities of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoic acids and their corresponding sodium salts in water, methanol and N,N'-Dimethylformamide, an aliquot of the corresponding saturated solution was filtered through a glass filter, adequately diluted and the absorbance of the resulting solution was measured using a computerised PV8700 UV/VIS Scanning Spectrophotometer. The corresponding concentration and therefore, solubility was read from a calibration curve of molarity versus molar absorbance, prepared from a number of well known electrolyte concentration solutions. Plotted molar absorbance and electrolyte concentrations yielded the different extinction coefficients of haptens in water, methanol and N,N'-Dimethylformamide at 298.15 K. These results are
shown in chapter 4.

b) Calorimetric Titration of Cyclodextrins

Solubilities of α, β and γ-Cyclodextrin in N,N'-Dimethylformamide at 298.15 K were obtained using the Hart Scientific 5021 isoperibol calorimeter. Aliquots of the saturated solutions of cyclodextrins were removed, filtered through a glass filter, and adequately diluted. Solutions of \textit{meta} (parahydroxy phenylazo) sodium benzoate (50 ml) were titrated against cyclodextrins until no heat was released inside the reaction vessel of the calorimeter. Heats released were corrected to heat effect due to dilution of the titrant and the titrate at 298.15 K. Combinations of heat released, Q, the corresponding equilibrium constant, $K_e$, and the molar enthalpy change of complexation of \textit{meta} (parahydroxy phenylazo) sodium benzoate with the cyclodextrin in question yielded the corresponding concentration and therefore, the solubility of the cyclodextrins.
CHAPTER 3
DISSOCIATION & ION PAIR FORMATION
CONSTANTS OF HAPTENS IN WATER,
METHANOL AND DMF
CHAPTER 3: DISSOCIATION & ION-PAIR FORMATION
CONSTANTS OF HAPTENS

3.1 Dissociation Constants of Acids

Dissociation constants of acids, generally referred to as ionisation constants ($pK_a = -\log K_a$), are used to measure the strength of acids and bases.

These data are of great importance because, not only do they show the strength of an acid but, they also reveal the proportions of the different species into which a species is present in solution at a given pH. Also, dissociation constants are valuable information in preparative chemistry, by defining the pH range in which a substance is least ionised, as well as the conditions under which this substance can be isolated in maximal yield. Additionally, dissociation constants are important in the calculation of solution free energies of the dissociated acid in a given solvent.

The determination of dissociation constants of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoic acids in water is of particular interest. This is because these acids are used as haptens. Therefore, data on their dissociation constants are required in the study of antigen-antibody reactions involving these acids. In addition, $pK_a$ values of benzoic and substituted benzoic acids have been reported in the literature, and it is of great interest to study the effect of substituent groups which have not been previously reported.

This study requires the investigation of the group responsible for ionisation as well as the number of ionic species in water. Given the rather complex nature of the structure of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoic acids, it is not obvious to predict, with a great deal of certainty, the behaviour of these acids in solution. In order to establish the groups responsible for ionisation, as well as the number of ionised species in water, spectrophotometric (UV) studies of these acids in water, and in aqueous solutions of hydrochloric acid,
were carried out. The latter was performed in order to confirm the number of ionic species which could be present in water.

The results shown in Fig 3.1 indicate that there are no differences in the two spectra. These results are further confirmed by conductance measurements as will be seen at a later stage in this Chapter. Therefore, it is concluded that the only ionising group in water is the carboxylate group of the acid and the process under investigation involves a monobasic acid (HA).

![Figure 3.1 A Spectrophotometric Scanning of m-pOHPPhN₂ Benzoic Acid in 0.1 M HCl](image)
The dissociation for the monobasic acid (HA) may be expressed by:—

\[
HA + H_2O \rightleftharpoons A^- + H_3O^+
\]

3.1

For simplicity, equation 3.1 is written as:—

\[
HA \rightleftharpoons A^- + H^+
\]

3.2

The thermodynamic dissociation constant, \(K_d^T\), for process 3.2 is given by:—

\[
K_d^T = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}}
\]

3.3

where \(a_{H^+}\), \(a_{A^-}\), and \(a_{HA}\) are the notations used to indicate the activities of the species \(H^+\), \(A^-\), and \(HA\), respectively. Equation 3.3 can be written in terms of concentrations (molar scale) and molar ionic activity coefficient, \(\gamma_\pm\). Thus,

\[
K_d^T = ([H^+][A^-]/[HA]).(\gamma_\pm^2/\gamma_{\pm HA})
\]

3.4

The activity coefficient for the undissociated acid, \(\gamma_\pm\), may be regarded as unity. Therefore, \(K_d^T\) may be expressed as:—

\[
K_d^T = K_d^C \cdot \gamma_\pm^2
\]

3.5

where \(K_d^C\) is the concentration equilibrium constant. Taking logarithms on both sides and multiplying by -1, equation 3.5 leads to:—

\[
-logK_d^T = -logK_d^C - 2\log\gamma_\pm
\]

3.6

Since \(-logK_d^T = pK_d^T\) and \(-logK_d^C = pK_d^C\), the resulting expression is:—

\[
pK_d^T = pK_d^C - 2\log\gamma_\pm
\]

3.7
With the lack of better approximation, $\gamma_\pm$ values were derived from the Debye-Hückel equation in its extended form:

$$-\log \gamma_\pm = \frac{(A \cdot z^+ z^- \sqrt{I})}{(1 + B \cdot a^0 \sqrt{I})}$$  \hspace{1cm} 3.8

A and B are the Debye-Hückel constants of the solvent; $a^0$ is the ion-size parameter; $z^+$ and $z^-$ are the valences of the positive and negative species in solution, I is the ionic strength defined by:

$$I = \frac{\Sigma c_i z_i^\pm}{2}$$  \hspace{1cm} 3.9

For 1:1 dissociated electrolytes, the ionic strength is equal to the ionic concentration, $c_i$.

Many methods have been developed to determine ionisation constants. Among these are:

a) Potentiometric titration
b) Conductimetry
c) Spectrophotometry

A brief description of each method is given.
3.1.1 Potentiometric Titration Method

This method requires the measurement of the pH of a solution as a function of the added volume (moles) of the titrant. The pH is measured potentiometrically using an electrochemical cell composed of two half cells known as electrodes. One electrode, known as the indicator electrode, is reversible to hydrogen ions, so its potential changes when the hydrogen concentration varies. The other electrode is termed "reference electrode" whose potential remains known and invariant throughout.

The hydrogen ion concentration (activity) is therefore obtained from measurements of hydrogen ion activity. Thus, the pH of an unknown solution can be calculated at 298.15 K from the following expression:

\[ pH = -\log a_{H^+} = \frac{(E_o - E_{ref})}{0.0591} \]

where \( E_o \) is the observed potential and \( E_{ref} \) is the potential of the reference electrode (e.g. calomel electrode) under the experimental conditions.

The pK_a value of a monobasic acid is related to the pH by the expression:

\[ pK_a = pH + \log a_{HA}/a_{A^-} \]

Equation 3.11 is a rearrangement of the Henderson-Hasselbalch equation, used for the calculation of pH of buffer solutions formed by a weak acid (HA) and its conjugated base (A^-). When 50% of the acid HA is dissociated, we have \( a_{HA} = a_{A^-} \) and therefore, \( pK_a = pH \).

The potentiometric titration technique is known to be fast and reliable.
3.1.2 Conductimetric Method

The conductimetric method consists in measuring the specific conductivity (κ) of electrolytes in solution at different concentrations and at a given temperature. Then, these values are used to determine the corresponding molar conductance (Λc). Ostwald applied the Law of Mass Action to the ionisation of carboxylic acids and derived the expression given by eqn. 3.12.

\[ K_d^C = \frac{\alpha^2 c}{(1 - \alpha)} \]  

3.12

Arrhenius showed that the degree of ionisation of an acid (α) can be expressed as:

\[ \alpha = \frac{\Lambda^T}{\Lambda^o} \]  

3.13

where Λo is the molar conductance at infinite dilution. Kohlrausch derived the expression of \( K_d^C \) in terms of conductivities.

The conductimetric method has a number of applications, since conductance measurements can be used for the determination of:

a) The ionisation constants of the acids (reciprocal of association constants).

b) The molar conductance of electrolytes at infinite dilution. These data are useful in the determination of the composition of salts (1:1 or 2:1 or 3:1 electrolytes etc.).

c) Ionic limiting conductivities (\( \lambda_o \) and \( \lambda_o^- \)).

d) Transfer numbers.

e) Ion-size parameters.

These data are very important. For instance, the limiting conductance (Λo) gives information about mobility of ions, reflecting solute-solvent interactions; when together with transport numbers, it enables the separation of cation and anion
numbers, it enables the separation of cation and anion contributions to the mobility of the electrolyte. The ion size parameter \((a^\circ)\), which is the distance separating two oppositely charged ions when they collide, enables to explain to what extent an ion is able to displace solvent molecules from the solvation sheath of the counter-ion when these ions approach each other.

### 3.1.3 Spectrophotometric Method

The determination of ionisation constants by ultraviolet or visible spectrophotometry depends upon the direct determination of the ratio of molecular species (neutral molecule) to ionised species in a series of non-absorbing buffer solutions, whose pH values are either known or measured. For this purpose, the spectrum of the molecular species must first be obtained in a buffer solution whose pH is so chosen that the substance to be measured is present wholly as this species. This spectrum is compared with that of the pure ionised species similarly isolated at another suitable pH. A wavelength is chosen at which the greatest difference between the absorbance of the two species is observed. This is called the "analytical wavelength". Measurements of the optical density, at this wavelength, of the substance, in question, at intermediate pH, enable the determination of the ratio of ionised to molecular species.

Assuming that Beer’s law is obeyed, the observed optical density, \(d\), is given by:

\[
d = d_i + d_m
\]

3.14

where \(d_i\) and \(d_m\) are the optical densities of the ionised and molecular species, respectively. Thus, for a monobasic acid, the \(pK_a\) value is given by:

\[
pK_a = pH + \log \left( \frac{d_i - d}{d_m - d} \right) \quad \text{if} \ d_m > d_i
\]

3.15

\[
pK_a = pH + \log \left( \frac{d_m - d}{d - d_i} \right) \quad \text{if} \ d_m < d_i
\]

3.16
However, the determination of ionisation constants by spectrophotometry is more time-consuming than by potentiometry. Nevertheless, the spectrophotometric method is an ideal method when a substance is too insoluble for potentiometry or when its $pK_a$ value is particularly low or high.

In this work, the potentiometric titration method was selected to determine the ionisation constants of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoic acids in water.

### 3.2 $pK_a$-values of $p$-OHPPh$_2$ and chloro-Substituted $p$-OHPPh$_2$ Benzoic Acids in Water at 298.15 K

$pK_a$ values of acids obtained from potentiometric titration data (pH, volume of titrant, V) can be determined using a) a graphical method or b) a numerical method.

#### 3.2.1 Graphical Method

For the graphical method, plots of pH vs volume of added titrant (V) or its derivative $\Delta$pH/$\Delta$V vs V are considered (see Fig 3.2 and 3.3). The latter one is preferably used. From this plot ($\Delta$pH/$\Delta$V vs V), the volume at which the end point of the titration of the acid in question occurs, can be determined. The end point of a titration corresponds to the necessary volume of titrant for 100% neutralisation of the substance in question. For a monobasic acid, the $pK_a$ value corresponds to the value of the pH at which 50% of the substance has ionised (see eq 3.11). Typical plots for graphical determination of $pK_a$ are shown in Fig 3.2 and 3.3.
Figure 3.2 A Typical Potentiometric Titration Curve of pH vs V

Figure 3.3 Typical Potentiometric Titration Curve of $\Delta p\text{H}/\Delta V$ vs V. The number of peaks corresponds to the number of ionised species.
3.2.2 Numerical Method

The numerical method involves complicated mathematical treatments to find the pK₄ values. The delicacy of the calculations require computer programs. There are a number of computer programs available for the calculation of the pK₄ values. Among these are, MINIQUAD¹⁴⁴,¹⁴⁵, SOGS¹⁴⁶ and LETAGROP¹⁴⁷ computer programs.

SOGS¹⁴⁶ and LETAGROP¹⁴⁷ are excellent programs and can be used to determine pK₄ values. However, MINIQUAD has several advantages over the other programs. These are:-

1) The use of the Gauss-Newton method of refinement. This method¹⁴⁸ is preferred to Newton-Raphson method, in spite of the better ultimate theoretical convergence properties of the latter. LETAGROP effectively uses the Newton-Raphson method.

2) The refinement is protected against divergence by the linear optimisation of shifts. Indeed, it has been shown¹⁴⁹ that optimisation of shifts confers a guaranteed convergence property on the refinement. Consequently, the initial estimates for the parameters need not be very accurate, and "guessed" values are usually satisfactory.

3) All differential coefficients are calculated from analytical expressions. This is an advantage since errors inevitably introduced during numerical differentiation, (such as occurs in both SOGS and LETAGROP), are demonstrated. It also avoids the problem of choosing suitable increments for the differentiating formulae.

Furthermore, SOGS is capable of dealing with multi-reactants systems but can only use pH titration data; LETAGROP can deal with many types of data, but each requires the use of one or more specific sub-programs. Additionally, both have
certain mathematical defects which could cause the failure of convergence to produce satisfactory solutions.

The potentiometric titration data of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoic acids in water at 298.15 K were analysed using the MINIQUAD\textsuperscript{144,145} computer program. The obtained pK\textsubscript{a} values are shown in Table 3.1.

Table 3.1 pK\textsubscript{a} values of p-OHPhN\textsubscript{2} and chloro-Substituted p-OHPhN\textsubscript{2} Benzoic Acids
in Water at 298.15 K as Obtained by MINIQUAD\textsuperscript{144,145}.

<table>
<thead>
<tr>
<th>Acid</th>
<th>pK\textsubscript{a} ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>5.31 ± 0.10</td>
</tr>
<tr>
<td>meta (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>5.08 ± 0.08</td>
</tr>
<tr>
<td>para (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>4.55 ± 0.08</td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>4.93 ± 0.07</td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>3.93 ± 0.06</td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>3.58 ± 0.04</td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN\textsubscript{2}) benzoic acid</td>
<td>4.63 ± 0.08</td>
</tr>
</tbody>
</table>

\footnote{Average of at least 3 measurements.}
3.2.3 Hammett Substituent Constant of Acids

The ionisation of substituted benzoic acids in water was the model used by Hammett\textsuperscript{150-152} and by Burckhardt and co-workers\textsuperscript{153,154}, to establish the electron-donating and electron-withdrawing properties of substituent groups\textsuperscript{155}.

Hammett drew attention to the fact that a plot of log$K_a$ for benzoic acid against log$K$ for ester hydrolysis, over many substituent is reasonably linear, which means that all substituents are exerting a similar effect in each of these quite dissimilar reactions. Substituents located at \textit{meta} or \textit{para} positions in the benzene ring fall on that line, whereas rates and equilibrium constants for \textit{ortho} substituted compounds do not.

The effect of each substituent, referred to as the Hammett substituent, $\sigma_x$, relative to that of hydrogen, may be obtained by a comparison of free energy change (hence $K_a$) for the dissociation process involving substituted benzoic acids, $K_x$, with corresponding data for the parent compound, benzoic acid, $K_h$, thus:

$$\sigma_x = \Delta G_x - \Delta G_h = pK_a(H) - pK_a(X)$$ \hfill \text{3.17}

In equation 3.17, $\sigma_x$ is a characteristic of the strength of the acid. Thus, electron-withdrawing substituents are characterised by negative $\sigma_x$ values and electron-donating ones by positive $\sigma$-values. Hydrogen, as a reference point, was given a value of $\sigma$= 0.

In this thesis, $X$ refers to the \textit{para}hydroxyphenylazo substituent groups. The corresponding Hammett substituent constants ($\sigma_x$) are determined as the difference between the $pK_a$ of benzoic acid (taken as 4.20 at 298.15 K)\textsuperscript{156-159} and the $pK_a$ values of the \textit{para}hydroxyphenylazo and chloro-substituted \textit{para}hydroxyphenylazo benzoic acids obtained from potentiometric titration data. The obtained values of $\sigma_x$ are shown in Table 3.2.
Table 3.2 The Hammett Constants ($\sigma$) of $p$-OHPhN$_2$ and chloro-Substituted
$p$-OHPhN$_2$ Substituents Groups in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_d$</th>
<th>$pK_a$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>4.20</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>ortho ($p$OHPhN$_2$)</td>
<td>5.31</td>
<td>-1.11</td>
<td></td>
</tr>
<tr>
<td>meta ($p$OHPhN$_2$)</td>
<td>5.08</td>
<td>-0.88</td>
<td></td>
</tr>
<tr>
<td>para ($p$OHPhN$_2$)</td>
<td>4.55</td>
<td>-0.36</td>
<td></td>
</tr>
<tr>
<td>$5CI$-2 ($p$OHPhN$_2$)</td>
<td>4.93</td>
<td>4.94</td>
<td>-0.73</td>
</tr>
<tr>
<td>$6CI$-2 ($p$OHPhN$_2$)</td>
<td>3.93</td>
<td>4.03</td>
<td>0.27</td>
</tr>
<tr>
<td>$2CI$-4 ($p$OHPhN$_2$)</td>
<td>3.58</td>
<td>3.27</td>
<td>0.62</td>
</tr>
<tr>
<td>$4CI$-3 ($p$OHPhN$_2$)</td>
<td>4.63</td>
<td>4.84</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

* Value obtained from ref 275-276.  ^ Values reported in Table 3.1.
^ Calculated values of $pK_d$ for the corresponding acids using the Hammett equation,
$\text{pK}_d (X) = \text{pK}_d (H) + \sigma_x$. 
3.2.4 Discussion

The introduction of a substituent on the phenyl group will result (depending on the nature of the substituent) in an increase or decrease of the ionisation of the acid which will be reflected in the $pK_d$ values. Thus, an increase in acidity (lower $pK_d$ values) is expected to be observed when the substituted group is electron-withdrawing and a decrease (higher $pK_d$ values) for an electron-donating substituent. It is clear from the $pK_d$ values listed in Table 3.1 and 3.2 that the introduction of the para-hydroxyphenylazo group in the structure of benzoic acid has an electron-donating mesomeric effect and therefore, ortho, meta and para (para-hydroxyphenylazo) benzoic acids are weaker (higher $pK_d$ values) than benzoic acid in water. This effect is greater for ortho (para-hydroxyphenylazo) benzoic acid ($pK_d = 5.31 \pm 0.10$) and lower for para (para-hydroxyphenylazo) benzoic acid ($pK_d = 4.55 \pm 0.08$).

The Hammett substituent ($\sigma$) calculated from data given in Table 3.1 and the literature $pK_d$ value of benzoic acid in water at 298.15 $K$ are $-1.11$, $-0.88$ and $-0.36$ for ortho, meta and para (para-hydroxyphenylazo) benzoic acids, respectively. One of the most interesting features of these results emerges when these constants ($\sigma_x$) are compared with those reported in the literature for azophenyl substituents, ($PhN\equiv$) ($\sigma_n = 0.29$ and $\sigma_p = 0.32$) since an opposite effect (electron-withdrawing) is observed. This effect, observed and reported for the first time in a recent publication, is the result of this work.

The $pK_d$ values observed for the chloro-substituted para-hydroxyphenylazo benzoic acids are in excellent agreement with the calculated values obtained from combination between the appropriate unsubstituted para-hydroxyphenylazo benzoic acid and the corresponding $\sigma$ values given in the literature for chlorine substituents ($\sigma_n = 0.37$, $\sigma_p = 0.24$ and $\sigma_o = 1.28$). Thus:

$$pK_d [(pOHPhN_2)B.A] + \sigma_{cl} = pK_d [Cl(pOHPhN_2)]$$  \hspace{1cm} 3.18
Using equation 3.18, 𝜎-values for the chloro-substituted para-hydroxyphenylazo benzoic acids were calculated (Table 3.2).

The obtained pKₐ values of the chloro-substituted para-hydroxyphenylazo benzoic acids and therefore, the calculated values of their corresponding Hammett constants (𝜎), suggest that the strength of these acids [5CI-2, 6CI-2, 2CI-4 and 4CI-3-(para-hydroxyphenylazo benzoic acid)] is as a result of contributions of the p-OHPhN₂ group and the powerful electronegative group, Cl. This seems to depend very much upon the position of chlorine in the benzene ring of the benzoic acid molecule. When the chlorine is in the meta or para position [5CI-2 and 4Chloro-3-(para-hydroxyphenylazo) benzoic acid], the para-hydroxyphenylazo substituent group is in control and the chlorine group seems to have little effect on the acidity and therefore, the acid is being weakened by mesomeric effect. However, in the case of 6chloro-2 and 2chloro-4 (para-hydroxy phenylazo) benzoic acid, it is the chlorine group which is in control and therefore, the acid is strengthened (pKₐ = 3.93 ± 0.06 and pKₐ = 3.58 ± 0.04) by inductive effect. The acid gets stronger when the para-hydroxyphenylazo group is positioned further away from the carboxylate group.
3.3 Ion-Pair Formation Constants of Electrolytes

An ion-pair may be said to exist when a cation and an anion are sufficiently close as a result of the electrostatic attraction between the two ions. The forces stabilising ion-pairs are primarily long-range electrostatic attractions as it is usually shown by their association constants, $K_a$, which in some cases seem to vary inversely with the dielectric constant of the solvent. Other intermolecular forces such as charge transfer and hydrogen bonding, between ions and solvent molecules are also important.

The formation of an ion-pair, a dipolar rather than a charged species is probably accompanied by some release of solvent which is thermodynamically favourable. Ion-pair formation can therefore be seen as competitive with solvation in lowering the free energy of the system. The stability of an ion-pair (association constant) with respect to free ions will, in general, diminish as the temperature is raised. Also, since an ion-pair in solution has a larger molar volume than the separated ions, due to the reduction in solvation, its stability will diminish with an increase in pressure.

The ion-pair formation process involved may be represented by the equation:

$$M^+_{\text{Solv}} + X^-_{\text{Solv}} \rightleftharpoons M^+X^-_{\text{Solv}} \quad 3.19$$

The thermodynamic ion-pair formation constant ($K_a$) of $M^+X^-$ may be given by the equation:

$$K_a = \frac{a_{M^+X^-}}{a_{M^+}a_{X^-}} \quad 3.20$$

where $a_{M^+X^-}$, $a_{M^+}$, and $a_{X^-}$ are the activities of the ion-pair ($M^+X^-$), the cation ($M^+$) and the anion species ($X^-$), respectively.
Evidence for the existence of ion-pairs rests on sound experimental evidence. The different analytical method used to determine ion-pair formation are given:

3.3.1 Conductance Measurements

The molar conductivity of electrolytes decreases with concentration. This was first recognised and interpreted by Bjerrum in 1926 and by Fuoss as a result of the electrical neutrality of the ion-pair and consequently of its inability to carry a current. Conductivity measurements may be used to determine $K_a$, and often reveal, through deviations of a simple equilibrium constant with concentration, the presence of higher ion aggregates. Variation of $\log K_a$ with $1/T$ should be linear, the slope yielding the enthalpy change for association. Again, these plots are frequently curved, evidently due to the occurrence of more than one complex equilibrium.

3.3.2 Spectrometry

The ultraviolet or visible spectra of certain organic ions show changes attributable to ion-pairing and to the type of ion-pair. Loose ion-pairs have spectra which are independent of the counterion, whereas the spectra of contact ion-pairs tend to show shifts of $\lambda_{max}$.

3.3.3 Electron Spin Resonance

Proton resonance spectra of organic anions and electron paramagnetic resonance spectra of radical anions and the proximity of magnetic ions can be discerned from direct coupling or from line broadening and the chemical shifts induced. The temperature dependence of these effects can yield information concerning the energetics and dynamic properties of the ion-pairs present, i.e. their lifetime, and may indicate the presence of more than one type of loose ion-pair.
3.3.4 Others

Abundant chemical evidence both from kinetic and from product studies implicates ion-pairs as intermediate species during the course of chemical reactions.

The conductivity measurement technique was selected to determine ion pair formation constants of para hydroxyphenylazo and chloro-substituted para hydroxyphenylazo sodium benzoate in water, methanol and N,N'-Dimethylformamide at 298.15K.
3.4 Ion-Pair Formation Constants of \( p\)-OHPhN\(_2\) and chloro-Substituted \( p\)-OHPhN\(_2\) Sodium Benzoate in Water, Methanol and DMF at 298.15K.

3.4.1 Specific Conductivity, \( \kappa \)

Ohm's Law as applied to a metallic conductor states that:

\[ V = I R \tag{3.21} \]

where \( V \) (volts) is the potential difference across the conductor, \( I \) is the current (amperes) and \( R \) is the resistance in ohms. The resistance of the metallic conductor can be defined by:

\[ R = \rho \frac{l}{A} \tag{3.22} \]

In equation 3.22, \( \rho \), \( l \) and \( A \) are the notation used to indicate specific resistivity (\( \Omega \cdot \text{cm} \)), length (cm) and cross-sectional area (cm\(^2\)) of the metallic conductor, respectively. These concepts can be extended to electrolyte solutions. In order to do so, specific resistivity is replaced by specific conductivity, \( \kappa \).

\[ \kappa = \frac{1}{\rho} \tag{3.23} \]

The specific conductivity, \( \kappa \), of a solution is usually determined by measuring the electrical resistance, \( R \) of a sample placed between two electrodes in a conductivity cell. Taking into account eqns 3.22 and 3.23, \( R \) may be given by:

\[ R = \frac{1}{\kappa} \cdot \frac{l}{A} \tag{3.24} \]

In equation 3.24, \( l \) is the distance between the electrodes and \( A \) is the cross sectional area of the electrodes. The ratio \( (l/A) \) is known as the cell constant and in this thesis will be referred to as \((\xi)\). Since calculating specific conductivity from the corresponding resistance of the sample and the cell dimensions are not reliable, the
cell constant was obtained by calibrating the cell using a solution of known conductivity. Then if the sample has a resistance value, $R$, in the same cell, its specific conductivity, $K$, is therefore,

$$K = \frac{\xi}{R}$$ \hspace{1cm} \text{(3.25)}

From equation 3.24, it is clear that the resistance $R$ of the sample increases with an increase in $l$ and a decrease in $A$. The value for the cell constant, $\xi$, is given in cm$^{-1}$.

The standard method used to measure the resistance, hence conductivity, of a solution consists of incorporating the conductivity cell into one arm of a Wheatstone bridge to search for the balance point. Alternating current must be used because a direct current would lead to electrolysis and to polarization, the charging of the layers of solution in contact with the electrodes. The use of alternating current avoids this polarization because the charging that occurs on one half of the cycle is undone during the second half.

3.4.2 Molar Conductivity, $\Lambda$

The specific conductivity, $K$, of a solution, which is due to contributions from both cations and anions, depends on the number of ions present in solution. Therefore, it is normal to express the conductivity as a molar quantity. The molar conductivity, $\Lambda$, is given by:-

$$\Lambda = 1000.K/c$$ \hspace{1cm} \text{(3.26)}

c is the electrolyte concentration expressed mol.dm$^{-3}$ and $\Lambda$ in $\Omega^{-1}.cm^{2}.mol^{-1}$.
3.4.3 Conductivity Cell Constant, \( \xi \)

The constant of the conductivity cell was determined according to the method described by Jones and Bradshaw\(^ {141} \). Since potassium chloride has normal behaviour in solution and its specific conductivity at known concentration is well established in the literature, this was used to determine the conductivity cell constant, \( \xi \). The molar conductances of KCl were calculated using both Lind \( et \) al.\(^ {170} \) and Fuoss-Hsia\(^ {71} \) equations corrected to the absolute ohm, the temperature scale and the molar mass of potassium chloride as reported by Kay and co-workers\(^ {172} \). The molar conductance of KCl is then used to calculate corresponding specific conductance using the equation:

\[
\kappa = \Lambda c/1000
\]  

3.27

In order to measure the cell constant, \( \xi \), specific conductivities of KCl, at various concentrations, were carried out. The corresponding theoretical values were obtained from eq. 3.27. Comparison between observed and theoretical values of the specific conductivities of KCl, at different concentrations, allowed the evaluation of the cell constant, \( c \). Details of calculations of the cell constant using different equations for conductance measurements of KCl in water at 298.15K are shown in Tables 3.5-3.8.
Table 3.5 Constant of the Conductivity Cell as Obtained Using Lind et al.\textsuperscript{70} Conductance Equation for KCl in Water 298.15K.

<table>
<thead>
<tr>
<th>c (mol.dm\textsuperscript{-3})</th>
<th>$\Lambda$ \textsuperscript{a}</th>
<th>$\kappa_{obs}$</th>
<th>$\kappa_{calc}$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48x10\textsuperscript{-4}</td>
<td>148.16</td>
<td>203.5x10\textsuperscript{-4}</td>
<td>5.16x10\textsuperscript{-5}</td>
<td>0.26836</td>
</tr>
<tr>
<td>5.85x10\textsuperscript{-4}</td>
<td>147.78</td>
<td>338.4x10\textsuperscript{-4}</td>
<td>5.16x10\textsuperscript{-5}</td>
<td>0.26435</td>
</tr>
<tr>
<td>7.80x10\textsuperscript{-4}</td>
<td>147.30</td>
<td>433.8x10\textsuperscript{-4}</td>
<td>11.49x10\textsuperscript{-5}</td>
<td>0.27197</td>
</tr>
<tr>
<td>1.05x10\textsuperscript{-3}</td>
<td>146.89</td>
<td>599.5x10\textsuperscript{-4}</td>
<td>15.42x10\textsuperscript{-5}</td>
<td>0.26224</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $\Lambda$ values were obtained from Lind et al.\textsuperscript{70} equation for KCl at 298.15K. It is given by:

\[ \Lambda = 149.93 - 94.65.c^{10} + 58.74.c.logc + 198.4.c \]

\[ \kappa_{wate} = 11.37x10^{-6} \, \Omega^{-1} \text{cm}^{-1} \]

Average value of the conductivity cell constant, $\xi = 0.26673 \pm 0.00374 \, \text{cm}^{-1}$

Table 3.6 Constant of the Conductivity Cell as Obtained from Lind et al.\textsuperscript{72} Equation for KCl in Water Corrected to the Absolute ohm, Temperature Scale and Molar Mass of Potassium Chloride at 298.15K.

<table>
<thead>
<tr>
<th>c (mol.dm\textsuperscript{-3})</th>
<th>$\Lambda$ \textsuperscript{b}</th>
<th>$\kappa_{obs}$</th>
<th>$\kappa_{calc}$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48x10\textsuperscript{-4}</td>
<td>148.16</td>
<td>203.5x10\textsuperscript{-4}</td>
<td>5.16x10\textsuperscript{-5}</td>
<td>0.26836</td>
</tr>
<tr>
<td>5.85x10\textsuperscript{-4}</td>
<td>147.78</td>
<td>338.4x10\textsuperscript{-4}</td>
<td>8.65x10\textsuperscript{-5}</td>
<td>0.26435</td>
</tr>
<tr>
<td>7.80x10\textsuperscript{-4}</td>
<td>147.30</td>
<td>433.8x10\textsuperscript{-4}</td>
<td>11.49x10\textsuperscript{-5}</td>
<td>0.27197</td>
</tr>
<tr>
<td>1.05x10\textsuperscript{-3}</td>
<td>146.89</td>
<td>599.5x10\textsuperscript{-4}</td>
<td>15.42x10\textsuperscript{-5}</td>
<td>0.26224</td>
</tr>
</tbody>
</table>

\textsuperscript{b} $\Lambda$ values were calculated from Lind et al.\textsuperscript{72} as corrected by R. L. Kay\textsuperscript{72}. This is given by:

\[ \Lambda = 149.873 - 94.60.c^{10} + 58.72.c.logc + 198.3.c \]

Average value of the conductivity cell constant, $\xi = 0.26657 \pm 0.00578 \, \text{cm}^{-1}$

79
Table 3.7 Constant of the conductivity cell as obtained using Fuoss and Hsia conductance equation for KCl in water at 298.15K.

<table>
<thead>
<tr>
<th>c (mol dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$ mol$^{-1}$)</th>
<th>$\kappa_{obs}$ (Ω cm$^{-1}$)</th>
<th>$\kappa_{calc}$ (Ω cm$^{-1}$)</th>
<th>$\xi$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48x10$^{-4}$</td>
<td>148.17</td>
<td>203.5x10$^{-6}$</td>
<td>5.156x10$^{-4}$</td>
<td>0.26836</td>
</tr>
<tr>
<td>5.85x10$^{-4}$</td>
<td>147.66</td>
<td>338.4x10$^{-6}$</td>
<td>8.638x10$^{-4}$</td>
<td>0.26413</td>
</tr>
<tr>
<td>7.80x10$^{-4}$</td>
<td>147.31</td>
<td>433.8x10$^{-6}$</td>
<td>11.490x10$^{-4}$</td>
<td>0.27200</td>
</tr>
<tr>
<td>1.05x10$^{-3}$</td>
<td>146.90</td>
<td>599.5x10$^{-6}$</td>
<td>15.425x10$^{-4}$</td>
<td>0.26227</td>
</tr>
</tbody>
</table>

$^c$ $\Lambda$ values were calculated from the Fuoss and Hsia$^{71}$ conductance equation for KCl in water at 298.15K. This is given by:

$$\Lambda = 149.936 - 94.88.c^{12} + 25.48.c.logc + 221.0.c - 229.c^{32}$$

The average value of the conductivity cell constant, $\xi = 0.26669 \pm 0.00378 \text{ cm}^{-1}$

Table 3.8 Constant of the conductivity cell as obtained using Fuoss and Hsia$^{72}$ conductance equation for KCl in water corrected to the absolute ohm, temperature scale and molar mass of KCl at 298.15K.

<table>
<thead>
<tr>
<th>c (mol dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$ mol$^{-1}$)</th>
<th>$\kappa_{obs}$ (Ω cm$^{-1}$)</th>
<th>$\kappa_{calc}$ (Ω cm$^{-1}$)</th>
<th>$\xi$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48x10$^{-4}$</td>
<td>148.12</td>
<td>203.5x10$^{-6}$</td>
<td>5.154x10$^{-4}$</td>
<td>0.26826</td>
</tr>
<tr>
<td>5.85x10$^{-4}$</td>
<td>147.60</td>
<td>338.4x10$^{-6}$</td>
<td>8.635x10$^{-4}$</td>
<td>0.26404</td>
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<tr>
<td>7.80x10$^{-4}$</td>
<td>147.26</td>
<td>433.8x10$^{-6}$</td>
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<td>1.05x10$^{-3}$</td>
<td>146.85</td>
<td>599.5x10$^{-6}$</td>
<td>15.419x10$^{-4}$</td>
<td>0.26270</td>
</tr>
</tbody>
</table>

$^d$ $\Lambda$ values were calculated using Fuoss and Hsia conductance equation for KCl in water corrected to the absolute ohm, temperature scale and molar mass of KCl at 298.15K. This is given by$^{72}$

$$\Lambda = 149.879 - 94.84.c^{12} + 58.65.c.logc + 220.9.c - 228.9.c^{32}$$

The average value of the conductivity cell constant, $\xi = 0.26673 \pm 0.00362 \text{ cm}^{-1}$

All the values of the constant of the conductivity cell, $\xi$, obtained from different equations for conductance measurements of KCl in water are in excellent agreement.
3.4.4 Measurements of Conductance of Haptens in Water, Methanol and DMF at 298.15K.

In order to determine the ion-pair formation constants of sodium [para hydroxyphenylazo and chloro-substituted para hydroxyphenylazo] benzoate in water, methanol and N,N'-Dimethylformamide at 298.15K, conductance measurements at different concentrations of these electrolytes in these solvents were carried out. The conductivity cell used was a Tip-type glass cell with bright platinum electrodes. A detailed description of the apparatus is given in chapter 2, section 2.5. Molar conductances of each hapten at different concentrations in the different solvents were recorded. The results are shown in Tables 3.9-3.29. Analysis of these data yielded association constants, $K_a$, and molar conductances at infinite dilution, $\Lambda^\circ$. The method of analysis and the results ($K_a$, $\Lambda^\circ$) are shown in section 3.4.5 of this chapter.
<table>
<thead>
<tr>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$mol$^{-1}$)</th>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$mol$^{-1}$)</th>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.32x10$^{-4}$</td>
<td>82.89</td>
<td>13.73x10$^{-4}$</td>
<td>81.79</td>
<td>26.46x10$^{-4}$</td>
<td>79.82</td>
</tr>
<tr>
<td>6.33x10$^{-4}$</td>
<td>82.58</td>
<td>15.42x10$^{-4}$</td>
<td>81.57</td>
<td>27.74x10$^{-4}$</td>
<td>79.60</td>
</tr>
<tr>
<td>8.28x10$^{-4}$</td>
<td>82.06</td>
<td>17.05x10$^{-4}$</td>
<td>81.43</td>
<td>28.37x10$^{-4}$</td>
<td>79.26</td>
</tr>
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<td>80.88</td>
<td>30.79x10$^{-4}$</td>
<td>79.10</td>
</tr>
<tr>
<td>11.08x10$^{-4}$</td>
<td>81.60</td>
<td>18.63x10$^{-4}$</td>
<td>80.44</td>
<td>31.37x10$^{-4}$</td>
<td>78.95</td>
</tr>
<tr>
<td>12.86x10$^{-4}$</td>
<td>81.95</td>
<td>25.13x10$^{-4}$</td>
<td>79.91</td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.9 Conductivity Measurements for Sodium [ortho (parahydroxyphenylazo)] Benzoate in Water at 298.15K.

<table>
<thead>
<tr>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$mol$^{-1}$)</th>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$mol$^{-1}$)</th>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω cm$^2$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18x10$^{-4}$</td>
<td>72.32</td>
<td>1.09x10$^{-4}$</td>
<td>70.23</td>
<td>2.07x10$^{-4}$</td>
<td>69.61</td>
</tr>
<tr>
<td>0.33x10$^{-4}$</td>
<td>72.82</td>
<td>1.32x10$^{-4}$</td>
<td>69.85</td>
<td>2.27x10$^{-4}$</td>
<td>69.23</td>
</tr>
<tr>
<td>0.49x10$^{-4}$</td>
<td>71.65</td>
<td>1.50x10$^{-4}$</td>
<td>69.62</td>
<td>2.47x10$^{-4}$</td>
<td>68.92</td>
</tr>
<tr>
<td>0.68x10$^{-4}$</td>
<td>70.09</td>
<td>1.71x10$^{-4}$</td>
<td>68.99</td>
<td>2.68x10$^{-4}$</td>
<td>68.29</td>
</tr>
<tr>
<td>0.88x10$^{-4}$</td>
<td>70.78</td>
<td>1.89x10$^{-4}$</td>
<td>69.81</td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.10 Conductivity Measurements for Sodium [meta (parahydroxyphenylazo)] Benzoate in Water at 298.15K.
Table 3.11 Conductivity Measurements for Sodium [para (parahydroxyphenylazo)] Benzoate in Water at 298.15K.

<table>
<thead>
<tr>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.07x10(^{-4})</td>
<td>78.44</td>
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<td>76.79</td>
<td>9.08x10(^{-4})</td>
<td>76.55</td>
</tr>
<tr>
<td>6.47x10(^{-4})</td>
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<td>8.01x10(^{-4})</td>
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<td>9.43x10(^{-4})</td>
<td>76.51</td>
</tr>
<tr>
<td>6.87x10(^{-4})</td>
<td>77.33</td>
<td>8.37x10(^{-4})</td>
<td>76.60</td>
<td>9.77x10(^{-4})</td>
<td>76.44</td>
</tr>
<tr>
<td>7.25x10(^{-4})</td>
<td>77.01</td>
<td>8.73x10(^{-4})</td>
<td>76.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.12 Conductivity Measurements for Sodium [5-chloro-2-(parahydroxyphenylazo)] Benzoate in Water at 298.15K.

<table>
<thead>
<tr>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13x10(^{-3})</td>
<td>83.07</td>
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<td>2.50x10(^{-3})</td>
<td>75.88</td>
</tr>
<tr>
<td>0.38x10(^{-3})</td>
<td>82.57</td>
<td>1.50x10(^{-3})</td>
<td>77.88</td>
<td>5.00x10(^{-3})</td>
<td>73.28</td>
</tr>
<tr>
<td>0.75x10(^{-3})</td>
<td>77.18</td>
<td>2.00x10(^{-3})</td>
<td>76.38</td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.13 Conductivity Measurements of Sodium [6-chloro-2 (parahydroxyphenylazo)] Benzoate in Water at 298.15K.

<table>
<thead>
<tr>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
<th>c (mol dm(^{-3}))</th>
<th>(\Lambda) ((\Omega\cdot\text{cm}^2\text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20x10(^{-3})</td>
<td>79.87</td>
<td>1.50x10(^{-3})</td>
<td>77.88</td>
<td>3.00x10(^{-3})</td>
<td>73.88</td>
</tr>
<tr>
<td>0.50x10(^{-3})</td>
<td>77.88</td>
<td>2.00x10(^{-3})</td>
<td>75.38</td>
<td>4.00x10(^{-3})</td>
<td>74.63</td>
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<td>1.00x10(^{-3})</td>
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<td>2.50x10(^{-3})</td>
<td>75.48</td>
<td>5.00x10(^{-3})</td>
<td>73.09</td>
</tr>
</tbody>
</table>
Table 3.14 Conductivity Measurements for Sodium [2-chloro-4 (parahydroxy phenylazo)] Benzoate in Water at 298.15K.

<table>
<thead>
<tr>
<th>c (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω⋅cm$^{2}$⋅mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23x10$^{-4}$</td>
<td>88.27</td>
</tr>
<tr>
<td>0.31x10$^{-4}$</td>
<td>88.13</td>
</tr>
<tr>
<td>0.45x10$^{-4}$</td>
<td>87.04</td>
</tr>
<tr>
<td>0.68x10$^{-4}$</td>
<td>85.94</td>
</tr>
<tr>
<td>0.91x10$^{-4}$</td>
<td>85.30</td>
</tr>
<tr>
<td>1.18x10$^{-4}$</td>
<td>84.58</td>
</tr>
<tr>
<td>1.43x10$^{-4}$</td>
<td>85.66</td>
</tr>
<tr>
<td>1.69x10$^{-4}$</td>
<td>82.79</td>
</tr>
</tbody>
</table>

Table 3.15 Conductivity Measurements for Sodium [4-chloro-3-(parahydroxy phenylazo)] Benzoate in Water at 298.15K.

<table>
<thead>
<tr>
<th>c (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω⋅cm$^{2}$⋅mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.43x10$^{-5}$</td>
<td>78.13</td>
</tr>
<tr>
<td>3.10x10$^{-4}$</td>
<td>75.77</td>
</tr>
<tr>
<td>3.59x10$^{-4}$</td>
<td>75.66</td>
</tr>
<tr>
<td>4.06x10$^{-4}$</td>
<td>75.44</td>
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<td>76.50</td>
</tr>
<tr>
<td>4.99x10$^{-4}$</td>
<td>76.23</td>
</tr>
</tbody>
</table>

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### Table 3.16 Conductivity Measurements for Sodium [ortho (parahydroxyphenylazo)]

Benzoate in Methanol at 298.15K.

<table>
<thead>
<tr>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω$^{-1}$cm$^2$mol$^{-1}$)</th>
<th>$c$ (mol.dm$^{-3}$)</th>
<th>$\Lambda$ (Ω$^{-1}$cm$^2$mol$^{-1}$)</th>
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### Table 3.17 Conductivity Measurements for Sodium [meta (parahydroxyphenylazo)]

Benzoate in Methanol at 298.15K.

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Table 3.19 Conductivity Measurements for Sodium [\textit{5-chloro-2 (parahydroxy phenylazo)}] Benzoate in Methanol at 298.15K.

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Table 3.20 Conductivity Measurements for Sodium [6-chloro-2 (parahydroxy phenylazo)] Benzoate in Methanol at 298.15K.

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Table 3.21 Conductivity Measurements for Sodium [2-chloro-4 (parahydroxy phenylazo)] Benzoate in Methanol at 298.15K.

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Table 3.23 Conductivity Measurements for Sodium [ortho (parahydroxyphenylazo)] Benzoate in N,N'-Dimethylformamide at 298.15K.

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Table 3.25 Conductivity Measurements for Sodium [para (parahydroxyphenylazo)] Benzoate in N,N’-Dimethylformamide at 298.15K.

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Table 3.27 Conductivity Measurements for Sodium [6-Chloro-2-(parahydroxyphenylazo)] Benzoate in N,N'-Dimethylformamide at 298.15K.

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Table 3.28 Conductivity Measurements for Sodium [2-chloro-4 (parahydroxy phenylazo)] Benzoate in N,N'-Dimethylformamide at 298.15K.

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<td>1.95x10⁴</td>
<td>43.99</td>
<td>5.20x10⁴</td>
<td>39.30</td>
<td>7.94x10⁴</td>
<td>36.66</td>
</tr>
<tr>
<td>2.65x10⁴</td>
<td>43.04</td>
<td>5.83x10⁴</td>
<td>38.77</td>
<td>8.48x10⁴</td>
<td>36.28</td>
</tr>
<tr>
<td>3.31x10⁴</td>
<td>41.59</td>
<td>6.37x10⁴</td>
<td>38.13</td>
<td>9.13x10⁴</td>
<td>35.77</td>
</tr>
<tr>
<td>3.99x10⁴</td>
<td>40.65</td>
<td>6.90x10⁴</td>
<td>37.57</td>
<td>9.70x10⁴</td>
<td>35.39</td>
</tr>
</tbody>
</table>

Table 3.29 Conductivity Measurements for Sodium [4-chloro-3 (parahydroxy phenylazo)] Benzoate in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>c (mol.dm⁻³)</th>
<th>Λ (Ω⁻¹cm²mol⁻¹)</th>
<th>c (mol.dm⁻³)</th>
<th>Λ (Ω⁻¹cm²mol⁻¹)</th>
<th>c (mol.dm⁻³)</th>
<th>Λ (Ω⁻¹cm²mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06x10⁴</td>
<td>48.26</td>
<td>3.74x10⁴</td>
<td>41.55</td>
<td>5.95x10⁴</td>
<td>38.28</td>
</tr>
<tr>
<td>1.57x10⁴</td>
<td>46.52</td>
<td>4.22x10⁴</td>
<td>40.82</td>
<td>6.34x10⁴</td>
<td>38.28</td>
</tr>
<tr>
<td>2.16x10⁴</td>
<td>44.93</td>
<td>4.67x10⁴</td>
<td>40.18</td>
<td>6.71x10⁴</td>
<td>37.31</td>
</tr>
<tr>
<td>2.72x10⁴</td>
<td>43.71</td>
<td>5.12x10⁴</td>
<td>39.40</td>
<td>7.07x10⁴</td>
<td>37.01</td>
</tr>
<tr>
<td>3.23x10⁴</td>
<td>42.66</td>
<td>5.54x10⁴</td>
<td>38.74</td>
<td>7.43x10⁴</td>
<td>36.60</td>
</tr>
</tbody>
</table>
3.4.5 Analysis of Conductance Data. The Fuoss - Hsia Equation

The results of the conductance theories may be expressed in a general form by the equation:-

\[ \Lambda = \Lambda^0 - \alpha \Lambda^0 \cdot c^{1/2} / (1 + ka)(1 + ka/\sqrt{2}) - \beta \cdot c^{1/2} / (1 + ka) + G(ka) \quad 3.28 \]

where \( G(Ka) \) is, in general, a complicated function of the variable. However, in order to simplify the analysis of the experimental results, often an equation of the form:-

\[ \Lambda = \Lambda^0 - S \cdot \sqrt{c} + E \cdot c \cdot \ln c + J_1 \cdot c - J_2 \cdot c^{3/2} \ldots \quad 3.29 \]

is employed. This is obtained by expanding the general equation using the expressions:-

\[ e^x = 1 + x + x^2/2! + \ldots \quad 3.30 \]
\[ 1/(1 + x) = 1 - x + x^2 \ldots \quad 3.31 \]
\[ E_1(x) = -\Gamma - \ln x + x - \ldots \quad 3.32 \]

where \( \Gamma \) is Euler’s constant, and neglecting those terms which depend on a power of concentration higher than \( c^{3/2} \). \( S \), the limiting low coefficient derived by Onsager\(^{173} \), is given for symmetrical electrolytes by:-

\[ S = \alpha \Lambda^0 + \beta \quad 3.33 \]
\[ \alpha = 82.046 \times 10^4 Z^2 / (e \cdot T)^{3/2} \quad 3.34 \]
\[ \beta = 82.487 Z^2 / \eta (e \cdot T)^{1/2} \quad 3.35 \]

\( \alpha \) and \( \beta \) are characteristics of the solvent, \( \eta \) the viscosity of the solution (poise) and \( T \) the operating temperature (K).

The term \( E \) in equation 3.29, originates in the expansion of the exponential
integrals contained in the function $G(Ka)$. It also depends on the solvent physical properties and on the charge of the electrolytes. $E$ is expressed by:

$$E = E_1 - E_2$$  \hspace{1cm} (3.36)

$$E_1 = k(ab)^2/24.c = 2.94257 \times 10^{12}.z^2/(\varepsilon.T)^9$$ \hspace{1cm} (3.37)

$$E_2 = kab\beta/16.c^{1/2} = 4.33244 \times 10^7.z^2/\eta(\varepsilon.T)^2$$ \hspace{1cm} (3.38)

$$ba = (z.e)^2/e.k.T = 16.7099 \times 10^5.z^2/(\varepsilon.T)$$ \hspace{1cm} (3.39)

$$k = 50.2916.z.\sqrt{c/(\varepsilon.T)^{1/2}}$$ \hspace{1cm} (3.40)

Many equations of conductance were developed to fit the experimental data $(\Lambda^\circ,C)$. The association constant, $K_a$, the limiting conductance, $\Lambda^\circ$ and the ion-size parameter, $a^\circ$ are determined as parameters that best fit the experimental data. Among the equations used to determine these parameters, the Fuoss-Hsia equation, which has evolved from the older Fuoss-Onsager equations corrected is often used in the expanded form due to Fernandez-Prini. Another equation is that of Pitts. The difference between the Fuoss-Hsia equation and that of Pitts is that the latter implies smaller interionic effects for ions of the same size. This results in smaller association constants and smaller contact distances for Pitts than for Fuoss-Hsia. However, both equations take into account the "electrophoretic effect" and the "relaxation field effect". In addition, both have been expressed in the same form as in equation 3.29 limited to the term $c^{3/2}$.

$$\Lambda = \Lambda^\circ - S.\sqrt{c} + E.c.Lnc + J_1.c - J_2.c^{3/2}$$ \hspace{1cm} (3.29)

The terms $J_1$ and $J_2$ are given by the equations:-

$$J_1 = 2.E_1.\Lambda^\circ[\ln(ka/c^{1/2}) + \Delta_1] + 2.E_2[\Delta_2 - \ln(ka/c^{1/2})]$$ \hspace{1cm} (3.41)

$$J_2 = (kab/C^{1/2})[4.E_1.\Lambda^\circ.\Delta_3 + 2.E_2.\Delta_4] - \Delta_5$$ \hspace{1cm} (3.42)

$J_1$ and $J_2$ depend on the same parameters as $S$ and $E$, but also on the closest distance of approach of two ions, $a^\circ$.  

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The \( \Delta_i \) terms are expressed as functions of the parameter, \( b \). Table 3.4 shows the different expressions of \( \Delta_i \) obtained by Pitts and Fuoss-Hsia equations.

**Table 3.4 \( \Delta_i \) Terms of Pitts and Fuoss-Hsia Conductance Equations**

<table>
<thead>
<tr>
<th></th>
<th>Pitts</th>
<th>Fuoss-Hsia</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_1 )</td>
<td>( \frac{2}{b} + 1.7718 )</td>
<td>( \frac{1}{b^3}[2b^2 + 2b - 1] + 0.090735 )</td>
</tr>
<tr>
<td>( \Delta_2 )</td>
<td>( \frac{8}{b} + 0.01387 )</td>
<td>( \frac{22}{3b} + 0.01420 )</td>
</tr>
<tr>
<td>( \Delta_3 )</td>
<td>( \frac{1.2929}{b^2} + 1.5732/b )</td>
<td>( \frac{0.9571}{b^3} + \frac{1.1187}{b^2} + 0.1523/b )</td>
</tr>
<tr>
<td>( \Delta_4 )</td>
<td>( \frac{8}{b^2} + 1.4073/b )</td>
<td>( \frac{1}{b^3}[0.5738b^2 + 7.0572b - 2/3] - 0.6461 )</td>
</tr>
<tr>
<td>( \Delta_5 )</td>
<td>0</td>
<td>( \left[\frac{4}{3b} - 2.2194\right]E_2\beta/\Lambda^o )</td>
</tr>
</tbody>
</table>

The Fuoss-Hsia equation for conductance measurements, in its expanded form due to Fernandez Prini using a pit-mapping method, was used to analyse the experimental conductance data \( \Lambda_{\text{obs}}, \alpha \) for the sodium [parahydroxyphenylazo and chloro substituted parahydroxyphenylazo] benzoates in water, methanol and N,N'-Dimethylformamide at 298.15K. The corresponding association constants, \( K_a \), the limiting molar conductivities, \( \Lambda^o \) and the ion-size parameters of these electrolytes were obtained by minimising the sum of the square of the standard errors, \( s \). This is given by the equation:

\[
s^2 = \Sigma (\Lambda_{\text{obs}} - \Lambda_{\text{calc}})^2 \tag{3.43}
\]

\( \Lambda_{\text{obs}} \) and \( \Lambda_{\text{calc}} \) are the observed and the calculated molar conductivities respectively.

The procedure involves solving equations 3.44 and 3.45 using the least square method.

\[
\Delta = \Lambda^o \cdot S\sqrt{(\alpha \gamma) + E(\alpha \gamma) \text{Ln}(\alpha \gamma) + J_1(\alpha \gamma) - J_2(\alpha \gamma) + K_a \cdot \alpha \gamma^2} \cdot \alpha \gamma^2 \tag{3.44}
\]

\[
\Delta \Delta = \Delta \Delta^0 + \left[(\partial J_1/\partial \alpha^0)\cdot c + (\partial J_2/\partial \alpha^0)\cdot c^{2\alpha^0}\right]\Delta \alpha^0 - \gamma^2 \cdot \Delta(\alpha \gamma) \cdot \Delta K_a \tag{3.45}
\]
The coefficients of $\Delta a^0$ and $\Delta K_*$ depend on $\Lambda^0$, $a^0$ and $K_*$. 

Preliminary values of $\Lambda^0$, $a^0$ and $K_*$ are necessary. $\Lambda^0$ and $K_*$ may be first obtained from a Shedlovsky plot of the conductance data and $a^0$ is guessed or made equal to the Bjerrum distance. A first approximation to the degree of dissociation at each concentration $\alpha_i$ is obtained using the limiting law:

$$\alpha_i = \Lambda_i/(\Lambda^0 - S\sqrt{c_i\Lambda_i/\Lambda^0}) \quad 3.46$$

subscript $i$ denotes values corresponding to concentration $c_i$. Then, a new approximation is obtained from:

$$\alpha_i = \Lambda_i/(\Lambda^0 - S\sqrt{(\alpha_i,c_i) + E_i(\alpha_i,c_i)\ln(\alpha_i,c_i) + J_1(\alpha_i,c_i) - J_2(\alpha_i,c_i)^{3/2}}) \quad 3.47$$

and this last procedure is repeated until the difference between two consecutive values of $\alpha_i$ is smaller than a certain value, for example 0.00001. Then, the Debye-Hückel equation is employed to obtain $\gamma_\pm$ using $a^0$ in its denominator; and $\Delta\Lambda_i$ becomes:

$$\Delta\Lambda_i = \Lambda_{\text{obs}} - \Lambda_{\text{calc}} \quad 3.48$$

Equation 3.45 is solved by the method of least squares obtaining $\Delta\Lambda^0$, $\Delta a^0$ and $\Delta K_*$. A second step starts by putting:

$$\Lambda^0 = \Lambda^0 + \Delta\Lambda^0 \quad 3.49$$
$$a^0 = a^0 + \Delta a^0 \quad 3.50$$
$$K_* = K_* + \Delta K_* \quad 3.51$$

New values of $S$, $E$ and of $J_1$ and $J_2$ and their derivatives are obtained, and the calculation is repeated starting from 3.47, with $\alpha_i$ equal to $\alpha_i$ as found in the previous step. The iteration is continued until $\Delta\Lambda^0$, $\Delta K_*$ and $\Delta a^0$ are smaller than or equal to the desired precision.
Diagram 3.1 represents a flow-chart used in this work for the procedure of calculation of \( \Lambda^0 \), \( K_a \) and \( a^0 \) using the Fuoss-Hsia equation of conductance in its extended form due to Fernandez Prini.

The conductance data for sodium [para hydroxyphenylazo and chloro substituted para hydroxyphenylazo] benzoate measured in water, methanol and N,N'-Dimethylformamide at 298.15K were analysed using the Fuoss-Hsia equation. A computer program provided by Dr. M. Salomon (USA army ETDL (LABCOM), Power Source Division), was used for this purpose. Another computer program, written in Fortran 77, was devised to calculate primarily values of \( \Lambda^0 \) and \( K_a \) using the Shedlovsky equation\(^{187} \) of conductance for pair-wise associated electrolytes. The slope gives \( K_a \) and the intercept yields \( \Lambda^0 \). The program is presented in appendix A. The association constants, \( K_a \), the limiting molar conductance, \( \Lambda^0 \) for sodium [para hydroxyphenylazo and chloro substituted para hydroxyphenylazo] benzoate in water, metanol and N,N'-Dimethylformamide at 298.15K are listed in Table 3.30. Standard deviation of molar conductance, \( \sigma_\Lambda \) are also included.
Diagram 3.1 A flow-chart showing the procedure of calculation of $\Lambda^0$, $K_a$ and $a^0$. 
Table 3.30 Limiting Molar Conductance, $\Lambda^o$, Association Constant, $K_a$, for Haptens in Water, Methanol and N,N'-Dimethlyformamide at 298.15K.

<table>
<thead>
<tr>
<th>Hapten</th>
<th>Solvent: Water</th>
<th>$\Lambda^o$</th>
<th>$K_a$</th>
<th>$\sigma_\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Omega^1.cm^2.mol^{-1}$</td>
<td>mol.dm^{-3}</td>
<td>$\Omega^1.cm^2.mol^{-1}$</td>
</tr>
<tr>
<td>ortho (pOHPhN$_2$)NaB</td>
<td></td>
<td>85.21</td>
<td>9.49</td>
<td>0.36</td>
</tr>
<tr>
<td>meta  (pOHPhN$_2$)NaB</td>
<td></td>
<td>72.65</td>
<td>179.73</td>
<td>0.57</td>
</tr>
<tr>
<td>para  (pOHPhN$_2$)NaB</td>
<td></td>
<td>86.16</td>
<td>54.99</td>
<td>0.31</td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN$_2$)NaB</td>
<td></td>
<td>81.45</td>
<td>8.28</td>
<td>2.25</td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN$_2$)NaB</td>
<td></td>
<td>81.05</td>
<td>10.67</td>
<td>0.94</td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN$_2$)NaB</td>
<td></td>
<td>87.67</td>
<td>95.80</td>
<td>1.25</td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN$_2$)NaB</td>
<td></td>
<td>77.96</td>
<td>3.46</td>
<td>0.53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hapten</th>
<th>Solvent: Methanol</th>
<th>$\Lambda^o$</th>
<th>$K_a$</th>
<th>$\sigma_\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Omega^1.cm^2.mol^{-1}$</td>
<td>mol.dm^{-3}</td>
<td>$\Omega^1.cm^2.mol^{-1}$</td>
</tr>
<tr>
<td>ortho (pOHPhN$_2$)NaB</td>
<td></td>
<td>77.36</td>
<td>1.82</td>
<td>0.28</td>
</tr>
<tr>
<td>meta  (pOHPhN$_2$)NaB</td>
<td></td>
<td>81.10</td>
<td>1.01</td>
<td>0.54</td>
</tr>
<tr>
<td>para  (pOHPhN$_2$)NaB</td>
<td></td>
<td>71.55</td>
<td>0.47</td>
<td>0.45</td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN$_2$)NaB</td>
<td></td>
<td>78.69</td>
<td>11.60</td>
<td>0.15</td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN$_2$)NaB</td>
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<td>75.23</td>
<td>0.90</td>
<td>0.15</td>
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<td>65.91</td>
<td>1.10</td>
<td>0.19</td>
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<tr>
<td>4Cl-3 (pOHPhN$_2$)NaB</td>
<td></td>
<td>73.88</td>
<td>7.68</td>
<td>0.26</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Hapten</th>
<th>Solvent: DMF</th>
<th>$\Lambda^o$</th>
<th>$K_a$</th>
<th>$\sigma_\Lambda$</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>$\Omega^1.cm^2.mol^{-1}$</td>
<td>mol.dm^{-3}</td>
<td>$\Omega^1.cm^2.mol^{-1}$</td>
</tr>
<tr>
<td>ortho (pOHPhN$_2$)NaB</td>
<td></td>
<td>59.41</td>
<td>100.0</td>
<td>0.17</td>
</tr>
<tr>
<td>meta  (pOHPhN$_2$)NaB</td>
<td></td>
<td>48.74</td>
<td>809.9</td>
<td>0.42</td>
</tr>
<tr>
<td>para  (pOHPhN$_2$)NaB</td>
<td></td>
<td>47.75</td>
<td>757.0</td>
<td>0.41</td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN$_2$)NaB</td>
<td></td>
<td>59.79</td>
<td>88.9</td>
<td>0.18</td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN$_2$)NaB</td>
<td></td>
<td>62.04</td>
<td>141.4</td>
<td>0.10</td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN$_2$)NaB</td>
<td></td>
<td>49.22</td>
<td>479.1</td>
<td>0.12</td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN$_2$)NaB</td>
<td></td>
<td>53.03</td>
<td>799.0</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Values of $\sigma_\Lambda$ were calculated using $\sigma_\Lambda = (\sum(\Lambda_{obs} - \Lambda_{calc})^2/(N - 3))^{1/2}$
Although it is shown by the $\sigma_A$ values (Table 3.30), that the present theoretical treatment (Fuoss-Hsia) does not fit the experimental results so precisely as expected, one has to consider (a) The complexity of the system under study and, (b) In the context of this work, $K_+$ values are ancillary data required for the calculation of the free energy of solution, $\Delta G^\circ$. Despite the variations in the limiting molar conductances ($\Lambda^\circ$) of these electrolytes, it can be argued that the obtained association constants, $K_+$ are acceptable for the purpose of this work. Danil de Namor and co-workers$^{188}$ have shown that variations in $K_+$ do not lead to significant changes in the $\Delta G^\circ$ values.

The obtained $K_+$ values for sodium [parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo] benzoates in water and methanol at 298.15K are relatively small and therefore, these electrolytes are considered to be highly dissociated in water and in methanol. However, this is not the case in N,N'-Dimethylformamide and the $K_+$ values of these electrolytes are much higher than those in water and in methanol. Thus, sodium [parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo] benzoate are considered to be fairly associated electrolytes in N,N'-Dimethylformamide at 298.15K.

In order to evaluate the contribution of the anion and cation to the limiting molar conductance ($\Lambda^\circ$), the ionic limiting molar conductance ($\lambda_+^\circ$ and $\lambda_-^\circ$) were calculated.

### 3.4.6 Ionic Molar Conductance and Ionic Radii

Kohlraush confirmed that the value of $\Lambda^\circ$, for any electrolyte, can be expressed as the sum of contributions from its individual ions. If the molar conductivity of the cation is denoted $\lambda_+$, and that of the anions $\lambda_-$ then:

$$\Lambda^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$  

3.52
\( v_+ \) and \( v_- \) are the numbers of cations and anions per formula unit of electrolyte. Eqn 3.52 is known as the Law of Independent Migration of ions.

Using literature data for the ionic molar conductances \( (\lambda_{\text{Na}^+}) \) for sodium in water\(^{196}\), in methanol\(^{199}\) and in N,N'-Dimethylformamide\(^{191}\), corresponding data for parahydroxyphenylazo and chloro substituted parahydroxyphenylazo benzoate ions (\( \lambda_\text{x} \)) in these solvents were calculated. Then, the ionic molar conductance of parahydroxyphenylazo benzoate anions (\( \lambda_\text{x} \)) may be expressed by:

\[
\lambda_\text{x} = \Lambda^0 - \lambda_{\text{Na}^+}
\]

These data (\( \lambda_\text{x} \)) were used to calculate the ionic radii (\( r_\text{x} \)) of para hydroxyphenylazo benzoate anions in water, methanol and N,N'-Dimethylformamide according to the Stokes Law\(^{192,193}\). The ionic radii, \( r_\text{x} \) is given by:

\[
r_\text{x} = 0.820xz_\text{r}^2/\lambda_\text{x}\eta
\]

where \( z_\text{r} \) is the valence of the ion and \( \eta \) is the viscosity of the solvent in question at 298.15K.

Table 3.31 contains the different limiting molar conductances of these anions in water, methanol and N,N'-Dimethylformamide at 298.15K. Ionic radii (\( r_\text{x} \)) of these anions is also included.
Table 3.31 Ionic Limiting Conductance, $\lambda_\chi$ and Ionic Radii, $r_i$, of parahydroxy phenylazo Benzoate Anions in Water, Methanol and N,N'-Dimethyl Formamide at 298.15K.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Solvent: Water</th>
<th>Solvent: Methanol</th>
<th>Solvent: DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_\chi$</td>
<td>$r_i$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Omega^{-1}.\text{cm}^2.\text{mol}^{-1}$</td>
<td>Å</td>
<td></td>
</tr>
<tr>
<td><strong>ortho</strong> (pOHPhN$_2$)B$^-$</td>
<td>35.11</td>
<td>2.62</td>
<td>29.50</td>
</tr>
<tr>
<td><strong>meta</strong> (pOHPhN$_2$)B$^-$</td>
<td>22.55</td>
<td>4.08</td>
<td>18.84</td>
</tr>
<tr>
<td><strong>para</strong> (pOHPhN$_2$)B$^-$</td>
<td>36.06</td>
<td>2.55</td>
<td>17.85</td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN$_2$)B$^-$</td>
<td>31.35</td>
<td>2.94</td>
<td>29.90</td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN$_2$)B$^-$</td>
<td>30.97</td>
<td>2.97</td>
<td>32.10</td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN$_2$)B$^-$</td>
<td>37.57</td>
<td>2.45</td>
<td>19.30</td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN$_2$)B$^-$</td>
<td>27.86</td>
<td>3.31</td>
<td>23.40</td>
</tr>
</tbody>
</table>
It can be seen, from data in Table 3.31, that the obtained $r_e$ of these anions are higher in methanol than in N,N'-Dimethylformamide than in water, suggesting that these anions are more solvated in methanol than in N,N'-Dimethylformamide than in water. A better interpretation could be provided if the crystal radii, $r_c$, of these anions were available. It is currently suggested, if the Stokes radii is greater than the crystal radii, that this is an indication of solvation\textsuperscript{196}. However, crystal radii of these anions are not available and therefore, it cannot be taken as an indication for the degree of solvation. Clearly, this statement will be illustrated by the single-ion values for the transfer of these anions from water to N,N'-Dimethylformamide in Chapter 5, Table 5.45.
CHAPTER 4
SOLUTION CALORIMETRY
CHAPTER 4: SOLUTION CALORIMETRY

4.1 Calorimetry

A calorimeter is an instrument used to measure the change in internal energy or enthalpy, which occurs when a chemical system changes from an initial state to a final state. For practical purposes, different calorimeters have been used. They are classified as:-

**Adiabatic:** Whereby, the chemical system under investigation is perfectly insulated, thermally, from its surroundings. In practice, this is impossible to achieve.

**Isothermal:** Or heat conduction calorimeter whereby, the temperature of the system remains constant. This is practically achieved by perfectly connecting, thermally, the calorimeter with its surroundings.

**Isoperibol:** Whereby, heat exchanges between the system and the surroundings are minimised, but are nevertheless considered.

Each type of calorimeter has its own area of specific application. For instance, the heat conduction calorimeter, is at its best for rapid chemical reactions, whereas the adiabatic has distinct advantages for the study of slow processes. They may all be adapted to operate in either a batch addition or continuous flow mode.

In this work, the LKB 8700, the Tronac 450 and the Hart Scientific calorimeters were used. They all operate as isoperibol calorimeters. The Hart Scientific calorimeter can also operate in isothermal mode.

Standard enthalpies of solution were obtained by using the LKB 8700 and the Tronac 450 calorimeters. The Hart Scientific calorimeter was used as a titration calorimeter to obtain stability constants and enthalpies of complexation of
cyclodextrins and haptens in aqueous and non-aqueous media. Descriptions of these calorimeters are given.

4.2 The LKB 8700 Calorimeter

The LKB 8700-1 precision calorimetry system is a commercial version of the constant temperature environment non-isothermal calorimeter, originally designed by Sunner and Wadsö\textsuperscript{194}. It enables a very precise comparison to be made between an electrical experiment (calibration run) and an actual experiment (reaction run), in which a well defined process takes place. The temperature is measured as a function of time, and conditions are chosen so as to give as identical a temperature change as possible in both reaction and calibration experiments.

A block diagram of the system is presented in Figure 4.1. It can be divided into three main parts. These include:

a) The Calorimeter

The calorimeter consists of a 100 cm\textsuperscript{3} reaction vessel, made of thin pyrex glass and fitted with a calibration heater, thermistor, stirrer, a sapphire-tipped pad for ampoule breaking, and an outer metal container made of stainless steel and maintained at a constant temperature in a thermostated bath.

The thermistor can be used in the temperature range of 278-310 K (lower range limit set by the Wheatstone bridge). It has a resistance value of 2000 ohms ± 5\% at 298.15 K. The heater resistance, $R_h$, is 50 ohms ± 0.5\%.

The stirrer made of 18 carat gold and plated with pure gold which holds glass ampoules (1ml), is fixed to a stirrer running at a speed of 500 rpm.
Figure 4.1 Block Diagram Representing The LKB 8700 Calorimeter
b) The Thermostatic Bath

The thermostatic bath has a capacity of 18 litres and it is well insulated. A magnetic stirrer is mounted on the bottom to ensure adequate circulation of water around the centrally located calorimeter. Good temperature stability is achieved by using a proportional electronic thermostat. This thermostat is controlled by the thermistor probe, a 70 ohms heater and an auxiliary cooling system. This system gives a temperature of 1-3 K below the set point. Under these conditions, the bath temperature can be maintained at 298.15 ± 0.001 K over a 48 hour period.

c) The Electronic Assembly

The electronic assembly consists mainly of the Wheatstone bridge with a range of 0.6 KΩ over six decades. The thermistor inside the calorimeter vessel forms one of the arms of the bridge. Thus, the temperature change is monitored in terms of the thermistor resistance. The out-of-balance voltage is measured on an electronic galvanometer which may be connected to a chart recorder.

4.3 The Tronac 450 Calorimeter

The Tronac 450 operates as an isoperibol calorimeter. It is one of the commercial versions of the solution calorimeter originally designed by Christensen and Izatt\(^{35}\). It can be divided into two main parts, the calorimeter assembly and the electronic assembly.

a) The Calorimeter Assembly

The calorimeter assembly consists of a constant temperature bath with capacity of 55 litres, a motor-driven stirrer, cooled-heated assembly and a precision temperature controller (PTC-40) which provides an environment of constant temperature for the titrant and reaction vessel (± 0.002 K). The insert assembly
holds the stirrer, motorised burette, titrant lines, a glass vacuum Dewar reaction vessel (50 ml) and an electrical junction box. The reaction vessel contains a stirrer, a thermistor and a heater. The stirrer is a stainless steel blade assembly that holds the ampoule in such a way that it does not touch the wall of the reaction vessel.

The burette consists of a syringe (2.5 cm³) with 0.1% accuracy. It is made of glass and teflon with a micrometer attached to it.

b) The Electronic Assembly

The electronic assembly consists of a Wheatstone bridge, heater circuit and power supply. There are eleven heating rates available for selection (0.418-836.8 mJ.s⁻¹) using the power select switch. The bridge voltage is adjustable in the 1.5-15 V range, and it is monitored on the digital voltmeter (DVM). The sensitivity of the thermistor increases as the bridge voltage increases. The heating power of the reaction is being measured directly by monitoring the voltages across the standard resistor and the calibration heater resistance (100.02 ± 0.01 Ω at 298.15 K) during an electrical calibration run.

A strip chart recorder, with suitable span, is connected across the recorder terminals to ensure a continuous reading out of the process under investigation.

c) Specifications of the Tronac 450 Calorimeters

The precision obtained of the enthalpy measurement by using the Tronac 450 calorimeter is about ± 0.5% on heat values of 2 calories. A temperature resolution of ± 0.0001 K can be obtained with a 1 mV recorder (input impedance at least 100 KΩ). The response time, limited by the thermistor, is of 3 seconds.
d) Use of the Tronac 450 Calorimeter

The Tronac 450 calorimeter can be used as:-

i) A thermometric titrator for analytical applications.
ii) A conventional solution calorimeter, for enthalpy change measurements or any liquid-liquid or solid-liquid system.
iii) An incremental or continuous titration calorimeter, for enthalpy measurements involving proton ionisation, metal-ligand interaction and equilibrium constant determination.

In the present work, the Tronac 450 was used as a conventional solution calorimeter.
4.4 Characteristics of the Time-Temperature Curve

An analysis of the temperature-time curve has been published by Wadso. Figure 4.2 shows a typical temperature-time curve from a calorimetric experiment where heat is evolved, i.e., an exothermic reaction or an electrical calibration experiment. Temperature-time readings may start when the calorimetric system is thermally steady. From A to B (initial period) a linear behaviour is observed. The reaction is initiated at B and has been completed before point C. This is called the "reaction or main period". The calorimetric curve is linear again during the final period, C-D.

In Figure 4.2, Tj is the notation used to indicate the temperature of the surrounding thermostatic bath (the Jacket-calorimeter), and T∞ indicates the temperature which the calorimeter vessel will approach if the final period is prolonged to infinity. For the LKB reaction calorimeter, T∞ is normally about 0.005 degrees higher than Tj.
4.5 The True Temperature Change
4.5.1 Measurement of Temperature Change

Production and exchange of heat have always been considered in terms of temperature change but, what is really determined with the thermistor operated calorimeter are resistance changes.

A linear correlation between the resistance, R, and the temperature, T, is not accurate and it cannot be assumed that $\Delta T = \Delta R$.

However, the change in thermistor resistance, R, as a function of temperature, T, may be expressed as:

$$R = A \cdot e^{B/T}$$

where T is expressed in Kelvin and R is given in ohms. A and B are constants characteristic of each solvent. In practice, A and B are obtained by determining the thermistor resistance at two different temperatures.

Derivation of equation 4.1 will lead to:

$$\frac{dR}{dT} = -\frac{R \cdot B}{T^2}$$

or

$$\frac{\Delta R}{\Delta T} = -\frac{R_m \cdot B}{T_m^2}$$

In equation 4.3, $\Delta R$ and $\Delta T$ are the corrected resistance and temperature change respectively. $R_m$ and $T_m$ represent the mean value. Thus,

$$\Delta T \propto -T_m^2(\Delta R/R_m)$$

In order to use this expression, the bridge must be calibrated in temperature units. However, for a series of calorimetric experiments, $T_m$ should be constant and
approximately equal to the equilibrium temperature. This leads to the expression:

\[ \Delta T = k(\Delta R/R_m) \]  \hspace{1cm} (4.5)

where \( \Delta R = R_f - R_i \), \( R_m = (R_f + R_i)/2 \) and \( k \) has units of kelvin representing a constant combining \( B \) and \( T_m \) terms.

Wadsö\textsuperscript{96} showed that equation 4.5 is accurate for measurements up to 0.1% precision.

### 4.5.2 Determination of the Thermistor Constants

The thermistor constants \( A \) and \( B \) are characteristics of the solvent under investigation. These are determined by comparison between two resistance values of the thermistor at two different temperatures.

From eqn. 4.1, we have \( R = A \cdot e^{B/T} \). Thus, \( \ln R = \ln A + B/T \) \hspace{1cm} (4.6)

at \( T = T_1 \), \( R = R_1 \) and \( \ln R_1 = \ln A + B/T_1 \) \hspace{1cm} (4.7)

and \( T = T_2 \), \( R = R_2 \) and \( \ln R_2 = \ln A + B/T_2 \) \hspace{1cm} (4.8)

Solving equations 4.7 and 4.8 for \( A \) and \( B \) would lead to:-

\[ B = ((T_2 - T_1)/(T_1,T_2)) \cdot \ln(R_1/R_2) \] \hspace{1cm} (4.9)

and \[ A = R_1 + (R_1 - R_2) \cdot e^{(T_1 - T_2)/(T_1,T_2)} \] \hspace{1cm} (4.10)
4.5.3 The True Temperature Change

For an isoperibol calorimeter, in general, the temperature change obtained during the main period of an experiment, is not solely determined by the amount of heat liberated or absorbed by the process under investigation. A certain part of the change is due to:

i) The exchange with the environment.

ii) Extraneous thermal effects within the calorimeter vessel, such as the heat of stirring, Joule heating by an electrical thermometer and heat due to ampoule breaking etc.

The true temperature change, $\Delta T_{\text{corr}}$, is defined as the observed temperature change, $\Delta T_{\text{obs}}$, that the calorimeter would have experienced in the absence of the above-mentioned perturbations, $\Delta T$. Thus, if the thermal gradients within the calorimeter are neglected, it can be written that:

$$\Delta T_{\text{corr}} = \Delta T_{\text{obs}} - \Delta T$$  \hspace{1cm} (4.11)

Dickinson, Regnault and Pfaudler and Gunn described numerical methods for the calculations of the true temperature change of the calorimeter. Wadsö has recommended to apply the Regnault-Pfaudler method to reactions with a reaction time over 5 minutes and the Dickinson method of extrapolation with reactions that have a reaction time less than 5 minutes.

In this work, the numerical Dickinson’s method of extrapolation and the Regnault-Pfaudler method were applied to heat of solution measurements obtained by the LKB 8700 calorimeter. To facilitate the application of these two numerical methods, a computer program written in Fortran77 was devised for each method (see Appendix B). The graphical Dickinson’s method of extrapolation was also implemented in order to determine heats of solution obtained from the Tronac 450
4.5.3.1 Heat Exchange Between the Calorimeter and its Surroundings

The heat exchange between a calorimeter and its surrounding jacket is due to:

1. Conduction via solid connections between them (e.g., support pegs and electrical lead wires).
2. Convection and conduction by gas molecules (normally air) occupying the interspace.
3. Radiation.
4. Evaporation losses from an unsealed calorimeter containing liquid.

Points (1), (2) and (3) are dependent on the existence of a temperature difference between the calorimeter and its jacket. Evaporation losses are preferably eliminated by using a sealed calorimeter.

Provided that the convection heat transfer is minimised, by suitably designing the calorimeter and jacket assembly, and that the thermal head between the calorimeter and its jacket is no more than a few degrees, the heat exchange between calorimeter and environment may obey Newton’s Law of Cooling. This can be expressed as:

\[
\frac{dT}{dt} = K (T_j - T)
\]

where \( T \) is the calorimetric temperature at time, \( t \). \( T_j \) is the jacket temperature (maintained at a constant value) \( K \) is the leakage modulus of the system.
a) Calculation of Heat Exchange

![Time-Temperature Curve](image)

**Fig 4.3 Time-Temperature Curve for a Calorimetric Experiment.**

(Reprinted from Coops, Jessup and van Nes, 1956).

$T_a$ and $T_b$ denote the calorimeter temperatures at the beginning and at the end of the main period.

$T_e - T_b$ is the "observed" temperature change.

$T_i$ is the mean temperature of the initial period.

$T_a$ and $T_b$ denote the calorimeter temperatures at the beginning and at the end of the final period.

$T_f$ is the mean temperature of the final period.

$T_j$ is the temperature of the thermostatic bath, but also the temperature of the jacket.

$T_{\infty}$ is the temperature at which the time-temperature curve levels off.

The total rate of temperature rise, $g$, due to stirring and leakage is given by:

$$g = \frac{dT}{dt} = u + K(T_j - T) \quad 4.13$$

At $T = T_{\infty}$, we have:

$$\frac{dT}{dt} = 0$$

Therefore,

$$u = -K(T_j - T_{\infty}) \quad 4.14$$

$$g = \frac{dT}{dt} = K(T_{\infty} - T) \quad 4.15$$
b) The Thermal Leakage Modules, K

The thermal leakage modulus, K, is characteristic of each calorimetric vessel provided that its heat capacity remains constant. It provides useful information on the accuracy of the heat measurement. A deviation in the value of K indicates that thermal disturbances took place during the main period of the experiment. It can also be used to check that a chemical reaction has ended.

Let \( g_i \) and \( g_f \) be the measured values of \( dT/dt \) at the mean temperatures, \( T_i \) and \( T_f \) of the initial and final periods. Then by making use of equation 4.10 and on the assumption that \( K \) remains constant, this would lead to:

\[
g_i = K (T_\infty - T_i) \tag{4.16}
\]

\[
g_f = K (T_\infty - T_f) \tag{4.17}
\]

By subtracting 4.16 from 4.17, the thermal leakage constant can be obtained:

\[
K = (g_i - g_f)/(T_f - T_i) \tag{4.18}
\]

4.5.3.2 Correction Term for the Temperature Change

The correction term for the temperature change of an isoperibol calorimeter can be obtained by integration of the rate of the temperature change over the time limits of the main period of the time-temperature curve.

\[
\Delta T = K \int_{t_i}^{t_f} (T_\infty - T) \, dt \tag{4.19}
\]

\[
\Delta T = K \int_{t_i}^{t_m} (T_\infty - T) \, dt + K \int_{t_m}^{t_f} (T_\infty - T) \, dt \tag{4.20}
\]

Equation 4.19 can be solved by applying the mean value theorem. Thus,

\[
\Delta T = K.(T_\infty - T_m) \Delta t \tag{4.21}
\]
$T_\infty$ can be derived from equations 4.16 and 4.17. It is given by:

$$T_\infty = \frac{g_f}{K} + T_i = \frac{g_f}{K} + T_f \quad 4.22.a$$

Replacing $T_\infty$ by its value in equation 4.21 will lead to:

$$\Delta T = [g_i + K(T_i - T_m)] \Delta t \quad 4.22$$

$$\Delta T = [g_e + K(T_f - T_m)] \Delta t \quad 4.23$$

Equations 4.22 and 4.33 are known as the Regnault-Pfaudler equations.

4.5.3.3 Finding of the Mean Temperature, $T_m$

The mean temperature of the main period of an actual reaction run or of a calibration run, $T_m$ can be obtained by either a graphical or a numerical method. $T_m$ is obtained in such a way that Area I is made equal to Area II (see Figure 4.5). $T_m$ may be determined by using Dickinson’s method of extrapolation or the Regnault-Pfaudler method (Fig. 4.4)
I. The Regnault-Pfaudler Method

a) Graphical Method

Fig. 4.4 Diagram showing the graphical Regnault-Pfaudler method to determine $T_m$.

The area below the curve of the main period of an actual reaction run or an electrical calibration run should be divided into a suitable number of trapezia so that the time-temperature curve is approximated. For each of these trapezia, a mean temperature is evaluated, and their weighted mean value is taken as:

$$T_m = \frac{(a \cdot T_m' + b \cdot T_m'' + c \cdot T_m''' + \ldots)}{(a + b + c + \ldots)} \quad 4.24$$

b) Integration Method

This method requires the measurement of $n$ temperatures, $T_r$, at equal time intervals $\Delta t$, over the main period of the calorimetric run. The average temperature, $T_m$, is given by:

$$T_m = \frac{\sum_{r=2}^{n} T_r + (T_B + T_C)/2) \cdot \Delta t/(t_i - t_j)} \quad 4.25$$

Or,

$$T_m = \frac{\sum_{r=2}^{n} T_r + (T_B + T_C)/2)/(n-1)} \quad 4.26$$
A computer program for the Regnault-Pfaudler method, written in Fortran77 Language, was devised and used to calculate the mean temperature, $T_m$ (see Appendix B).

**II- The Dickinson's Method of Extrapolation**

**b) Graphical Method**

![Graphical Method Diagram](image)

Fig. 4.5 Typical resistance vs time plot showing the graphical method of Dickinson.

The graphical method of Dickinson involves taking the pre and post-period of the time-temperature curves. An extrapolation to a defined time, such as that the difference of their values at that time is equal to the corrected temperature change. This "extrapolation time" is determined from a graphical integration of the time-temperature curve during (Figure 4.5) the main period of a calorimetric run. Such a method has significant advantages in many fields of calorimetry. Foremost amongst these is the rapidity of the calculation. Another advantage is the adaptability of the method to modern instrumental technique.
b) Numerical Method

i) Reaction Experiment

Dickinson assumed that the resistance change follows an exponential path.

Let \( R_f = 0 \) such that \( \Delta R = R_i \) and \( t_i = 0 \) (see Figure 4.5.3)

Then

\[
\text{Area I} = R_i t_m - \int_0^{t_m} R_i e^{kt} \, dt
\]

\[= R_i (t_m + (1/k)(e^{kt_m} - 1)) \quad 4.27a
\]

\[
\text{Area II} = \int_0^{\infty} R_i e^{kt} \, dt = R_i / k \cdot e^{kt_m} \quad 4.28
\]

When \( \text{Area I} = \text{Area II} \)

Then

\( t_m = 1/k \quad 4.29\)

and

\( R_m = R_i e^{kt_m} = R_i / e \quad 4.30\)

Therefore, a fraction of the total resistance change at \( t_m \) is equal to:

\[
\frac{(R_i - R_i/e)/R_i}{1 - 1/e} = 0.63 \quad 4.31
\]

This means that the mean temperature of the main reaction would occur at 63% of heat evolution. In another term if \( R_m \) is unknown e.g. a back-off experiment, then \( t_m = t_i/(2 \ln 2) \) (\( t_i/\ln 2 \) half-life time). After \( 7t_i/\ln 2 \) more than 99% of the reaction takes place. Therefore,

\[
t_m = t_i + (t_f - t_i)/7 \ln 2 = t_i + (t_f - t_i)/5 \quad 4.32
\]

ii) Calibration Experiment

Dickinson assumed that the resistance change follows a linear path. Therefore, a fraction of the total resistance change at \( t_m = 0.5 \). In other words if \( R_m \) is not known, then:

\[
t_m = t_i + (t_f - t_i)/2 \quad 4.33
\]
A computer program for the Dickinson's Method of Extrapolation, written in Fortran77 Language, was used (see Appendix B).

4.6 Electrical Calibration - Heat Capacity

In order to determine the heat capacity of the calorimetric system, an electrical calibration must be carried out before or after the actual reaction takes place. For this, electrical heat is introduced over a precisely timed interval and the temperature change in the system is measured. The calibration experiment was carried out over the same range of temperature change as in the reaction experiment so that a maximum accuracy could be achieved.

a) Calibration Before Reaction

If the electrical calibration is carried out before the reaction has taken place, the obtained heat capacity (ε) value will refer to the isothermal process at the final temperature of the experiment. This can be explained as follows:-

Assuming that the starting system is S, the product is P and the calibration is performed between temperatures T₁ and T₂, then:

<table>
<thead>
<tr>
<th>Calibration: S(T₁)</th>
<th>S(T₂)</th>
<th>ΔH = Q'ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(T₁)</td>
<td>P(T₂)</td>
<td>ΔH = 0</td>
</tr>
<tr>
<td>S(T₂)</td>
<td>P(T₂)</td>
<td>ΔH₁₂ = -Q'ε</td>
</tr>
</tbody>
</table>

Equation 4.34 shows an increase in enthalpy equal to the calibration heat. Equation 4.35 shows that there is no enthalpy change (ΔH = 0, this is because heat evolved is kept within the calorimetric system). Then ε-value is obtained at T₂ (the temperature of the final period of the experiment).
b) Calibration After Reaction

When calibration is carried out after the reaction run, the following steps are considered:

Reaction: \[ S(T_i) \rightarrow P(T_f) \quad \Delta H = 0 \]  
Calibration: \[ P(T_i) \rightarrow P(T_f) \quad \Delta H = Q'' \]  
\[ S(T_i) \rightarrow P(T_f) \quad \Delta H_{T_1} = -Q'' \]

In this case, \( \varepsilon \)-value is referred to \( T_1 \) (the temperature of the initial period of the experiment). If, calibration and reaction experiments are carried out over the same range of temperature \( (T_1 - T_2) \) therefore,

\[
\begin{align*}
T_{1c} & \approx T_{1r} \\
T_{2c} & \approx T_{2r} \\
\Delta T_c & \approx \Delta T_R
\end{align*}
\]

and \( \varepsilon \)-value of calibration = \( \varepsilon \)-value of reaction

4.7 Enthalpy Change Measurements By Using The LKB 8700 Solution Calorimeter

4.7.1 Heat Measurements

a) Calibration Experiment

The amount of heat released during a calibration, \( Q_c \), is obtained from the expression:

\[ Q_c = I_c^2 R_H t \]

where \( I_c \) is the current measured in amperes (A), \( R_H \) is the heater resistance (\( \Omega \)) and \( t \) is the heating time in seconds.
b) Reaction Experiment

The heat released or absorbed during the main period of a reaction experiment, $Q_r$, may be expressed by:

$$Q_r = \varepsilon \Delta T_{\text{corr}} = \varepsilon \frac{\Delta R}{R_{\text{mo}}}$$

where $\varepsilon$ is the heat capacity of the calorimetric system and it is expressed in J.K$^{-1}$ units. $\Delta T_r$ is the notation used to indicate the true temperature change, expressed in kelvin (K).

Assuming that the calibration experiment is performed over the same range of temperature change as the actual reaction experiment, the heat capacity, $\varepsilon$, can then be derived from the calibration experiment. The amount of heat released during a calibration experiment can also be expressed as:

$$Q_c = \varepsilon \Delta T_{\text{corr}}$$

Therefore, $\varepsilon = Q_c / \Delta T_{\text{corr}}$ ; and $Q_r = Q_c \Delta T_{r,\text{corr}} / \Delta T_{c,\text{corr}}$

4.7.2 Measurement of Molar Enthalpy

The molar enthalpy is related to the amount of heat evolved during the reaction main period experiment, $Q_r$, as given in the following equation:

$$\Delta H = \frac{Q_r}{n}$$

where $n$ is the number of moles of the solute dissolved in the calorimetric system under investigation. The number of moles is given by:
\[ n = \frac{m}{M} \quad 4.49 \]

\( m \) and \( M \) are the mass and the molecular weight of the solute in question, respectively.

4.8 Enthalpy Change Measurements from the Tronac 450 Solution Calorimeter

The temperature-time plots, to measure the enthalpy change of solution, as obtained by using the Tronac 450 calorimeter were analysed by the graphical method of extrapolation, suggested by Dickinson\(^*\).

The heat capacity of the calorimetric system can be determined from the temperature change (\( \Delta T \)) and the amount of heat added to the system (\( Q_c \)) using the relation:

\[ \varepsilon = \frac{Q_c}{\Delta T} = \frac{Q_c}{d_c} \quad 4.50 \]

\( Q_c \), which is the heat of calibration is calculated using the equation:

\[ Q_c = P \cdot R \cdot t \quad 4.51 \]

\( t \), is time in seconds during which the current is passed, and the term \( P \cdot R \) is the power dissipated in the heater as given by:

\[ P = \frac{V_1 \cdot V_2}{R} \quad 4.52 \]

\( V_1 \) and \( V_2 \) are the voltage readings taken in the heater voltage positions. \( R(100.02 \Omega) \) is the heater resistance.

For a reaction experiment, the heat of reaction, is calculated by:-
\[ Q_r = Q_c \frac{d_R}{d_c} \]

where \( Q_c \) is the calibration heat giving a calibration distance, \( d_c \), and a reaction giving a reaction distance, \( d_R \), as measured from the temperature-time curve in mm.

The enthalpy change of a reaction, \( \Delta H_r \), is then calculated from the expression:

\[ \Delta H_r = \frac{Q_r}{n} \]

where \( n \) is the number of moles of the solute.

4.9 Miscellaneous Corrections

When determining heat measurements, corrections for extra heats must be made. These are heat effects associated with:

1) The initiation of the reaction: this is due to ampoule breaking and ampoule holder or its shaft movement.

2) Incompletely filled ampoule: which could cause the evaporation of the calorimetric liquid as well as partial evaporation of ampoule content, if volatile.

3) Change in vapor pressure of the calorimetric liquid: this is caused by either change in temperature of the calorimetric liquid or as a result of dissolution of the ampoule content.

4) Evolution of gas in the reaction: this would cause saturation of the calorimetric liquid with its vapor also extra heat would be evolved, if the gas released is soluble enough in the calorimetric liquid.
5) Partial vaporisation of volatile reaction components: this may call for a correction to make up for the corresponding heat of vaporisation. If part of the ampoule content vaporises, this must be taken into account when the molar enthalpy is calculated.

In the present work, only corrections due to ampoule breaking in methanol and N,N'-Dimethylformamide were applied. However, this was neglected in water.

4.10 Accuracy of Calorimetric Measurements

It is important to distinguish between the precision of the measurements and their accuracy. The term "precision" is a measure of the reproducibility of the experimental results, whereas "accuracy" defines how close the experimental results are to reality.

The measure of precision is based on the random errors in a series of experiments. Precision is thus an upper limit to accuracy, which will normally be less than the precision suggests. The usual measure of precision in modern calorimetry is the standard deviation of the mean, $\sigma$. This is given by:

$$\sigma = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n(n - 1)}}$$ 4.55

where $X_i = $ value of the $i$th measurement, $\bar{X} = $ average value of $n$ measurements and $n =$ total number of measurements.

If electrical calibration experiments yield a mean value $\bar{E}$ (subject to a standard deviation $= \sigma_E$) for the energy equivalent of the calorimeter and separate calorimetric measurements yield a mean value $Q$ (subject to a standard deviation $= \sigma_Q$) for the heat of the process under investigation, the overall standard deviation to be assigned to $Q$ is given by:-
\[ \sigma = Q \sqrt{\left(\sigma_E^2 + \sigma_Q^2\right)} \]

The uncertainty interval, equal to \(2\sigma\), is normally accepted as the overall uncertainty in the precision of measurement of the heat quantity, \(Q\).

Many of the items contributing to the overall accuracy of a given measurement can be independently assessed. These include the following:

1. Accuracy of weights and volume measurements.
2. Accuracy of measurements of time intervals.
3. Accuracy of temperature measurement.
4. Accuracy of electrical equipment used in electrical calibration.
5. Accuracy of the calorimeter in specific test processes.
6. Accuracy of "corrections applied".
7. Purity of chemical reagents used.
8. Analysis of the process presumed to occur in the calorimeter.

The most frequent causes of systematic errors, however, arise from impurities in the chemical reagents used(7) and to insufficient analysis of the process taking place in the calorimeter(8).

### 4.11 Calorimetric Measurements

#### 4.11.1 Experimental Procedure

a) Reaction Experiment

An accurate dry amount, of the chemical under investigation, was weighed out in a cylindrical ampoule using a semi-microbalance with a precision of 0.00001g. The ampoule was then sealed with a rubber bung, placed into the ampoule holder and immersed into the reaction vessel in which an exact volume of solvent was poured using a pipette(grade A). Next, the temperature of the calorimetric
system was raised to a temperature of slightly less than 298.15 K. At this stage, the reaction vessel was placed into the jacket, immersed in the thermostated water bath and left for about 20 minutes to reach thermal equilibrium. After the system had reached thermal equilibrium, before, during and after which readings of resistance and time were taken, the ampoule was broken into the solvent (LKB 8700 Calorimeter). For measurements carried out with the Tronac 450 calorimeter, the process was monitored by a means of a chart recorder.

When measuring heat of solution of hygroscopic chemicals, extra care was taken. The chemicals were first dried under vacuum for several days, then placed in ampoules within a nitrogen box free of humidity. Weights of the ampoules were recorded, before and after filling the ampoule with the chemical outside the nitrogen box.

\textit{b) Electrical Calibration}

In order to obtain maximum precision of a heat of solution measurement, an electrical calibration was performed following every reaction experiment. This is achieved by passing a known current through a heater resistance for a selected time interval and measuring the corresponding temperature change. The electrical calibration experiment was carried out under the same conditions and for approximately the same temperature change as in the reaction experiment.

\textbf{4.11.2 Heat of Ampoule Breaking}

The heat of ampoule breaking was carried out by breaking an empty sealed ampoule (1ml) in the relevant solvent, and measuring its corresponding temperature change in the reaction vessel. The same experimental procedure, as described for a reaction experiment, was followed.

Heat of ampoule breaking determined in N,N'-Dimethylformamide, methanol
and different solvent mixtures of water and methanol at 298.15K using the Tronac 450 calorimeter are listed in Table 4.11.1.

Table 4.11.1 Heat of Ampoule Breaking in N,N'-Dimethylformamide, Methanol and Different Mixtures of Water and Methanol as Obtained using the Tronac 450 Calorimeter at 298.15 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Q&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Q&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Number of Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>-0.0518 ± 0.0025</td>
<td>0.01423</td>
<td>7</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.3235 ± 0.0031</td>
<td>0.26167</td>
<td>8</td>
</tr>
<tr>
<td>MeOH:H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:90</td>
<td>0.0312 ± 0.0070</td>
<td>0.0578 ± 0.0056</td>
<td>5</td>
</tr>
<tr>
<td>30:70</td>
<td>0.0445 ± 0.0160</td>
<td>0.0796 ± 0.0050</td>
<td>5</td>
</tr>
<tr>
<td>40:60</td>
<td>0.1209 ± 0.0060</td>
<td>0.1209 ± 0.0060</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup> This work.

<sup>b</sup> average heat of ampoule breaking taken from ref. 133
4.11.3 Calibration of the Calorimeter

The requirements for a standard reaction have been examined by Gunn and referred to a rapid, exothermic, non-gas liberating and highly precise reaction.

The heat of solution of potassium chloride, the heat of reaction of sulphuric acid with excess of sodium hydroxide and the heat of reaction of TRIS (hydroxymethyl) aminomethane, known as THAM or TRIS, with hydrochloric acid (0.1 mol.dm$^{-3}$) are used as standard chemical reactions in reaction calorimetry in order to check the accuracy and the reproducibility of a calorimeter.

The TRIS reaction suggested by Irving and Wadsö is the most commonly used standard chemical reaction. TRIS is a crystalline compound with a melting point of 444.25K. It is a weak base ($pK_b = 5.92$). It has a low degree of hygroscopicity and does not absorb carbon dioxide ($CO_2$). TRIS is readily soluble in water and has therefore, found use as a primary acidimetric standard. The heat associated with this, corresponds to the following process:

$$H_2NC(CH_2OH)_3 + H_3O^+ \rightarrow H_2N^+C(CH_2OH)_3 + H_2O$$

The reproducibility of the LKB 8700 and Tronac 450 calorimeters was checked by determining the $\Delta H$ values for the standard TRIS reaction with hydrochloric acid (0.1 mol.dm$^{-3}$). The obtained results listed in Tables 4.11.2 and 4.11.3 are in good agreement with the published values reported in Table 4.11.4. Details of calculations of the standard enthalpy of reaction of TRIS in HCl(0.1 mol.dm$^{-3}$) obtained by the LKB 8700 and the Tronac 450 are shown in Table 4.11.2 and 4.11.3.
### Table 4.11.2 Enthalpy of Solution of TRIS in 100 ml of Hydrochloric Acid (0.1 mol.dm\(^{-3}\)) obtained with the LKB 8700 Calorimeter at 298.15 K.

<table>
<thead>
<tr>
<th>Mass of THAM (g)</th>
<th>Heat Capacity (c) (J.K(^{-1}))</th>
<th>Heat Released (Q_R) (J)</th>
<th>(\Delta H^0) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50032</td>
<td>428.0</td>
<td>69.515</td>
<td>-29.75</td>
</tr>
<tr>
<td>0.56361</td>
<td>429.0</td>
<td>69.353</td>
<td>-29.75</td>
</tr>
<tr>
<td>0.53293</td>
<td>428.0</td>
<td>69.427</td>
<td>-29.72</td>
</tr>
<tr>
<td>0.59752</td>
<td>428.5</td>
<td>69.356</td>
<td>-29.72</td>
</tr>
<tr>
<td>0.54209</td>
<td>429.0</td>
<td>69.382</td>
<td>-29.77</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H^0\) = -29.74 ± 0.02 kJ.mol\(^{-1}\)

### Table 4.11.3 Enthalpy of Solution of TRIS in 50 ml Hydrochloric Acid (0.1 mol.dm\(^{-3}\)) obtained with the Tronac 450 Calorimeter at 298.15K.

<table>
<thead>
<tr>
<th>Mass of THAM (g)</th>
<th>(\Delta H^0) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26098</td>
<td>-29.71</td>
</tr>
<tr>
<td>0.26001</td>
<td>-29.62</td>
</tr>
<tr>
<td>0.25809</td>
<td>-29.64</td>
</tr>
<tr>
<td>0.25541</td>
<td>-29.77</td>
</tr>
<tr>
<td>0.24321</td>
<td>-29.61</td>
</tr>
<tr>
<td>0.24761</td>
<td>-29.67</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H^0\) = -29.70 ± 0.06 kJ.mol\(^{-1}\)
Table 4.11.4 Standard Enthalpy of Reaction of THAM with a Solution of 0.1 mol.dm$^3$ Hydrochloric Acid at 298.15K.

<table>
<thead>
<tr>
<th>Author</th>
<th>$\Delta H^\circ$, kJ.mol$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irving and Wadsö</td>
<td>-29.735 ± 0.017</td>
<td>205</td>
</tr>
<tr>
<td>Gunn S. R.</td>
<td>-29.735 ± 0.004</td>
<td>202</td>
</tr>
<tr>
<td>Sunner and Wadsö</td>
<td>-29.757 ± 0.008</td>
<td>206</td>
</tr>
<tr>
<td>Irving and Wadsö</td>
<td>-29.757 ± 0.008</td>
<td>208</td>
</tr>
<tr>
<td>Ojelund and Wadsö</td>
<td>-29.757 ± 0.017</td>
<td>207</td>
</tr>
<tr>
<td>Irving and Sonsa</td>
<td>-29.748 ± 0.004</td>
<td>208</td>
</tr>
<tr>
<td>Hill et al</td>
<td>-29.744 ± 0.004</td>
<td>209</td>
</tr>
<tr>
<td>Gunn S. R.</td>
<td>-29.736 ± 0.004</td>
<td>204</td>
</tr>
<tr>
<td>Ghousseni L. (Tronac)</td>
<td>-29.690 ± 0.071</td>
<td>136</td>
</tr>
<tr>
<td>Bdokhti H. N.</td>
<td>-29.748 ± 0.017</td>
<td>208</td>
</tr>
<tr>
<td>This work (LKB)</td>
<td>-29.740 ± 0.020</td>
<td></td>
</tr>
<tr>
<td>This work (Tronac)</td>
<td>-29.700 ± 0.060</td>
<td></td>
</tr>
</tbody>
</table>

These values, $\Delta H^\circ$(THAM) = -29.74 ± 0.02 kJ.mol$^{-1}$ and -29.70 ± 0.06 kJ.mol$^{-1}$, compares well with $\Delta H$ values previously reported for this reaction. It should be pointed out that most of the literature values refer to calorimetric measurements using the LKB calorimeter and not the Tronac.
CHAPTER 5
THERMODYNAMIC PARAMETERS
OF
HAPTENS AND CYCLODEXTRINS
IN
WATER, METHANOL
&
DMF
CHAPTER 5: THERMODYNAMIC PARAMETERS OF TRANSFER

5.1 Standard Thermodynamic Parameters for Transfer of Haptens from Water to Non-Aqueous Solvents at 298.15 K.

5.1.1 Solubilities and Derived Free Energies of Transfer of Haptens

The solubility of an electrolyte in any solvent is largely determined by the extent of solvation of the ions, solvent-solvent interactions and other effects such as volume energy. Solubility measurements provide useful data for evaluation of thermodynamics of ion-solvent interactions. For instance, from solubility data, solubility products, $pK_v^*$, free energies of solution, $\Delta G^\circ$, standard enthalpies of solution and entropies of solvation may be obtained. Reilly and Rae\textsuperscript{210} have discussed some aspects of solubility measurements. Also, an account of the factors that affect the solubility of electrolytes in different reaction media has been presented by Kolthoff and Elving\textsuperscript{211}.

Compilation of solubility data has been the subject of several publications. The most recent work in this field is illustrated in the Solubility Data Series organised by the Solubility Commission of the Analytical Chemistry Division of the International Union of Pure and Applied Chemistry (IUPAC). A number of volumes have been published on the solubility of electrolytes.

In determining the solubilities of electrolytes, various methods have been employed. The method used in this work has been described in the experimental part of this thesis (chapter 2). In order to analyse the amount of solid dissolved in the solvent, as a result of the equilibrium established between the solid and the saturated solution of the ions, several analytical techniques have been used. These include potentiometric titration, spectrophotometry, gravimetric analysis and atomic absorption. Solubilities of parahydroxyphenylazo and chloro-substituted para hydroxyphenylazo benzoic acids in water and methanol, and those of the
corresponding sodium salts were carried out in water, methanol and N,N'-Dimethylformamide at 298.15 K. The selected analytical technique used for this purpose was that of spectrophotometry. A calibration curve for each hapten, in each solvent, was carried out. Figures 5.1-5.42 show the different calibration curves of parahydroxyphenylazo and chloro substituted parahydroxyphenylazo benzoic acids and those of their sodium salts in water, methanol and N,N'-Dimethylformamide at 298.15K. Slopes of these plots represent the molar absorbance coefficients at the corresponding maximum wavelength of the haptens in these solvents.

The molar absorbance coefficients (ε) and maximum wavelength (λ_max) at which these electrolytes absorb UV light in water, methanol and N,N'-Dimethylformamide at 298.15K are listed in Table 5.1.

Table 5.2 contains the solubilities and wavelength of maximum absorbance of these electrolytes in the referred solvents. The reported solubilities are those at 298.15K.
Table 5.1 Molar Absorbance Coefficients, $\varepsilon$, and Maximum Wavelength of Haptens in Water, Methanol and $N,N'$-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>Water $\varepsilon$</th>
<th>$\lambda_{\text{max}}$ nm</th>
<th>MeOH $\varepsilon$</th>
<th>$\lambda_{\text{max}}$ nm</th>
<th>DMF $\varepsilon$</th>
<th>$\lambda_{\text{max}}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho ($p$OHPhN$_2$)B.A</td>
<td>$1.72 \times 10^4$</td>
<td>348.1</td>
<td>1.90$x10^4$</td>
<td>354.4</td>
<td>1.92$x10^4$</td>
<td>353.0</td>
</tr>
<tr>
<td>meta ($p$OHPhN$_2$)B.A</td>
<td>1.71$x10^4$</td>
<td>348.8</td>
<td>3.00$x10^4$</td>
<td>351.2</td>
<td>2.56$x10^4$</td>
<td>357.6</td>
</tr>
<tr>
<td>para ($p$OHPhN$_2$)B.A</td>
<td>2.16$x10^4$</td>
<td>355.0</td>
<td>3.02$x10^4$</td>
<td>359.8</td>
<td>1.35$x10^4$</td>
<td>368.5</td>
</tr>
<tr>
<td>5CI-2 ($p$OHPhN$_2$)B.A</td>
<td>1.55$x10^4$</td>
<td>354.4</td>
<td>2.21$x10^4$</td>
<td>358.2</td>
<td>2.04$x10^4$</td>
<td>359.0</td>
</tr>
<tr>
<td>6CI-2 ($p$OHPhN$_2$)B.A</td>
<td>2.17$x10^4$</td>
<td>353.5</td>
<td>2.56$x10^4$</td>
<td>358.9</td>
<td>2.40$x10^4$</td>
<td>363.5</td>
</tr>
<tr>
<td>2CI-4 ($p$OHPhN$_2$)B.A</td>
<td>2.52$x10^4$</td>
<td>355.2</td>
<td>1.20$x10^4$</td>
<td>359.5</td>
<td>2.64$x10^4$</td>
<td>367.2</td>
</tr>
<tr>
<td>4CI-3 ($p$OHPhN$_2$)B.A</td>
<td>3.76$x10^4$</td>
<td>354.4</td>
<td>2.35$x10^4$</td>
<td>360.0</td>
<td>2.33$x10^4$</td>
<td>367.8</td>
</tr>
<tr>
<td>ortho ($p$OHPhN$_2$)NaB</td>
<td>1.97$x10^4$</td>
<td>347.2</td>
<td>2.09$x10^4$</td>
<td>350.1</td>
<td>3.52$x10^4$</td>
<td>507.7</td>
</tr>
<tr>
<td>meta ($p$OHPhN$_2$)NaB</td>
<td>2.25$x10^4$</td>
<td>348.7</td>
<td>2.63$x10^4$</td>
<td>349.6</td>
<td>2.47$x10^4$</td>
<td>354.4</td>
</tr>
<tr>
<td>para ($p$OHPhN$_2$)NaB</td>
<td>2.33$x10^4$</td>
<td>355.0</td>
<td>2.85$x10^4$</td>
<td>356.8</td>
<td>2.67$x10^4$</td>
<td>361.5</td>
</tr>
<tr>
<td>5CI-2 ($p$OHPhN$_2$)NaB</td>
<td>2.22$x10^4$</td>
<td>354.4</td>
<td>2.38$x10^4$</td>
<td>356.0</td>
<td>2.33$x10^4$</td>
<td>501.9</td>
</tr>
<tr>
<td>6CI-2 ($p$OHPhN$_2$)NaB</td>
<td>1.93$x10^4$</td>
<td>353.1</td>
<td>2.25$x10^4$</td>
<td>355.2</td>
<td>2.08$x10^4$</td>
<td>367.8</td>
</tr>
<tr>
<td>2CI-4 ($p$OHPhN$_2$)NaB</td>
<td>2.41$x10^4$</td>
<td>355.2</td>
<td>2.72$x10^4$</td>
<td>358.1</td>
<td>2.60$x10^4$</td>
<td>368.0</td>
</tr>
<tr>
<td>4CI-3 ($p$OHPhN$_2$)NaB</td>
<td>1.83$x10^4$</td>
<td>354.5</td>
<td>2.26$x10^4$</td>
<td>357.8</td>
<td>2.10$x10^4$</td>
<td>363.1</td>
</tr>
<tr>
<td>Haptens</td>
<td>WATER mol.dm$^{-3}$</td>
<td>MeOH mol.dm$^{-3}$</td>
<td>DMF mol.dm$^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>-------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho (pOHPhN$_2$)B.A</td>
<td>4.67x10$^{-4}$</td>
<td>6.32x10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta (pOHPhN$_2$)B.A</td>
<td>1.41x10$^{-4}$</td>
<td>2.94x10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>para (pOHPhN$_2$)B.A</td>
<td>4.16x10$^{-5}$</td>
<td>7.60x10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN$_2$)B.A</td>
<td>1.39x10$^{-4}$</td>
<td>5.70x10$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN$_2$)B.A</td>
<td>1.01x10$^{-3}$</td>
<td>2.89x10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN$_2$)B.A</td>
<td>2.40x10$^{-3}$</td>
<td>6.87x10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN$_2$)B.A</td>
<td>8.33x10$^{-5}$</td>
<td>7.50x10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho (pOHPhN$_2$)NaB</td>
<td>1.07x10$^{-1}$</td>
<td>5.29x10$^{-2}$</td>
<td>3.53x10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta (pOHPhN$_2$)NaB</td>
<td>6.06x10$^{-3}$</td>
<td>5.98x10$^{-2}$</td>
<td>2.84x10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>para (pOHPhN$_2$)NaB</td>
<td>1.72x10$^{-2}$</td>
<td>4.02x10$^{-2}$</td>
<td>2.45x10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN$_2$)NaB</td>
<td>2.16x10$^{-2}$</td>
<td>1.33x10$^{-2}$</td>
<td>1.81x10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN$_2$)NaB</td>
<td>3.04x10$^{-4}$</td>
<td>7.29x10$^{-2}$</td>
<td>3.20x10$^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN$_2$)NaB</td>
<td>1.24x10$^{-3}$</td>
<td>2.10x10$^{-1}$</td>
<td>1.41x10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN$_2$)NaB</td>
<td>2.37x10$^{-2}$</td>
<td>2.17x10$^{-2}$</td>
<td>1.94x10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.1 Spectrometric Calibration Curve of ortho (p-OHPhN$_2$)BA in Water at 298.15 K.

Figure 5.2 Spectrometric Calibration Curve of ortho (p-OHPhN$_2$)BA in MeOH at 298.15 K.

Figure 5.3 Spectrometric Calibration Curve of ortho (p-OHPhN$_2$)BA in DMF at 298.15 K.
Figure 5.4 Spectrometric Calibration Curve of *ortho* (p-OHPhN$_2$)NaB in Water at 298.15 K.

Figure 5.5 Spectrometric Calibration Curve of *ortho* (p-OHPhN$_2$)NaB in MeOH at 298.15 K.

Figure 5.6 Spectrometric Calibration Curve of *ortho* (p-OHPhN$_2$)NaB in DMF at 298.15 K.
Figure 5.7 Spectrometric Calibration Curve of meta \((p-\text{OHPPhN}_2)\text{BA}\) in Water at 298.15 K.

Figure 5.8 Spectrometric Calibration Curve of meta \((p-\text{OHPPhN}_2)\text{BA}\) in MeOH at 298.15 K.

Figure 5.9 Spectrometric Calibration Curve of meta \((p-\text{OHPPhN}_2)\text{BA}\) in DMF at 298.15 K.
Figure 5.10 Spectrometric Calibration Curve of meta (p-OHPhN$_2$)NaB in Water at 298.15 K.

Figure 5.11 Spectrometric Calibration Curve of meta (p-OHPhN$_2$)NaB in MeOH at 298.15 K.

Figure 5.12 Spectrometric Calibration Curve of meta (p-OHPhN$_2$)NaB in DMF at 298.15 K.
Figure 5.13 Spectrometric Calibration Curve of \( \text{para} \ (p\text{-OHPhN}_2)\text{BA} \) in Water at 298.15 K.

Figure 5.14 Spectrometric Calibration Curve of \( \text{para} \ (p\text{-OHPhN}_2)\text{BA} \) in MeOH at 298.15 K.

Figure 5.15 Spectrometric Calibration Curve of \( \text{para} \ (p\text{-OHPhN}_2)\text{BA} \) in DMF at 298.15 K.
Figure 5.16 Spectrometric Calibration Curve of para (p-OHPhN$_2$)NaB in Water at 298.15 K.

Figure 5.17 Spectrometric Calibration Curve of para (p-OHPhN$_2$)NaB in MeOH at 298.15 K.

Figure 5.18 Spectrometric Calibration Curve of para (p-OHPhN$_2$)NaB in DMF at 298.15 K.
Figure 5.19 Spectrometric Calibration Curve of 5chloro-2(p-OHPn2)BA in Water at 298.15 K.

Figure 5.20 Spectrometric Calibration Curve of 5chloro-2(p-OHPn2)BA in MeOH at 298.15 K.

Figure 5.21 Spectrometric Calibration Curve of 5chloro-2(p-OHPn2)BA in DMF at 298.15 K.
Figure 5.22 Spectrometric Calibration Curve of 5chloro-2(p-OHPhN$_2$)NaB in Water at 298.15 K.

Figure 5.23 Spectrometric Calibration Curve of 5chloro-2(p-OHPhN$_2$)NaB in MeOH at 298.15 K.

Figure 5.24 Spectrometric Calibration Curve of 5chloro-2(p-OHPhN$_2$)NaB in DMF at 298.15 K.
Figure 5.25 Spectrometric Calibration Curve of 6chloro-2(p-OHPhN$_2$)BA in Water at 298.15 K.

Figure 5.26 Spectrometric Calibration Curve of 6chloro-2(p-OHPhN$_2$)BA in MeOH at 298.15 K.

Figure 5.27 Spectrometric Calibration Curve of 6chloro-2(p-OHPhN$_2$)BA in DMF at 298.15 K.
Figure 5.28 Spectrometric Calibration Curve of 6chloro-2(p-OHPPhN2)NaB in water at 298.15 K.

Figure 5.29 Spectrometric Calibration Curve of 6chloro-2(p-OHPPhN2)NaB in MeOH at 298.15 K.

Figure 5.30 Spectrometric Calibration Curve of 6chloro-2(p-OHPPhN2)NaB in DMF at 298.15 K.
Figure 5.31 Spectrometric Calibration Curve of 2chloro-4(p-OHPhN$_2$)BA in Water at 298.15 K.

Figure 5.32 Spectrometric Calibration Curve of 2chloro-4(p-OHPhN$_2$)BA in MeOH at 298.15K.

Figure 5.33 Spectrometric Calibration Curve of 2chloro-4(p-OHPhN$_2$)BA in DMF at 298.15 K.
Figure 5.34 Spectrometric Calibration Curve of 2chloro-4(p-OHPhN2)NaB in Water at 298.15 K.

Figure 5.35 Spectrometric Calibration Curve of 2chloro-4(p-OHPhN2)NaB in MeOH at 298.15K.

Figure 5.36 Spectrometric Calibration Curve of 2chloro-4(p-OHPhN2)NaB in DMF at 298.15 K.
Figure 5.37 Spectrometric Calibration Curve of 4chloro-3(p-OHPHn2)BA in Water at 298.15 K.

Figure 5.38 Spectrometric Calibration Curve of 4chloro-3(p-OHPHn2)BA in MeOH at 298.15 K.

Figure 5.39 Spectrometric Calibration Curve of 4chloro-3(p-OHPHn2)BA in DMF at 298.15 K.
Figure 5.40 Spectrometric Calibration Curve of 4chloro-3(p-OHPN₂)NaB in Water at 298.15 K.

Figure 5.41 Spectrometric Calibration Curve of 4chloro-3(p-OHPN₂)NaB in MeOH at 298.15 K.

Figure 5.42 Spectrometric Calibration Curve of 4chloro-3(p-OHPN₂)NaB in DMF at 298.15 K.
In order to calculate the solution free energy of the dissociated electrolyte \((M^+ + X^-)\) in the appropriate solvent (water, methanol and \(N,N'\)-Dimethylformamide), ionic concentrations, \(c_i\), are required. Therefore, solubility data were corrected for ion-pair formation in solution. This was done by taking into account association constants \((K_a\) values given in Table 3.1, chapter 3), as obtained from potentiometric titration and conductance measurements.

For a 1:1 electrolyte (e.g. para-hydroxyphenylazo and chloro-substituted para hydroxyphenylazo benzoic acids and their sodium salts), the equilibrium involved, between a solid hapten, \(MX\), and a saturated solution of its ions in a given solvent, provided that the electrolyte is fully dissociated in that solvent, refers to the process as described by:-

\[
MX_{\text{solid}} \rightarrow M^+_{\text{soln}} + X^-_{\text{soln}} \quad (5.1)
\]

The thermodynamic equilibrium constants, \(K^{\circ}_{sp}\), may be expressed by:-

\[
K^{\circ}_{sp} = a_{M^+}a_{X^-} \quad (5.2)
\]

where \(a_{M^+}\) and \(a_{X^-}\) represent the activities of the species \(M^+\) and \(X^-\) in solution, respectively. The activity of a solid is unity by convention. The activity, \(a\), on the molar scale, is related to the ionic molar concentration, \(c_i\), by the mean ionic molar activity coefficient, \(\gamma^\pm\). Thus:-

\[
a_i = \gamma^\pm c_i \quad (5.3)
\]

\[
K^{\circ}_{sp} = \gamma^\pm^2 c_i^2 \quad (5.4)
\]

\(K^{\circ}_{sp}\) is known as the ion-activity solubility product. \(\gamma^\pm\), may be obtained using the extended Debye-Hückel equation.
The change in free energy, \( \Delta G_n \), on dissolution of one mole of electrolyte, is given by:

\[
\Delta G_n = \Delta G^\circ_n + RT \ln K^\circ_{r\nu} \\
\Delta G_n = \Delta G^\circ_n + RT \ln c_i^2 \gamma^2
\]

As \( \Delta G_n = 0 \), when the solute is in equilibrium with a saturated solution of its ions, equation 5.6, may be written as:

\[
\Delta G^\circ_n = -RT \ln c_i^2 \gamma^2
\]

where \( \Delta G^\circ_n \) is the standard free energy of solution of the electrolyte.

However, in media where the electrolyte is not fully dissociated, ion-pair formation constants must be taken into account. Then, in order to calculate \( \Delta G^\circ_n \), the following equilibrium must be considered:

\[
M^+ \_{\text{solv}} + X^- \_{\text{solv}} \rightleftharpoons M^+X^- \_{\text{solv}}
\]

The ion-pair formation constant, \( K_s \), for the process described by the equation 5.8, is given by:

\[
K_s = a_{M^+X^-} / (a_{M^+}a_{X^-})
\]

\( K_s \) may be expressed in terms of the mean molar ionic activity coefficient. Thus, \( K_s \) becomes:

\[
K_s = (c_{ip} \gamma_{ip}^2) / (c_i^2 \gamma_i^2)
\]

\( c_{ip} \) is the molar concentration of ion-pairs (\( M^+X^- \)). However, the solubility, \( S \), corresponds to the total concentration of the free ions, \( c_i \), and ion-pairs, \( c_{ip} \), in
solution. Thus:

\[ S = c_i + c_{ip} \quad 5.11 \]

\[ c_{ip} = S - c_i \quad 5.12 \]

Assuming that \( \gamma_{\pm ip} \) is equal to 1, then equation 5.10 becomes:

\[ K_i = (S - c_i)/(c_i\gamma_{\pm i}^2) \quad 5.13 \]

This leads to a quadratic equation of the form:

\[ K_i\gamma_{\pm i}^2c_i^2 + c_i - S = 0 \quad 5.14 \]

\( \gamma_{\pm} \) is \( c_i \) dependent. Thus, the calculation of \( c_i \) is tedious and requires an iterative method of calculation (e.g. Trial and Error, Raphson-Newton, etc...). For this purpose, a computer program, written in Fortran Language and presented in Appendix C, was devised to evaluate the ionic concentration, \( c_i \), the thermodynamic solubility product (\( pK_i = c_i^2\gamma_{\pm i}^2 \)) and the corresponding change in free energy of solution, \( \Delta G^\circ \), for the dissociated 1:1 electrolytes. It should be pointed out that the mean ionic activity, \( \gamma_\pm \), was calculated using the Debye-Hückel equation in its extended form. \( \gamma_\pm \) is also an ion-size (\( a^0 \)) dependent. Values of 5.0 Å and 6.5 Å, for the acids and sodium salts respectively, were assigned to \( a^0 \). However, Danil de Namor and co-workers\(^{188,212} \) shown that \( \gamma_\pm \) values are not affected to any significant extent by ion-size parameter changes.

Solubilities, solubility products, reported as \( pK_i^\circ \), and standard free energies of solution of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoic acids, in water at 298.15 K, are reported in Table 5.3. Whereas, those of the sodium salts, in water, methanol and N,N'-Dimethylformamide, are reported in Tables 5.3-5.5. Table 5.6 lists a recapitulation of the free energies of solution of these electrolytes in these solvents.
Table 5.3 Solubilities and Free Energies of Solution of 1:1 Haptens in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>Solubility $K_s$</th>
<th>$K_s$ mol$^3$.dm$^3$</th>
<th>$pK^o_s$</th>
<th>$\Delta G^{o_s}$ kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho $(pOHPhN_2)B.A$</td>
<td>$4.67 \times 10^{-4}$</td>
<td>$2.04 \times 10^6$</td>
<td>8.69</td>
<td>49.57</td>
</tr>
<tr>
<td>meta $(pOHPhN_2)B.A$</td>
<td>$1.41 \times 10^{-4}$</td>
<td>$1.20 \times 10^5$</td>
<td>9.04</td>
<td>51.57</td>
</tr>
<tr>
<td>para $(pOHPhN_2)B.A$</td>
<td>$4.16 \times 10^{-5}$</td>
<td>$3.55 \times 10^4$</td>
<td>9.28</td>
<td>52.97</td>
</tr>
<tr>
<td>5Cl-2 $(pOHPhN_2)B.A$</td>
<td>$1.39 \times 10^{-4}$</td>
<td>$8.51 \times 10^4$</td>
<td>8.91</td>
<td>50.87</td>
</tr>
<tr>
<td>6Cl-2 $(pOHPhN_2)B.A$</td>
<td>$1.01 \times 10^{-3}$</td>
<td>$8.51 \times 10^3$</td>
<td>7.08</td>
<td>40.38</td>
</tr>
<tr>
<td>2Cl-4 $(pOHPhN_2)B.A$</td>
<td>$2.40 \times 10^{-3}$</td>
<td>$3.80 \times 10^3$</td>
<td>6.35</td>
<td>36.23</td>
</tr>
<tr>
<td>4Cl-3 $(pOHPhN_2)B.A$</td>
<td>$8.33 \times 10^{-5}$</td>
<td>$4.27 \times 10^2$</td>
<td>8.94</td>
<td>51.02</td>
</tr>
<tr>
<td>ortho $(pOHPhN_2)NaB$</td>
<td>$1.07 \times 10^{-1}$</td>
<td>9.45</td>
<td>2.47</td>
<td>14.10</td>
</tr>
<tr>
<td>meta $(pOHPhN_2)NaB$</td>
<td>$6.06 \times 10^{-2}$</td>
<td>180.00</td>
<td>3.62</td>
<td>20.66</td>
</tr>
<tr>
<td>para $(pOHPhN_2)NaB$</td>
<td>$1.72 \times 10^{-2}$</td>
<td>55.00</td>
<td>3.98</td>
<td>22.72</td>
</tr>
<tr>
<td>5Cl-2 $(pOHPhN_2)NaB$</td>
<td>$2.16 \times 10^{-2}$</td>
<td>8.00</td>
<td>3.55</td>
<td>20.26</td>
</tr>
<tr>
<td>6Cl-2 $(pOHPhN_2)NaB$</td>
<td>$3.04 \times 10^{-1}$</td>
<td>11.00</td>
<td>1.87</td>
<td>9.42</td>
</tr>
<tr>
<td>2Cl-4 $(pOHPhN_2)NaB$</td>
<td>$1.24 \times 10^{-2}$</td>
<td>96.00</td>
<td>4.31</td>
<td>24.60</td>
</tr>
<tr>
<td>4Cl-3 $(pOHPhN_2)NaB$</td>
<td>$2.37 \times 10^{-2}$</td>
<td>3.50</td>
<td>3.42</td>
<td>19.52</td>
</tr>
</tbody>
</table>

* Data derived from $pK_a$ values given in Table 3.1, Chapter3.
* Data obtained from conductance measurements, Table 3.30, Chapter3.
Table 5.4 Solubilities and Free Energies of Solution of 1:1 Haptens in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>Solubility $K_*$</th>
<th>$pK^o$,</th>
<th>$\Delta G^o$,</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol dm$^{-3}$</td>
<td>mol$^2$.dm$^{-3}$</td>
<td>kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>ortho $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$5.29 \times 10^{-2}$</td>
<td>2.0</td>
<td>3.19</td>
</tr>
<tr>
<td>meta $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$5.98 \times 10^{-2}$</td>
<td>0.0</td>
<td>3.10</td>
</tr>
<tr>
<td>para $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$4.02 \times 10^{-2}$</td>
<td>0.5</td>
<td>3.36</td>
</tr>
<tr>
<td>$5Cl-2$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$1.33 \times 10^{-2}$</td>
<td>11.0</td>
<td>4.16</td>
</tr>
<tr>
<td>$6Cl-2$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$7.29 \times 10^{-2}$</td>
<td>0.0</td>
<td>2.98</td>
</tr>
<tr>
<td>$2Cl-4$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$2.10 \times 10^{-1}$</td>
<td>0.0</td>
<td>2.33</td>
</tr>
<tr>
<td>$4Cl-3$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$2.17 \times 10^{-2}$</td>
<td>7.7</td>
<td>3.81</td>
</tr>
</tbody>
</table>

* Data obtained from conductance measurements, Table 3.30, Chapter 3.

Table 5.5 Solubilities and Free Energies of Solution of 1:1 Haptens in N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>Solubility $K_*$</th>
<th>$pK^o$,</th>
<th>$\Delta G^o$,</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol dm$^{-3}$</td>
<td>mol$^2$.dm$^{-3}$</td>
<td>kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>ortho $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$3.53 \times 10^{-2}$</td>
<td>100.7</td>
<td>3.79</td>
</tr>
<tr>
<td>meta $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$2.84 \times 10^{-1}$</td>
<td>809.2</td>
<td>3.50</td>
</tr>
<tr>
<td>para $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$2.45 \times 10^{-2}$</td>
<td>756.8</td>
<td>4.62</td>
</tr>
<tr>
<td>$5Cl-2$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$1.81 \times 10^{-2}$</td>
<td>88.9</td>
<td>4.15</td>
</tr>
<tr>
<td>$6Cl-2$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$3.20 \times 10^{-2}$</td>
<td>141.4</td>
<td>3.94</td>
</tr>
<tr>
<td>$2Cl-4$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$1.41 \times 10^{-1}$</td>
<td>479.1</td>
<td>3.61</td>
</tr>
<tr>
<td>$4Cl-3$ $(pO\text{OHPhN}_2)\text{NaB}$</td>
<td>$1.94 \times 10^{-2}$</td>
<td>799.1</td>
<td>4.75</td>
</tr>
</tbody>
</table>

* Data obtained from conductance measurements, Table 3.30, Chapter 3.
Table 5.6 Gibbs Free Energies of Solution of Sodium [parahydroxyphenylazo and chloro-Substituted parahydroxyphenylazo] Benzoates in Water, Methanol and N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>$\Delta G^\circ$, / kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2O$</td>
</tr>
<tr>
<td><strong>ortho</strong> $(pOHPhN_2)NaB$</td>
<td>14.10</td>
</tr>
<tr>
<td><strong>meta</strong> $(pOHPhN_2)NaB$</td>
<td>20.66</td>
</tr>
<tr>
<td><strong>para</strong> $(pOHPhN_2)NaB$</td>
<td>22.72</td>
</tr>
<tr>
<td>$5Cl-2$ $(pOHPhN_2)NaB$</td>
<td>20.26</td>
</tr>
<tr>
<td>$6Cl-2$ $(pOHPhN_2)NaB$</td>
<td>9.42</td>
</tr>
<tr>
<td>$2Cl-4$ $(pOHPhN_2)NaB$</td>
<td>24.60</td>
</tr>
<tr>
<td>$4Cl-3$ $(pOHPhN_2)NaB$</td>
<td>19.52</td>
</tr>
</tbody>
</table>

* Data from Table 5.3, Chapter 5.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta G^\circ$, / kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ortho</strong> $(pOHPhN_2)NaB$</td>
<td>14.10</td>
</tr>
<tr>
<td><strong>meta</strong> $(pOHPhN_2)NaB$</td>
<td>20.66</td>
</tr>
<tr>
<td><strong>para</strong> $(pOHPhN_2)NaB$</td>
<td>22.72</td>
</tr>
<tr>
<td>$5Cl-2$ $(pOHPhN_2)NaB$</td>
<td>20.26</td>
</tr>
<tr>
<td>$6Cl-2$ $(pOHPhN_2)NaB$</td>
<td>9.42</td>
</tr>
<tr>
<td>$2Cl-4$ $(pOHPhN_2)NaB$</td>
<td>24.60</td>
</tr>
<tr>
<td>$4Cl-3$ $(pOHPhN_2)NaB$</td>
<td>19.52</td>
</tr>
</tbody>
</table>

For a better interpretation of the data ($\Delta G^\circ$), inequalities attributed to the contribution of the crystal lattice energy must be eliminated. Therefore, Gibbs free energies for the transfer of these electrolytes, from water to methanol and from water to N,N'-Dimethylformamide, were calculated.

Standard free energy of transfer, $\Delta G^\circ$, for haptens (H), from water to non-aqueous media (S), is referred to the process as described by equation 5.15.

$$ H (H_2O) \xrightarrow{\text{process}} H (s) $$  \hspace{1cm} 5.15

The thermodynamic transfer constant, $K_T$, is defined as:

$$ K_T = \frac{a_H(s)}{a_H(H_2O)} $$  \hspace{1cm} 5.16
It must be pointed out that $K_r$ is referred to the process when the two solvents are in their pure state. Taking into account eqn 5.7, the transfer free energy may be expressed as:

$$
\Delta G^0_i = \Delta G^0_s (s) - \Delta G^0_i (H_2O)
$$

5.17

Standard free energies for the transfer of haptens (sodium [para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo] benzoate) from water to methanol and from water to N,N'-Dimethylformamide are listed in Table 5.7.
Table 5.7 Free Energies of Transfer of Sodium \([\text{parahydroxyphenylazo and chloro-Substituted parahydroxyphenylazo]}\) Benzoates from Water to Non-Aqueous Media at 298.15 K.

Water $\rightarrow$ MeOH

<table>
<thead>
<tr>
<th>Haptens</th>
<th>$\Delta G^\circ_\text{a} (\text{H}_2\text{O})$</th>
<th>$\Delta G^\circ_\text{b} (\text{MeOH})$</th>
<th>$\Delta G^\circ_\text{c} (\text{H}_2\text{O} \rightarrow \text{MeOH})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN$_2$)NaB</td>
<td>14.10 kJ.mol$^{-1}$</td>
<td>18.21 kJ.mol$^{-1}$</td>
<td>4.11 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>meta (pOHPhN$_2$)NaB</td>
<td>20.66 kJ.mol$^{-1}$</td>
<td>18.07 kJ.mol$^{-1}$</td>
<td>-2.59 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>para (pOHPhN$_2$)NaB</td>
<td>22.72 kJ.mol$^{-1}$</td>
<td>19.17 kJ.mol$^{-1}$</td>
<td>-3.55 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>5CI-2 (pOHPhN$_2$)NaB</td>
<td>20.26 kJ.mol$^{-1}$</td>
<td>23.73 kJ.mol$^{-1}$</td>
<td>3.47 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>6CI-2 (pOHPhN$_2$)NaB</td>
<td>9.42 kJ.mol$^{-1}$</td>
<td>16.98 kJ.mol$^{-1}$</td>
<td>7.56 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>2CI-4 (pOHPhN$_2$)NaB</td>
<td>24.60 kJ.mol$^{-1}$</td>
<td>13.27 kJ.mol$^{-1}$</td>
<td>-11.33 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>4CI-3 (pOHPhN$_2$)NaB</td>
<td>19.52 kJ.mol$^{-1}$</td>
<td>21.74 kJ.mol$^{-1}$</td>
<td>2.22 kJ.mol$^{-1}$</td>
</tr>
</tbody>
</table>

Water $\rightarrow$ DMF

<table>
<thead>
<tr>
<th>Haptens</th>
<th>$\Delta G^\circ_\text{a} (\text{H}_2\text{O})$</th>
<th>$\Delta G^\circ_\text{b} (\text{MeOH})$</th>
<th>$\Delta G^\circ_\text{c} (\text{H}_2\text{O} \rightarrow \text{DMF})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN$_2$)NaB</td>
<td>14.10 kJ.mol$^{-1}$</td>
<td>21.66 kJ.mol$^{-1}$</td>
<td>7.56 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>meta (pOHPhN$_2$)NaB</td>
<td>20.66 kJ.mol$^{-1}$</td>
<td>19.98 kJ.mol$^{-1}$</td>
<td>-0.68 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>para (pOHPhN$_2$)NaB</td>
<td>22.72 kJ.mol$^{-1}$</td>
<td>26.37 kJ.mol$^{-1}$</td>
<td>3.65 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>5CI-2 (pOHPhN$_2$)NaB</td>
<td>20.26 kJ.mol$^{-1}$</td>
<td>23.68 kJ.mol$^{-1}$</td>
<td>3.42 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>6CI-2 (pOHPhN$_2$)NaB</td>
<td>9.42 kJ.mol$^{-1}$</td>
<td>22.48 kJ.mol$^{-1}$</td>
<td>13.06 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>2CI-4 (pOHPhN$_2$)NaB</td>
<td>24.60 kJ.mol$^{-1}$</td>
<td>20.63 kJ.mol$^{-1}$</td>
<td>-3.97 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>4CI-3 (pOHPhN$_2$)NaB</td>
<td>19.52 kJ.mol$^{-1}$</td>
<td>27.13 kJ.mol$^{-1}$</td>
<td>7.61 kJ.mol$^{-1}$</td>
</tr>
</tbody>
</table>

* Data from Table 5.3; † Data from Table 5.4.

It is well reflected, from $\Delta G^\circ_\text{a} (\text{H}_2\text{O} \rightarrow \text{MeOH})$ data listed in Table 5.7, that the transfer of ortho, 5CI-2, 6CI-2 and 4CI-3 (pOHPhN$_2$) sodium benzoate from water
to methanol, is unfavourable ($\Delta G^\circ > 0$). Similarly, the transfer of haptens from water to N,N'-Dimethylformamide is also unfavourable except for meta and 2CI-4 (pOHPhNz) sodium benzoate ($\Delta G^\circ < 0$). However, it is rather dangerous to give an interpretation of the process on the basis of the free energy data without considering the contributions made by the transfer enthalpy, $\Delta H^\circ$, and transfer entropy, $\Delta S^\circ$, to the $\Delta G^\circ$ values. Thus, $\Delta H^\circ$ and $\Delta S^\circ$ parameters will be given.

5.1.2 Standard Enthalpies of Transfer of Haptens from Water to Non-Aqueous Solvents at 298.15 K.

Standard enthalpies of transfer of electrolytes, $\Delta H^\circ$, requires data on enthalpies of solution of these electrolytes in the solvents under investigation. The process involved refers to the following equation:

$$H(H_2O) \longrightarrow H(s)$$  \hspace{1cm} 5.18

The transfer enthalpy may be given by:

$$\Delta H^\circ = \Delta H^\circ(s) - \Delta H^\circ(H_2O)$$  \hspace{1cm} 5.19

where $\Delta H^\circ(s)$ and $\Delta H^\circ(H_2O)$ are the standard enthalpies of solution of the electrolyte in the solvent (s) and in water, respectively.

Standard enthalpies of solution of sodium [parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo] benzoate, $\Delta H^\circ$, were measured in water, methanol and N,N'-Dimethylformamide at 298.15 K. This has been achieved by measuring, calorimetrically, heats of solution, $\Delta H_s$, of these electrolytes, in these solvents, at various electrolyte concentration. A detailed description of this technique has been described in chapter 4. The experimental procedure was included in chapter 2. Standard enthalpy of solution was obtained from a plot of $\Delta H_s$ versus the square root of the final electrolyte concentration, $\sqrt{c}$, in the reaction vessel of the
calorimeter. The intercept gives $\Delta H^\circ_r$. For this purpose, a least square was devised. The program gives the standard deviation of the intercept, see appendix C.

Since anomalies in the charts of the heat of solution of sodium [meta, para and 4Cl-3 (parahydroxyphenylazo)] benzoates, in water, were observed, the standard enthalpies of solution of these electrolytes, in this solvent, were derived from relevant data, obtained in different mixtures of water and methanol, using a polynomial extrapolation method.

Standard deviation, $\sigma$, was calculated using:

$$\sigma = \sqrt{\frac{\sum(X_i - \bar{X})^2}{n(n-1)}}$$

where $X_i$ = value of the ith measurement

$\bar{X}$ = average value from n measurements, and

$n$ = total number of measurements.

Table 5.8 - 5.40 contains calorimetric measurements at various electrolyte concentration in water, methanol and N,N'-Dimethylformamide at 298.15 K. A recapitulation for the $\Delta H^\circ_r$ of haptens in the different solvents is presented in Table 5.41. Standard enthalpies for the transfer of these haptens from water to methanol and from water to N,N'-Dimethylformamide are listed in Table 5.42.
Table 5.8 Standard Enthalpy of Solution of Sodium [ortho (pOHPhN$_2$)] Benzoate in water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>c * (mol dm$^{-3}$)</th>
<th>$\sqrt{c}$ (mol$^{1/2}$ dm$^{-3/2}$)</th>
<th>$\Delta H_s$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05251</td>
<td>3.98x10$^{-3}$</td>
<td>6.31x10$^{-2}$</td>
<td>8.21</td>
</tr>
<tr>
<td>0.04424</td>
<td>3.35x10$^{-3}$</td>
<td>5.79x10$^{-2}$</td>
<td>8.18</td>
</tr>
<tr>
<td>0.02510</td>
<td>1.90x10$^{-3}$</td>
<td>4.36x10$^{-2}$</td>
<td>8.11</td>
</tr>
<tr>
<td>0.03916</td>
<td>2.97x10$^{-3}$</td>
<td>5.45x10$^{-2}$</td>
<td>8.16</td>
</tr>
<tr>
<td>0.08617</td>
<td>6.53x10$^{-3}$</td>
<td>8.08x10$^{-2}$</td>
<td>8.29</td>
</tr>
<tr>
<td>0.07665</td>
<td>5.81x10$^{-3}$</td>
<td>7.62x10$^{-2}$</td>
<td>8.26</td>
</tr>
<tr>
<td>0.08270</td>
<td>3.12x10$^{-3}$</td>
<td>5.58x10$^{-2}$</td>
<td>8.17</td>
</tr>
<tr>
<td>0.07101</td>
<td>2.69x10$^{-3}$</td>
<td>5.19x10$^{-2}$</td>
<td>8.15</td>
</tr>
<tr>
<td>0.14788</td>
<td>5.60x10$^{-3}$</td>
<td>7.48x10$^{-2}$</td>
<td>8.26</td>
</tr>
<tr>
<td>0.10032</td>
<td>3.80x10$^{-3}$</td>
<td>6.16x10$^{-2}$</td>
<td>8.19</td>
</tr>
<tr>
<td>0.05425</td>
<td>2.05x10$^{-3}$</td>
<td>4.53x10$^{-2}$</td>
<td>8.12</td>
</tr>
</tbody>
</table>

Average value, $\Delta H_s = 8.19 \pm 0.05$ kJ mol$^{-1}$

Standard value, $\Delta H^o_s = 7.90 \pm 0.04$ kJ mol$^{-1}$

* Final electrolyte concentration in the reaction vessel.
Table 5.9 Standard Enthalpy of Solution of Sodium [ortho (pOHPhN$_2$)] Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>c (mol.dm$^{-3}$)</th>
<th>$\sqrt{c}$ (mol$^{1/2}$.dm$^{-3/2}$)</th>
<th>$\Delta H_f$ (kJ.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03330</td>
<td>2.52x10$^{-3}$</td>
<td>5.02x10$^{-2}$</td>
<td>-12.48</td>
</tr>
<tr>
<td>0.04735</td>
<td>3.59x10$^{-3}$</td>
<td>5.99x10$^{-2}$</td>
<td>-12.69</td>
</tr>
<tr>
<td>0.06388</td>
<td>4.84x10$^{-3}$</td>
<td>6.96x10$^{-2}$</td>
<td>-12.92</td>
</tr>
<tr>
<td>0.10992</td>
<td>8.33x10$^{-3}$</td>
<td>9.13x10$^{-2}$</td>
<td>-13.41</td>
</tr>
<tr>
<td>0.07014</td>
<td>5.31x10$^{-3}$</td>
<td>7.29x10$^{-2}$</td>
<td>-12.99</td>
</tr>
<tr>
<td>0.09406</td>
<td>7.13x10$^{-3}$</td>
<td>8.44x10$^{-2}$</td>
<td>-13.25</td>
</tr>
<tr>
<td>0.08589</td>
<td>6.51x10$^{-3}$</td>
<td>8.07x10$^{-2}$</td>
<td>-13.17</td>
</tr>
<tr>
<td>0.12286</td>
<td>9.31x10$^{-3}$</td>
<td>9.65x10$^{-2}$</td>
<td>-13.53</td>
</tr>
</tbody>
</table>

Average value of $\Delta H_f = -13.05 \pm 0.33$ kJ.mol$^{-1}$
Standard value, $\Delta H^\circ_f = -11.34 \pm 0.02$ kJ.mol$^{-1}$

Table 5.10 Standard Enthalpy of Solution of Sodium ortho (pOHPhN$_2$) Benzoate in N$_2$N' Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>c (mol.dm$^{-3}$)</th>
<th>$\sqrt{c}$ (mol$^{1/2}$.dm$^{-3/2}$)</th>
<th>$\Delta H_f$ (kJ.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01926</td>
<td>0.73x10$^{-3}$</td>
<td>2.70x10$^{-2}$</td>
<td>1.68</td>
</tr>
<tr>
<td>0.01168</td>
<td>0.44x10$^{-3}$</td>
<td>2.10x10$^{-2}$</td>
<td>2.89</td>
</tr>
<tr>
<td>0.02617</td>
<td>0.99x10$^{-3}$</td>
<td>3.15x10$^{-2}$</td>
<td>-1.68</td>
</tr>
<tr>
<td>0.01486</td>
<td>0.56x10$^{-3}$</td>
<td>2.37x10$^{-2}$</td>
<td>1.87</td>
</tr>
<tr>
<td>0.03575</td>
<td>1.35x10$^{-3}$</td>
<td>3.68x10$^{-2}$</td>
<td>-3.48</td>
</tr>
<tr>
<td>0.02268</td>
<td>0.86x10$^{-3}$</td>
<td>2.93x10$^{-2}$</td>
<td>-1.11</td>
</tr>
<tr>
<td>0.06796</td>
<td>2.57x10$^{-3}$</td>
<td>5.07x10$^{-2}$</td>
<td>-4.42</td>
</tr>
<tr>
<td>0.05851</td>
<td>2.22x10$^{-3}$</td>
<td>4.71x10$^{-2}$</td>
<td>-4.42</td>
</tr>
<tr>
<td>0.04493</td>
<td>1.70x10$^{-3}$</td>
<td>4.13x10$^{-2}$</td>
<td>-3.05</td>
</tr>
</tbody>
</table>

Average value of $\Delta H_f = -1.30 \pm 2.82$ kJ.mol$^{-1}$
Standard value, $\Delta H^\circ_f = 7.43 \pm 0.99$ kJ.mol$^{-1}$
Table 5.11 Standard Enthalpy of Solution of Sodium [(pOHPhN_2)] Benzoate in Water:Methanol Mixture (30:70) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm(^{-3}))</th>
<th>√c (mol(^{1/2}) dm(^{-3/2}))</th>
<th>ΔH(_s) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02798</td>
<td>1.1x10(^{-3})</td>
<td>3.26x10(^{-2})</td>
<td>9.92</td>
</tr>
<tr>
<td>0.04667</td>
<td>1.8x10(^{-3})</td>
<td>4.20x10(^{-2})</td>
<td>8.87</td>
</tr>
<tr>
<td>0.04067</td>
<td>1.5x10(^{-3})</td>
<td>3.92x10(^{-2})</td>
<td>9.17</td>
</tr>
<tr>
<td>0.06014</td>
<td>4.6x10(^{-3})</td>
<td>6.75x10(^{-2})</td>
<td>10.99</td>
</tr>
</tbody>
</table>

Average value of ΔH\(_s\) = 9.74 ± 0.82 kJ mol\(^{-1}\)

Standard value, ΔH\(_s\) = 7.68 ± 1.4 kJ mol\(^{-1}\)

Table 5.12 Standard Enthalpy of Solution of Sodium [(pOHPhN_2)] Benzoate in Water:Methanol Mixture (60:40) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm(^{-3}))</th>
<th>√c (mol(^{1/2}) dm(^{-3/2}))</th>
<th>ΔH(_s) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03783</td>
<td>1.4x10(^{-3})</td>
<td>3.79x10(^{-2})</td>
<td>24.43</td>
</tr>
<tr>
<td>0.02382</td>
<td>0.9x10(^{-3})</td>
<td>3.00x10(^{-2})</td>
<td>24.32</td>
</tr>
<tr>
<td>0.04588</td>
<td>1.7x10(^{-3})</td>
<td>4.17x10(^{-2})</td>
<td>22.49</td>
</tr>
<tr>
<td>0.01815</td>
<td>0.7x10(^{-3})</td>
<td>2.62x10(^{-2})</td>
<td>22.65</td>
</tr>
</tbody>
</table>

Average value of ΔH\(_s\) = 23.57 ± 0.83 kJ mol\(^{-1}\)

Standard value, ΔH\(_s\) = 20.02 ± 2.16 kJ mol\(^{-1}\)
Table 5.13 Standard Enthalpy of Solution of Sodium \([meta (pOHPN_2)]\) Benzoate in Water:Methanol Mixture (75:25) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm(^{-3}))</th>
<th>(\sqrt{c}) (mol(^{1/2}) dm(^{-3/2}))</th>
<th>(\Delta H_s) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01552</td>
<td>0.6x10(^{-3})</td>
<td>2.42x10(^{-2})</td>
<td>28.64</td>
</tr>
<tr>
<td>0.02874</td>
<td>1.1x10(^{-3})</td>
<td>3.30x10(^{-2})</td>
<td>26.59</td>
</tr>
<tr>
<td>0.02144</td>
<td>0.8x10(^{-3})</td>
<td>2.84x10(^{-2})</td>
<td>26.84</td>
</tr>
<tr>
<td>0.03770</td>
<td>1.4x10(^{-3})</td>
<td>3.78x10(^{-2})</td>
<td>27.26</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s\) = 27.33 ± 0.79 kJ mol\(^{-1}\)
Standard value, \(\Delta H^\circ_s\) = 30.20 ± 2.78 kJ mol\(^{-1}\)

Table 5.14 Standard Enthalpy of Solution of Sodium \([meta (pOHPN_2)]\) Benzoate in Water:Methanol Mixture (90:10) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm(^{-3}))</th>
<th>(\sqrt{c}) (mol(^{1/2}) dm(^{-3/2}))</th>
<th>(\Delta H_s) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02012</td>
<td>0.8x10(^{-3})</td>
<td>2.76x10(^{-2})</td>
<td>20.37</td>
</tr>
<tr>
<td>0.03677</td>
<td>1.4x10(^{-3})</td>
<td>3.73x10(^{-2})</td>
<td>18.73</td>
</tr>
<tr>
<td>0.03028</td>
<td>1.1x10(^{-3})</td>
<td>3.39x10(^{-2})</td>
<td>18.10</td>
</tr>
<tr>
<td>0.04354</td>
<td>1.6x10(^{-3})</td>
<td>4.06x10(^{-2})</td>
<td>16.44</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s\) = 18.41 ± 1.41 kJ mol\(^{-1}\)
Standard value, \(\Delta H^\circ_s\) = 27.63 ± 3.13 kJ mol\(^{-1}\)

Table 5.15 Standard Enthalpy of Solution of Sodium \([meta (pOHPN_2)]\) Benzoate in Water at 298.15 K.

<table>
<thead>
<tr>
<th>% MeOH</th>
<th>(\Delta H_s) / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>13.99</td>
</tr>
<tr>
<td>70</td>
<td>9.74</td>
</tr>
<tr>
<td>40</td>
<td>23.56</td>
</tr>
<tr>
<td>25</td>
<td>27.33</td>
</tr>
<tr>
<td>10</td>
<td>18.41</td>
</tr>
<tr>
<td>0</td>
<td>23.85</td>
</tr>
</tbody>
</table>

\(\Delta H^\circ_s\) of \([meta (pOHPN_2)] NaB\) in Water = 23.85 ± 0.80 kJ mol\(^{-1}\)
Table 5.16 Standard Enthalpy of Solution of Sodium \([meta (pOHPhN)]\) Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm(^{-3}))</th>
<th>(\sqrt{c}) (mol(^{1/2}) dm(^{-3/2}))</th>
<th>(\Delta H_{s}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05244</td>
<td>4.0x10(^{-3})</td>
<td>6.3x10(^{-2})</td>
<td>-14.03</td>
</tr>
<tr>
<td>0.01188</td>
<td>0.9x10(^{-3})</td>
<td>3.0x10(^{-2})</td>
<td>-13.81</td>
</tr>
<tr>
<td>0.02112</td>
<td>1.6x10(^{-3})</td>
<td>4.0x10(^{-2})</td>
<td>-13.90</td>
</tr>
<tr>
<td>0.03981</td>
<td>3.0x10(^{-3})</td>
<td>5.5x10(^{-2})</td>
<td>-14.10</td>
</tr>
<tr>
<td>0.07260</td>
<td>5.5x10(^{-3})</td>
<td>7.5x10(^{-2})</td>
<td>-14.23</td>
</tr>
<tr>
<td>0.02640</td>
<td>2.0x10(^{-3})</td>
<td>4.5x10(^{-2})</td>
<td>-13.89</td>
</tr>
<tr>
<td>0.04752</td>
<td>3.6x10(^{-3})</td>
<td>6.0x10(^{-2})</td>
<td>-14.00</td>
</tr>
<tr>
<td>0.05927</td>
<td>4.5x10(^{-3})</td>
<td>4.5x10(^{-2})</td>
<td>-14.02</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_{s}\) = \(-13.99 \pm 0.12\) kJ mol\(^{-1}\)

Standard value, \(\Delta H^\circ_{s}\) = \(-13.57 \pm 0.09\) kJ mol\(^{-1}\)

Table 5.17 Standard Enthalpy of Solution of Sodium \([meta (pOHPhN)]\) Benzoate in \(N,N'\)-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm(^{-3}))</th>
<th>(\sqrt{c}) (mol(^{1/2}) dm(^{-3/2}))</th>
<th>(\Delta H_{s}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03091</td>
<td>2.34x10(^{-3})</td>
<td>4.84x10(^{-2})</td>
<td>-5.90</td>
</tr>
<tr>
<td>0.04145</td>
<td>3.14x10(^{-3})</td>
<td>5.60x10(^{-2})</td>
<td>-5.98</td>
</tr>
<tr>
<td>0.05543</td>
<td>4.20x10(^{-3})</td>
<td>6.48x10(^{-2})</td>
<td>-6.18</td>
</tr>
<tr>
<td>0.08075</td>
<td>6.12x10(^{-3})</td>
<td>7.82x10(^{-2})</td>
<td>-6.44</td>
</tr>
<tr>
<td>0.04426</td>
<td>3.35x10(^{-3})</td>
<td>5.79x10(^{-2})</td>
<td>-5.97</td>
</tr>
<tr>
<td>0.05040</td>
<td>3.82x10(^{-3})</td>
<td>6.18x10(^{-2})</td>
<td>-6.27</td>
</tr>
<tr>
<td>0.07193</td>
<td>5.45x10(^{-3})</td>
<td>7.38x10(^{-2})</td>
<td>-6.41</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_{s}\) = \(-6.16 \pm 0.21\) kJ mol\(^{-1}\)

Standard value, \(\Delta H^\circ_{s}\) = \(-4.89 \pm 0.19\) kJ mol\(^{-1}\)
Table 5.18 Standard Enthalpy of Solution of Sodium [(para (pOHPnN\textsubscript{3}))] Benzoate in Water:Methanol Mixture (30:70) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (\text{mol.dm}^{-3})</th>
<th>(\sqrt{c}) (\text{mol}^{1/2}.\text{dm}^{-3/2})</th>
<th>(\Delta H) (\text{kJ.mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02049</td>
<td>(8 \times 10^{-3})</td>
<td>(2.79 \times 10^{-2})</td>
<td>13.98</td>
</tr>
<tr>
<td>0.02907</td>
<td>(1.1 \times 10^{-2})</td>
<td>(3.32 \times 10^{-2})</td>
<td>14.28</td>
</tr>
<tr>
<td>0.05722</td>
<td>(2.2 \times 10^{-2})</td>
<td>(4.66 \times 10^{-2})</td>
<td>14.49</td>
</tr>
<tr>
<td>0.03753</td>
<td>(1.4 \times 10^{-2})</td>
<td>(3.77 \times 10^{-2})</td>
<td>13.30</td>
</tr>
<tr>
<td>0.04464</td>
<td>(1.7 \times 10^{-2})</td>
<td>(4.11 \times 10^{-2})</td>
<td>12.54</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H\) = 13.72 ± 0.72 kJ.mol\(^{-1}\)
Standard value, \(\Delta H^°\) = 14.14 ± 2.42 kJ.mol\(^{-1}\)

Table 5.19 Standard Enthalpy of Solution of Sodium [(para (pOHPnN\textsubscript{3}))] Benzoate in Water:Methanol Mixture (60:40) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (\text{mol.dm}^{-3})</th>
<th>(\sqrt{c}) (\text{mol}^{1/2}.\text{dm}^{-3/2})</th>
<th>(\Delta H) (\text{kJ.mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02476</td>
<td>(0.9 \times 10^{-3})</td>
<td>(3.06 \times 10^{-2})</td>
<td>18.34</td>
</tr>
<tr>
<td>0.03212</td>
<td>(1.2 \times 10^{-3})</td>
<td>(3.49 \times 10^{-2})</td>
<td>18.81</td>
</tr>
<tr>
<td>0.03755</td>
<td>(1.4 \times 10^{-3})</td>
<td>(3.77 \times 10^{-2})</td>
<td>18.46</td>
</tr>
<tr>
<td>0.04670</td>
<td>(1.8 \times 10^{-3})</td>
<td>(4.21 \times 10^{-2})</td>
<td>17.71</td>
</tr>
<tr>
<td>0.05374</td>
<td>(2.0 \times 10^{-3})</td>
<td>(4.51 \times 10^{-2})</td>
<td>17.66</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H\) = 18.20 ± 0.44 kJ.mol\(^{-1}\)
Standard value, \(\Delta H^°\) = 20.76 ± 1.21 kJ.mol\(^{-1}\)
Table 5.20 Standard Enthalpy of Solution of Sodium \([(para \ (pOHPhN_2)\)]\) Benzoate in Water:Methanol Mixture (90:10) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>$c$ mol.dm$^{-3}$</th>
<th>$\sqrt{c}$ mol$^{1/2}$.dm$^{-3/2}$</th>
<th>$\Delta H_s$ kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02232</td>
<td>$0.8 \times 10^{-3}$</td>
<td>$2.91 \times 10^{-2}$</td>
<td>21.36</td>
</tr>
<tr>
<td>0.02917</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$3.32 \times 10^{-2}$</td>
<td>21.44</td>
</tr>
<tr>
<td>0.03980</td>
<td>$1.5 \times 10^{-3}$</td>
<td>$3.88 \times 10^{-2}$</td>
<td>22.93</td>
</tr>
<tr>
<td>0.04720</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$4.23 \times 10^{-2}$</td>
<td>23.60</td>
</tr>
<tr>
<td>0.05724</td>
<td>$2.2 \times 10^{-3}$</td>
<td>$4.66 \times 10^{-2}$</td>
<td>24.60</td>
</tr>
</tbody>
</table>

Average value of $\Delta H_s = 22.79 \pm 1.25$ kJ.mol$^{-1}$

Standard value, $\Delta H^\circ_s = 15.31 \pm 0.84$ kJ.mol$^{-1}$

Table 5.21 Standard Enthalpy of Solution of Sodium \([(para \ (pOHPhN_2)\)]\) Benzoate in Water at 298.15 K.

<table>
<thead>
<tr>
<th>% MeOH</th>
<th>$\Delta H^\circ_s$ / kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-10.60</td>
</tr>
<tr>
<td>70</td>
<td>13.72</td>
</tr>
<tr>
<td>40</td>
<td>18.20</td>
</tr>
<tr>
<td>10</td>
<td>22.79</td>
</tr>
<tr>
<td>0</td>
<td>28.03</td>
</tr>
</tbody>
</table>

$\Delta H^\circ_s$ of \([(para \ (pOHPhN_2))\) NaB in water = 28.03 \pm 0.84$ kJ.mol$^{-1}$
Table 5.22 Standard Enthalpy of Solution of Sodium \([\text{para} (p\text{OHPhN}_2)]\) Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (\text{mol.dm}^{-3})</th>
<th>(\sqrt{c}) (\text{mol}^{1/2}\text{.dm}^{-3/2})</th>
<th>(\Delta H_s) (\text{kJ.mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02850</td>
<td>(2.16\times10^{-3})</td>
<td>(4.65\times10^{-2})</td>
<td>-10.12</td>
</tr>
<tr>
<td>0.06247</td>
<td>(4.73\times10^{-3})</td>
<td>(6.88\times10^{-2})</td>
<td>-10.51</td>
</tr>
<tr>
<td>0.03777</td>
<td>(2.86\times10^{-3})</td>
<td>(5.35\times10^{-2})</td>
<td>-10.25</td>
</tr>
<tr>
<td>0.07937</td>
<td>(6.01\times10^{-3})</td>
<td>(7.75\times10^{-2})</td>
<td>-10.91</td>
</tr>
<tr>
<td>0.05429</td>
<td>(4.11\times10^{-3})</td>
<td>(6.41\times10^{-2})</td>
<td>-10.44</td>
</tr>
<tr>
<td>0.08365</td>
<td>(6.33\times10^{-3})</td>
<td>(7.96\times10^{-2})</td>
<td>-10.61</td>
</tr>
<tr>
<td>0.11034</td>
<td>(8.36\times10^{-3})</td>
<td>(9.14\times10^{-2})</td>
<td>-10.89</td>
</tr>
<tr>
<td>0.13796</td>
<td>(1.05\times10^{-2})</td>
<td>(1.02\times10^{-1})</td>
<td>-11.05</td>
</tr>
</tbody>
</table>

Average of \(\Delta H_s = -10.60 \pm 0.31 \text{ kJ.mol}^{-1}\)

Standard value, \(\Delta H^\circ_s = -9.36 \pm 0.16 \text{ kJ.mol}^{-1}\)

---

Table 5.23 Standard Enthalpy of Solution of Sodium \([\text{para} (p\text{OHPhN}_2)]\) Benzoate in \(\text{N,N}'\text{-Dimethylformamide}\) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (\text{mol.dm}^{-3})</th>
<th>(\sqrt{c}) (\text{mol}^{1/2}\text{.dm}^{-3/2})</th>
<th>(\Delta H_s) (\text{kJ.mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02167</td>
<td>(1.64\times10^{-3})</td>
<td>(4.05\times10^{-2})</td>
<td>-2.89</td>
</tr>
<tr>
<td>0.04287</td>
<td>(3.25\times10^{-3})</td>
<td>(5.69\times10^{-2})</td>
<td>-2.99</td>
</tr>
<tr>
<td>0.07265</td>
<td>(5.50\times10^{-3})</td>
<td>(7.42\times10^{-2})</td>
<td>-3.14</td>
</tr>
<tr>
<td>0.05565</td>
<td>(4.22\times10^{-3})</td>
<td>(6.49\times10^{-2})</td>
<td>-3.06</td>
</tr>
<tr>
<td>0.08300</td>
<td>(6.29\times10^{-3})</td>
<td>(7.93\times10^{-2})</td>
<td>-3.16</td>
</tr>
<tr>
<td>0.06150</td>
<td>(4.66\times10^{-3})</td>
<td>(6.83\times10^{-2})</td>
<td>-3.11</td>
</tr>
<tr>
<td>0.05961</td>
<td>(4.52\times10^{-3})</td>
<td>(6.72\times10^{-2})</td>
<td>-3.08</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s = -3.06 \pm 0.08 \text{ kJ.mol}^{-1}\)

Standard value, \(\Delta H^\circ_s = -2.58 \pm 0.03 \text{ kJ.mol}^{-1}\)
Table 5.24 Standard Enthalpy of Solution of Sodium \([5Cl-2 (pOHPPhN_2)]\) Benzoate in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>(c) mol.dm(^{-3})</th>
<th>(\sqrt{c}) mol(^{1/2}).dm(^{3/2})</th>
<th>(\Delta H_s) kJ.mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09881</td>
<td>3.31x10(^{-3})</td>
<td>5.75x10(^{-2})</td>
<td>13.76</td>
</tr>
<tr>
<td>0.07409</td>
<td>2.48x10(^{-3})</td>
<td>4.98x10(^{-2})</td>
<td>13.44</td>
</tr>
<tr>
<td>0.08978</td>
<td>3.01x10(^{-3})</td>
<td>5.48x10(^{-2})</td>
<td>13.65</td>
</tr>
<tr>
<td>0.16759</td>
<td>5.61x10(^{-3})</td>
<td>7.49x10(^{-2})</td>
<td>14.48</td>
</tr>
<tr>
<td>0.16133</td>
<td>5.40x10(^{-3})</td>
<td>7.35x10(^{-2})</td>
<td>14.42</td>
</tr>
<tr>
<td>0.05435</td>
<td>3.64x10(^{-3})</td>
<td>6.03x10(^{-2})</td>
<td>13.88</td>
</tr>
<tr>
<td>0.07861</td>
<td>5.27x10(^{-3})</td>
<td>7.25x10(^{-2})</td>
<td>14.38</td>
</tr>
<tr>
<td>0.08330</td>
<td>5.58x10(^{-3})</td>
<td>7.47x10(^{-2})</td>
<td>14.47</td>
</tr>
<tr>
<td>0.04813</td>
<td>3.22x10(^{-3})</td>
<td>5.68x10(^{-2})</td>
<td>13.73</td>
</tr>
<tr>
<td>0.04234</td>
<td>2.84x10(^{-3})</td>
<td>5.36x10(^{-2})</td>
<td>13.60</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s\) = 13.98 ± 0.39 kJ.mol\(^{-1}\)
Standard value, \(\Delta H^0_s\) = 11.39 ± 0.03 kJ.mol\(^{-1}\)

Table 5.25 Standard Enthalpy of Solution of Sodium \([5Cl-2 (pOHPPhN_2)]\) Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>(c) mol.dm(^{-3})</th>
<th>(\sqrt{c}) mol(^{1/2}).dm(^{3/2})</th>
<th>(\Delta H_s) kJ.mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03707</td>
<td>2.48x10(^{-3})</td>
<td>4.98x10(^{-2})</td>
<td>-4.10</td>
</tr>
<tr>
<td>0.06481</td>
<td>4.34x10(^{-3})</td>
<td>6.59x10(^{-2})</td>
<td>-4.18</td>
</tr>
<tr>
<td>0.04283</td>
<td>2.87x10(^{-3})</td>
<td>5.36x10(^{-2})</td>
<td>-4.15</td>
</tr>
<tr>
<td>0.08174</td>
<td>5.48x10(^{-3})</td>
<td>7.40x10(^{-2})</td>
<td>-4.25</td>
</tr>
<tr>
<td>0.13768</td>
<td>9.22x10(^{-3})</td>
<td>9.60x10(^{-2})</td>
<td>-4.36</td>
</tr>
<tr>
<td>0.11289</td>
<td>7.56x10(^{-3})</td>
<td>8.70x10(^{-2})</td>
<td>-4.44</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s\) = -4.25 ± 0.12 kJ.mol\(^{-1}\)
Standard value, \(\Delta H^0_s\) = -3.77 ± 0.10 kJ.mol\(^{-1}\)
Table 5.26 Standard Enthalpy of Solution of Sodium \([5Cl-2 (pOHPhN)]\) Benzoate in N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (mol.dm(^{-3}))</th>
<th>(\sqrt{c}) (mol(^{1/2}).dm(^{-3/2}))</th>
<th>(\Delta H_s) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03940</td>
<td>1.32\times10^{-3}</td>
<td>3.63\times10^{-3}</td>
<td>0.87</td>
</tr>
<tr>
<td>0.02149</td>
<td>0.72\times10^{-3}</td>
<td>0.85\times10^{-2}</td>
<td>1.99</td>
</tr>
<tr>
<td>0.01701</td>
<td>0.57\times10^{-3}</td>
<td>0.75\times10^{-2}</td>
<td>2.84</td>
</tr>
<tr>
<td>0.04618</td>
<td>1.50\times10^{-3}</td>
<td>3.93\times10^{-2}</td>
<td>0.67</td>
</tr>
<tr>
<td>0.03499</td>
<td>1.20\times10^{-3}</td>
<td>3.42\times10^{-2}</td>
<td>0.99</td>
</tr>
<tr>
<td>0.03070</td>
<td>1.00\times10^{-3}</td>
<td>3.20\times10^{-2}</td>
<td>1.13</td>
</tr>
<tr>
<td>0.04374</td>
<td>1.50\times10^{-3}</td>
<td>3.83\times10^{-2}</td>
<td>0.71</td>
</tr>
<tr>
<td>0.01845</td>
<td>0.60\times10^{-3}</td>
<td>2.49\times10^{-2}</td>
<td>1.51</td>
</tr>
<tr>
<td>0.01200</td>
<td>0.40\times10^{-3}</td>
<td>2.01\times10^{-2}</td>
<td>1.72</td>
</tr>
<tr>
<td>0.02232</td>
<td>0.70\times10^{-3}</td>
<td>2.73\times10^{-2}</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s = 1.379 \pm 0.64\) kJ.mol\(^{-1}\)

Standard value, \(\Delta H^\circ_s = 2.87 \pm 0.17\) kJ.mol\(^{-1}\)

Table 5.27 Standard Enthalpy of Solution of Sodium \([6Cl-2 (pOHPhN)]\) Benzoate in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (mol.dm(^{-3}))</th>
<th>(\sqrt{c}) (mol(^{1/2}).dm(^{-3/2}))</th>
<th>(\Delta H_s) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02611</td>
<td>1.75\times10^{-3}</td>
<td>4.18\times10^{-2}</td>
<td>-24.99</td>
</tr>
<tr>
<td>0.04283</td>
<td>2.87\times10^{-3}</td>
<td>5.36\times10^{-2}</td>
<td>-25.02</td>
</tr>
<tr>
<td>0.03376</td>
<td>2.26\times10^{-3}</td>
<td>4.76\times10^{-2}</td>
<td>-24.99</td>
</tr>
<tr>
<td>0.05033</td>
<td>3.37\times10^{-3}</td>
<td>5.81\times10^{-2}</td>
<td>-25.06</td>
</tr>
<tr>
<td>0.06606</td>
<td>4.43\times10^{-3}</td>
<td>6.65\times10^{-2}</td>
<td>-25.04</td>
</tr>
<tr>
<td>0.06285</td>
<td>2.10\times10^{-3}</td>
<td>4.59\times10^{-2}</td>
<td>-24.98</td>
</tr>
<tr>
<td>0.08667</td>
<td>2.90\times10^{-3}</td>
<td>5.39\times10^{-2}</td>
<td>-25.02</td>
</tr>
<tr>
<td>0.03730</td>
<td>1.25\times10^{-3}</td>
<td>3.53\times10^{-2}</td>
<td>-24.97</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H_s = -25.01 \pm 0.03\) kJ.mol\(^{-1}\)

Standard value, \(\Delta H^\circ_s = -24.86 \pm 0.03\) kJ.mol\(^{-1}\)
Table 5.28 Standard Enthalpy of Solution of Sodium \([\text{6Cl-2 (pOHPPhN}_2\text{)}]\) Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (\text{mol dm}^{-3})</th>
<th>(\sqrt{c}) (\text{mol}^{1/2}\text{dm}^{-3/2})</th>
<th>(\Delta H_s) kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01981</td>
<td>1.33x10(^3)</td>
<td>3.64x10(^{-2})</td>
<td>-47.91</td>
</tr>
<tr>
<td>0.04272</td>
<td>2.86x10(^3)</td>
<td>5.35x10(^{-2})</td>
<td>-48.59</td>
</tr>
<tr>
<td>0.07938</td>
<td>5.32x10(^3)</td>
<td>7.29x10(^{-2})</td>
<td>-49.37</td>
</tr>
<tr>
<td>0.02367</td>
<td>1.59x10(^3)</td>
<td>3.98x10(^{-2})</td>
<td>-48.30</td>
</tr>
<tr>
<td>0.05682</td>
<td>3.81x10(^3)</td>
<td>6.17x10(^{-2})</td>
<td>-49.16</td>
</tr>
<tr>
<td>0.03703</td>
<td>2.48x10(^3)</td>
<td>4.98x10(^{-2})</td>
<td>-48.63</td>
</tr>
<tr>
<td>0.10686</td>
<td>7.16x10(^3)</td>
<td>8.46x10(^{-2})</td>
<td>-49.87</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H^o_s\) = -48.83 ± 0.62 kJ mol\(^{-1}\)
Standard value, \(\Delta H^o_s\) = -46.67 ± 0.18 kJ mol\(^{-1}\)

Table 5.29 Standard Enthalpy of Solution of Sodium \([\text{6Cl-2 (pOHPPhN}_2\text{)}]\) Benzoate in \(\text{N,N'-Dimethylformamide}\) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(c) (\text{mol dm}^{-3})</th>
<th>(\sqrt{c}) (\text{mol}^{1/2}\text{dm}^{-3/2})</th>
<th>(\Delta H_s) kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04322</td>
<td>1.45x10(^3)</td>
<td>3.81x10(^{-2})</td>
<td>-49.51</td>
</tr>
<tr>
<td>0.06590</td>
<td>2.21x10(^3)</td>
<td>4.70x10(^{-2})</td>
<td>-49.44</td>
</tr>
<tr>
<td>0.10845</td>
<td>3.63x10(^3)</td>
<td>6.03x10(^{-2})</td>
<td>-48.97</td>
</tr>
<tr>
<td>0.08425</td>
<td>2.82x10(^3)</td>
<td>5.31x10(^{-2})</td>
<td>-49.19</td>
</tr>
</tbody>
</table>

Average value of \(\Delta H^o_s\) = -49.28 ± 0.21 kJ mol\(^{-1}\)
Standard value, \(\Delta H^o_s\) = -50.53 ± 0.25 kJ mol\(^{-1}\)
Table 5.30 Standard Enthalpy of Solution of Sodium [2Cl- (pOHPhN)] Benzoate in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm⁻³)</th>
<th>√c (mol¹².dm⁻³²)</th>
<th>ΔH (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02315</td>
<td>0.80x10⁻³</td>
<td>2.78x10⁻²</td>
<td>17.96</td>
</tr>
<tr>
<td>0.01635</td>
<td>0.50x10⁻³</td>
<td>2.34x10⁻²</td>
<td>19.10</td>
</tr>
<tr>
<td>0.03888</td>
<td>1.30x10⁻³</td>
<td>3.61x10⁻²</td>
<td>16.92</td>
</tr>
<tr>
<td>0.03305</td>
<td>1.10x10⁻³</td>
<td>3.33x10⁻²</td>
<td>20.02</td>
</tr>
<tr>
<td>0.01909</td>
<td>0.60x10⁻³</td>
<td>2.53x10⁻²</td>
<td>19.18</td>
</tr>
<tr>
<td>0.01662</td>
<td>0.59x10⁻³</td>
<td>2.36x10⁻²</td>
<td>18.13</td>
</tr>
</tbody>
</table>

Average value of ΔH = 18.55 ± 0.99 kJ mol⁻¹  
Standard value, ΔH° = 20.08 ± 2.86 kJ mol⁻¹

Table 5.31 Standard Enthalpy of Solution of Sodium [2Cl- (pOHPhN)] Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm⁻³)</th>
<th>√c (mol¹².dm⁻³²)</th>
<th>ΔH (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01595</td>
<td>1.07x10⁻³</td>
<td>3.27x10⁻²</td>
<td>-49.88</td>
</tr>
<tr>
<td>0.03744</td>
<td>2.51x10⁻³</td>
<td>5.01x10⁻²</td>
<td>-51.05</td>
</tr>
<tr>
<td>0.02355</td>
<td>1.58x10⁻³</td>
<td>3.97x10⁻²</td>
<td>-50.25</td>
</tr>
<tr>
<td>0.04629</td>
<td>3.10x10⁻³</td>
<td>5.57x10⁻²</td>
<td>-51.13</td>
</tr>
<tr>
<td>0.05967</td>
<td>4.00x10⁻³</td>
<td>6.32x10⁻²</td>
<td>-51.30</td>
</tr>
<tr>
<td>0.07308</td>
<td>4.90x10⁻³</td>
<td>7.00x10⁻²</td>
<td>-51.69</td>
</tr>
<tr>
<td>0.10468</td>
<td>7.01x10⁻³</td>
<td>8.37x10⁻²</td>
<td>-52.29</td>
</tr>
</tbody>
</table>

Average value of ΔH = -51.08 ± 0.76 kJ mol⁻¹  
Standard value, ΔH° = -48.50 ± 0.20 kJ mol⁻¹
Table 5.32 Standard Enthalpy of Solution of Sodium [2Cl-4 (pOHPhN)] Benzoate in N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>c mol.dm$^{-3}$</th>
<th>$\sqrt{c}$ mol$^{1/2}$.dm$^{-3/2}$</th>
<th>$\Delta H_s$ kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02798</td>
<td>0.94x10$^{-3}$</td>
<td>3.06x10$^{-2}$</td>
<td>0</td>
</tr>
<tr>
<td>0.04838</td>
<td>1.62x10$^{-3}$</td>
<td>4.03x10$^{-2}$</td>
<td>0</td>
</tr>
<tr>
<td>0.06824</td>
<td>2.29x10$^{-3}$</td>
<td>4.78x10$^{-2}$</td>
<td>0</td>
</tr>
<tr>
<td>0.09185</td>
<td>3.08x10$^{-3}$</td>
<td>5.55x10$^{-2}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Heat of solution of Sodium [2Cl-4 (pOHPhN)] Benzoate in N,N'-Dimethylformamide, at 298.15 K, was found to be zero.

Table 5.33 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPhN)] Benzoate in Water:Methanol Mixture (30:70) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>c mol.dm$^{-3}$</th>
<th>$\sqrt{c}$ mol$^{1/2}$.dm$^{-3/2}$</th>
<th>$\Delta H_s$ kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02225</td>
<td>0.7x10$^{-3}$</td>
<td>2.73x10$^{-2}$</td>
<td>3.01</td>
</tr>
<tr>
<td>0.01681</td>
<td>0.6x10$^{-3}$</td>
<td>2.37x10$^{-2}$</td>
<td>3.77</td>
</tr>
<tr>
<td>0.03097</td>
<td>1.0x10$^{-3}$</td>
<td>3.22x10$^{-2}$</td>
<td>2.43</td>
</tr>
<tr>
<td>0.03823</td>
<td>1.3x10$^{-3}$</td>
<td>3.58x10$^{-2}$</td>
<td>3.38</td>
</tr>
<tr>
<td>0.04546</td>
<td>1.5x10$^{-3}$</td>
<td>3.90x10$^{-2}$</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Average value of $\Delta H_s = 3.15 \pm 0.44$ kJ.mol$^{-1}$

Standard value, $\Delta H^0_s = 3.96 \pm 1.40$ kJ.mol$^{-1}$
Table 5.34 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPnN)] Benzoate in Water:Methanol Mixture (60:40) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol.dm⁻³)</th>
<th>( \sqrt{c} ) (mol¹².dm⁻⁶²)</th>
<th>( \Delta H_s ) (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01816</td>
<td>0.6x10⁻³</td>
<td>2.47x10⁻²</td>
<td>11.10</td>
</tr>
<tr>
<td>0.02657</td>
<td>0.9x10⁻³</td>
<td>2.98x10⁻²</td>
<td>7.92</td>
</tr>
<tr>
<td>0.03476</td>
<td>1.2x10⁻³</td>
<td>3.41x10⁻²</td>
<td>9.78</td>
</tr>
<tr>
<td>0.04222</td>
<td>1.4x10⁻³</td>
<td>3.76x10⁻²</td>
<td>9.41</td>
</tr>
<tr>
<td>0.01189</td>
<td>0.4x10⁻³</td>
<td>2.00x10⁻²</td>
<td>9.69</td>
</tr>
</tbody>
</table>

Average value of \( \Delta H_s = 9.58 ± 1.01 \) kJ.mol⁻¹
Standard value, \( \Delta H^o_s = 10.93 ± 2.65 \) kJ.mol⁻¹

Table 5.35 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPnN)] Benzoate in Water:Methanol Mixture (80:20) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol.dm⁻³)</th>
<th>( \sqrt{c} ) (mol¹².dm⁻⁶²)</th>
<th>( \Delta H_s ) (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01560</td>
<td>0.5x10⁻³</td>
<td>2.29x10⁻²</td>
<td>22.34</td>
</tr>
<tr>
<td>0.02967</td>
<td>1.0x10⁻³</td>
<td>3.15x10⁻²</td>
<td>19.67</td>
</tr>
<tr>
<td>0.02097</td>
<td>0.7x10⁻³</td>
<td>2.65x10⁻²</td>
<td>20.03</td>
</tr>
<tr>
<td>0.02516</td>
<td>0.8x10⁻³</td>
<td>2.90x10⁻²</td>
<td>21.19</td>
</tr>
<tr>
<td>0.03761</td>
<td>1.3x10⁻³</td>
<td>3.55x10⁻²</td>
<td>20.44</td>
</tr>
</tbody>
</table>

Average value of \( \Delta H_s = 3.15 ± 0.44 \) kJ.mol⁻¹
Standard value, \( \Delta H^o_s = 3.96 ± 1.40 \) kJ.mol⁻¹

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Table 5.36 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPhN)₃] Benzoate in Water:Methanol Mixture (45:55) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass ( g )</th>
<th>( c ) ( \text{mol.dm}^{-3} )</th>
<th>( \sqrt{c} ) ( \text{mol}^{1/2} \cdot \text{dm}^{3/2} )</th>
<th>( \Delta H_{s} ) ( \text{kJ.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01550</td>
<td>0.5x10⁻³</td>
<td>2.28x10⁻²</td>
<td>10.91</td>
</tr>
<tr>
<td>0.02309</td>
<td>0.8x10⁻³</td>
<td>2.78x10⁻²</td>
<td>10.81</td>
</tr>
<tr>
<td>0.03577</td>
<td>1.2x10⁻³</td>
<td>3.46x10⁻²</td>
<td>12.21</td>
</tr>
<tr>
<td>0.02982</td>
<td>1.0x10⁻³</td>
<td>3.16x10⁻²</td>
<td>10.76</td>
</tr>
</tbody>
</table>

Average value of \( \Delta H_{s} = 11.17 \pm 0.6 \text{kJ.mol}^{-1} \)
Standard value, \( \Delta H^{o}_{s} = 8.62 \pm 2.20 \text{kJ.mol}^{-1} \)

Table 5.37 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPhN)₃] Benzoate in Water:Methanol Mixture (70:30) at 298.15 K.

<table>
<thead>
<tr>
<th>Mass ( g )</th>
<th>( c ) ( \text{mol.dm}^{-3} )</th>
<th>( \sqrt{c} ) ( \text{mol}^{1/2} \cdot \text{dm}^{3/2} )</th>
<th>( \Delta H_{s} ) ( \text{kJ.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02092</td>
<td>0.7x10⁻³</td>
<td>2.65x10⁻²</td>
<td>21.55</td>
</tr>
<tr>
<td>0.01277</td>
<td>0.4x10⁻³</td>
<td>2.07x10⁻²</td>
<td>21.21</td>
</tr>
<tr>
<td>0.02729</td>
<td>0.9x10⁻³</td>
<td>3.02x10⁻²</td>
<td>24.48</td>
</tr>
<tr>
<td>0.03635</td>
<td>1.2x10⁻³</td>
<td>3.49x10⁻²</td>
<td>22.68</td>
</tr>
</tbody>
</table>

Average value of \( \Delta H_{s} = 22.48 \pm 1.28 \text{kJ.mol}^{-1} \)
Standard value, \( \Delta H^{o}_{s} = 18.19 \pm 3.89 \text{kJ.mol}^{-1} \)
Table 5.38 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPhN₂)] Benzoate in Water at 298.15 K.

<table>
<thead>
<tr>
<th>% MeOH</th>
<th>ΔH°, / kJ.mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-17.64</td>
</tr>
<tr>
<td>70</td>
<td>3.15</td>
</tr>
<tr>
<td>55</td>
<td>11.17</td>
</tr>
<tr>
<td>40</td>
<td>9.58</td>
</tr>
<tr>
<td>30</td>
<td>22.48</td>
</tr>
<tr>
<td>20</td>
<td>20.73</td>
</tr>
<tr>
<td>0</td>
<td>23.43</td>
</tr>
</tbody>
</table>

ΔH°, of 4Cl-3 (pOHPhN₂) NaB in Water = 23.43 ± 0.50 kJ.mol⁻¹

Table 5.39 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPhN₂)] Benzoate in Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>c mol.dm⁻³</th>
<th>√c mol¹².dm⁻³²</th>
<th>ΔHₙ kJ.mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02321</td>
<td>1.56x10⁻³</td>
<td>3.94x10⁻²</td>
<td>-17.36</td>
</tr>
<tr>
<td>0.03720</td>
<td>2.49x10⁻³</td>
<td>4.99x10⁻²</td>
<td>-17.80</td>
</tr>
<tr>
<td>0.04990</td>
<td>3.34x10⁻³</td>
<td>5.78x10⁻²</td>
<td>-18.12</td>
</tr>
<tr>
<td>0.01233</td>
<td>0.83x10⁻³</td>
<td>2.87x10⁻²</td>
<td>-16.85</td>
</tr>
<tr>
<td>0.01833</td>
<td>1.23x10⁻³</td>
<td>3.50x10⁻²</td>
<td>-17.16</td>
</tr>
<tr>
<td>0.03036</td>
<td>2.03x10⁻³</td>
<td>4.51x10⁻²</td>
<td>-17.59</td>
</tr>
<tr>
<td>0.06473</td>
<td>4.34x10⁻³</td>
<td>6.59x10⁻²</td>
<td>-18.56</td>
</tr>
</tbody>
</table>

Average value of ΔHₙ = -17.64 ± 0.54 kJ.mol⁻¹
Standard value, ΔH°ₙ = -15.58 ± 0.04 kJ.mol⁻¹
Table 5.40 Standard Enthalpy of Solution of Sodium [4Cl-3 (pOHPhN2)] Benzoate in N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>e (mol.dm⁻³)</th>
<th>sqrt(e) (mol⁻¹.dm⁻³)</th>
<th>ΔHᵥ (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05321</td>
<td>1.78x10⁻³</td>
<td>4.22x10⁻²</td>
<td>-14.82</td>
</tr>
<tr>
<td>0.04268</td>
<td>1.43x10⁻³</td>
<td>3.78x10⁻²</td>
<td>-14.93</td>
</tr>
<tr>
<td>0.06937</td>
<td>2.32x10⁻³</td>
<td>4.82x10⁻²</td>
<td>-15.33</td>
</tr>
<tr>
<td>0.11066</td>
<td>3.71x10⁻³</td>
<td>6.09x10⁻²</td>
<td>-15.55</td>
</tr>
</tbody>
</table>

Average value of ΔHᵥ = -15.16 ± 0.30 kJ.mol⁻¹
Standard value, ΔHᵥ = -13.69 ± 0.47 kJ.mol⁻¹

Table 5.41 Standard Enthalpies of Solution of Haptens in Water, Methanol and N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>ΔHᵥ (H₂O) (kJ.mol⁻¹)</th>
<th>ΔHᵥ (MeOH) (kJ.mol⁻¹)</th>
<th>ΔHᵥ (DMF) (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN₂)NaB</td>
<td>7.90 ± 0.04</td>
<td>-11.34 ± 0.02</td>
<td>7.43 ± 1.00</td>
</tr>
<tr>
<td>meta (pOHPhN₂)NaB</td>
<td>23.85 ± 0.80</td>
<td>-13.57 ± 0.09</td>
<td>-4.89 ± 0.19</td>
</tr>
<tr>
<td>para (pOHPhN₂)NaB</td>
<td>28.03 ± 0.84</td>
<td>-9.36 ± 0.16</td>
<td>-2.58 ± 0.03</td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN₂)NaB</td>
<td>11.39 ± 0.02</td>
<td>-3.77 ± 0.10</td>
<td>-2.87 ± 0.17</td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN₂)NaB</td>
<td>-24.86 ± 0.03</td>
<td>-46.67 ± 0.18</td>
<td>-50.53 ± 0.25</td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN₂)NaB</td>
<td>18.55 ± 0.99</td>
<td>-48.50 ± 0.20</td>
<td>0</td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN₂)NaB</td>
<td>23.43 ± 0.50</td>
<td>-15.58 ± 0.04</td>
<td>-13.69 ± 0.47</td>
</tr>
</tbody>
</table>
Table 5.42 Standard Enthalpies of Transfer of Haptens from Water to Non-Aqueous Solvents at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>$\Delta H^\circ$, (H$_2$O) $^a$</th>
<th>$\Delta H^\circ$, (MeOH) $^a$</th>
<th>$\Delta H^\circ$, (H$_2$O$\rightarrow$MeOH) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ.mol$^{-1}$</td>
<td>kJ.mol$^{-1}$</td>
<td>kJ.mol$^{-1}$</td>
</tr>
<tr>
<td><strong>WATER $\rightarrow$ MeOH</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho $(pOHPhN_2)NaB$</td>
<td>7.90</td>
<td>-11.34</td>
<td>-19.24</td>
</tr>
<tr>
<td>meta $(pOHPhN_2)NaB$</td>
<td>23.85</td>
<td>-13.57</td>
<td>-37.42</td>
</tr>
<tr>
<td>para $(pOHPhN_2)NaB$</td>
<td>28.03</td>
<td>-9.36</td>
<td>-37.39</td>
</tr>
<tr>
<td>5Cl-2 $(pOHPhN_2)NaB$</td>
<td>11.39</td>
<td>-3.77</td>
<td>-15.16</td>
</tr>
<tr>
<td>6Cl-2 $(pOHPhN_2)NaB$</td>
<td>-24.86</td>
<td>-46.67</td>
<td>-21.81</td>
</tr>
<tr>
<td>2Cl-4 $(pOHPhN_2)NaB$</td>
<td>18.55</td>
<td>-48.50</td>
<td>-67.05</td>
</tr>
<tr>
<td>4Cl-3 $(pOHPhN_2)NaB$</td>
<td>23.43</td>
<td>-15.58</td>
<td>-39.01</td>
</tr>
<tr>
<td><strong>WATER $\rightarrow$ DMF</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho $(pOHPhN_2)NaB$</td>
<td>7.90</td>
<td>7.43</td>
<td>-0.48</td>
</tr>
<tr>
<td>meta $(pOHPhN_2)NaB$</td>
<td>23.85</td>
<td>-4.89</td>
<td>-28.74</td>
</tr>
<tr>
<td>para $(pOHPhN_2)NaB$</td>
<td>28.03</td>
<td>-2.58</td>
<td>-30.62</td>
</tr>
<tr>
<td>5Cl-2 $(pOHPhN_2)NaB$</td>
<td>11.39</td>
<td>-2.87</td>
<td>-8.52</td>
</tr>
<tr>
<td>6Cl-2 $(pOHPhN_2)NaB$</td>
<td>-24.86</td>
<td>-50.53</td>
<td>-25.67</td>
</tr>
<tr>
<td>2Cl-4 $(pOHPhN_2)NaB$</td>
<td>18.55</td>
<td>0</td>
<td>-18.55</td>
</tr>
<tr>
<td>4Cl-3 $(pOHPhN_2)NaB$</td>
<td>23.43</td>
<td>-13.69</td>
<td>-37.12</td>
</tr>
</tbody>
</table>

$^a$ Data from Table 5.41.

$^b$ Data obtained using equation 5.19.
It is seen that the enthalpies transfer data (Table 5.42) of sodium \([para\ hydroxyphenylazo\ and\ chloro-substituted\ \textit{para}hydroxyphenylazo]\) benzoate from water to methanol and from water to N,N'-Dimethylformamide, result in a favourable enthalpy \(\Delta H^\circ\). The enthalpies for the transfer from water to methanol are more negative than those for the transfer from Water to N,N'-Dimethylformamide suggesting that these electrolytes (haptens) are enthalpically more stable in methanol than N,N'-Dimethylformamide. Undoubtedly, there is a number of contributions to the transfer enthalpy that must be taken into account. Among these are:-

a) The breaking of solvent-solvent bonds as a result of the introduction of the solute in the solvent (endothermic process).

b) The solute-solvent interactions (exothermic process).

The former contribution (a) is likely to predominate. This contribution arises from the different energetic requirements for cavity formation in water and N,N'-Dimethylformamide. Water is a highly structured solvent and therefore, it has a much more ordered structure than methanol or N,N'-Dimethylformamide. Therefore, the energy required to break solvent-solvent bonds in water as a result of the solute entering the solvent is expected to be much higher for water than for others. Naturally, the overall process of transfer results in an exothermic reaction.

5.1.3 Standard Entropies of Haptens from Water to Non-Aqueous Solvent at 298.15 K.

Standard entropies of transfer, \(\Delta S^\circ\), for electrolytes from a reference solvent (water) to another solvent (non-aqueous) involve the chemical process described by eqn 5.18. \(\Delta S^\circ\), may be expressed by:-

\[
\Delta S^\circ = \Delta S^\circ, (s) - \Delta S^\circ, (H_2O) \tag{5.21}
\]
where $\Delta S^\circ, (s)$ and $\Delta S^\circ, (H_2O)$ are the standard entropies of solution of the electrolyte in question in the solvent (s) and in water, respectively. A combination between free energies and enthalpies of solution could also yield entropies of solution using the equation:

$$\Delta S^\circ_i = \frac{(\Delta H^\circ, - \Delta G^\circ)}{T}$$  \hspace{1cm} 5.22

The obtained results for the standard entropies of solution of sodium [para hydroxyphenylazo and chloro-substituted para hydroxyphenylazo] benzoate in water, methanol and N,N’-Dimethylformamide, at 298.15K, are shown in Table 5.43. Table 5.44 contains the standard entropies of transfer of these haptens from water to methanol and water to N,N’-Dimethylformamide at 298.15 K.
Table 5.43 Standard Thermodynamic Parameters of solution (ΔG°, ΔH°, and ΔS°,) of Sodium [parahydroxyphenylazo and chloro-Substituted para hydroxyphenylazo] Benzoate in Water, Methanol and N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>Solvent</th>
<th>ΔG°, kJ.mol⁻¹</th>
<th>ΔH°, kJ.mol⁻¹</th>
<th>ΔS°, J.mol⁻¹.K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>14.10</td>
<td>7.90</td>
<td>-21</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>18.21</td>
<td>-11.34</td>
<td>-99</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>21.66</td>
<td>7.43</td>
<td>-48</td>
</tr>
<tr>
<td><strong>ortho (pOHPhN₂)NaB</strong></td>
<td></td>
<td>14.10</td>
<td>7.90</td>
<td>-21</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>18.07</td>
<td>-13.57</td>
<td>-106</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>21.98</td>
<td>-4.89</td>
<td>-83</td>
</tr>
<tr>
<td><strong>meta (pOHPhN₂)NaB</strong></td>
<td></td>
<td>20.66</td>
<td>23.85</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>19.17</td>
<td>-9.36</td>
<td>-96</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>19.98</td>
<td>-4.89</td>
<td>-83</td>
</tr>
<tr>
<td><strong>para (pOHPhN₂)NaB</strong></td>
<td></td>
<td>22.72</td>
<td>28.03</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>23.73</td>
<td>-3.77</td>
<td>-92</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>26.37</td>
<td>-2.58</td>
<td>-97</td>
</tr>
<tr>
<td><strong>5Cl-2 (pOHPhN₂)NaB</strong></td>
<td></td>
<td>20.26</td>
<td>11.39</td>
<td>-30</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>23.68</td>
<td>2.87</td>
<td>-70</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>23.68</td>
<td>2.87</td>
<td>-70</td>
</tr>
<tr>
<td><strong>6Cl-2 (pOHPhN₂)NaB</strong></td>
<td></td>
<td>9.42</td>
<td>-24.86</td>
<td>-115</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>16.98</td>
<td>-46.67</td>
<td>-213</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>22.48</td>
<td>-50.53</td>
<td>-245</td>
</tr>
<tr>
<td><strong>2Cl-4 (pOHPhN₂)NaB</strong></td>
<td></td>
<td>24.60</td>
<td>18.55</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>13.27</td>
<td>-48.50</td>
<td>-207</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>20.63</td>
<td>0</td>
<td>-69</td>
</tr>
<tr>
<td><strong>4Cl-3 (pOHPhN₂)NaB</strong></td>
<td></td>
<td>19.52</td>
<td>23.43</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>21.74</td>
<td>-15.58</td>
<td>-125</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>27.13</td>
<td>-13.69</td>
<td>-137</td>
</tr>
</tbody>
</table>
Table 5.44 Standard Thermodynamic Parameters of Transfer ($\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$) of Sodium [para-hydroxyphenylazo and chloro-Substituted para hydroxyphenylazo] Benzoate from Water to Methanol and Water to N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Haptens</th>
<th>$\Delta G^\circ$, kJ.mol$^{-1}$</th>
<th>$\Delta H^\circ$, kJ.mol$^{-1}$</th>
<th>$\Delta S^\circ$, J.mol$^{-1}$.K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>4.11</td>
<td>-19.24</td>
<td>-78</td>
</tr>
<tr>
<td>meta $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>-2.59</td>
<td>-37.42</td>
<td>-117</td>
</tr>
<tr>
<td>para $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>-3.55</td>
<td>-37.39</td>
<td>-114</td>
</tr>
<tr>
<td>5Cl-2 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>3.47</td>
<td>-15.16</td>
<td>-62</td>
</tr>
<tr>
<td>6Cl-2 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>7.56</td>
<td>-21.81</td>
<td>-99</td>
</tr>
<tr>
<td>2Cl-4 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>-11.33</td>
<td>-67.05</td>
<td>-187</td>
</tr>
<tr>
<td>4Cl-3 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>2.22</td>
<td>-39.01</td>
<td>-138</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Haptens</th>
<th>$\Delta G^\circ$, kJ.mol$^{-1}$</th>
<th>$\Delta H^\circ$, kJ.mol$^{-1}$</th>
<th>$\Delta S^\circ$, J.mol$^{-1}$.K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>7.56</td>
<td>-0.48</td>
<td>-27</td>
</tr>
<tr>
<td>meta $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>-0.68</td>
<td>-28.74</td>
<td>-94</td>
</tr>
<tr>
<td>para $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>3.65</td>
<td>-30.62</td>
<td>-115</td>
</tr>
<tr>
<td>5Cl-2 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>3.42</td>
<td>-8.52</td>
<td>-40</td>
</tr>
<tr>
<td>6Cl-2 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>13.06</td>
<td>-25.67</td>
<td>-130</td>
</tr>
<tr>
<td>2Cl-4 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>-3.97</td>
<td>-18.55</td>
<td>-49</td>
</tr>
<tr>
<td>4Cl-3 $(p\text{OHPhN}_2)\text{NaB}$</td>
<td>7.61</td>
<td>-37.12</td>
<td>-150</td>
</tr>
</tbody>
</table>

The transfer entropies for these haptens, shown in Table 5.44, from Water to methanol and water to N,N'-Dimethylformamide are all negative ($\Delta S^\circ < 0$). This may be attributed to the degree of structure of the solvents (water, methanol and N,N'-Dimethylformamide) which seem to play a major role in the unfavourable entropies observed for the transfer of these electrolytes from water to methanol and
from water to N,N'-Dimethylformamide.

Since the transfer of these haptens from water to methanol and N,N'-Dimethylformamide is enthalpically favourable (ΔH° < 0) and entropically unfavourable (ΔS° < 0) therefore, it is indeed the rather unfavourable transfer entropy which overcomes the enthalpy contribution and lead to a positive transfer free energy, ΔG°.

However, the transfer parameters are referred to the dissociated electrolytes and therefore, cation and anion contributions are involved. In attempt to analyse the anion contribution, single-ion quantities were calculated.

5.1.4 Single-Ion Thermodynamic Parameters for the Transfer of p-OHPhN₂ and chloro-Substituted p-OHPhN₂ Benzoate Anions from Water to Non-Aqueous Solvents at 298.15 K. Data Based on the Ph₄AsPh₄B Convention.

In order to calculate the single-ion thermodynamic quantities of transfer (ΔG°, (X), ΔH°, (X) and ΔS°, (X)) of parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo benzoate anions, from water to methanol and water to N,N'-Dimethylformamide, the following equations were used:

\[
\Delta G°, (X)_{\text{H}_2\text{O}} \rightarrow s = \Delta G°, (\text{Na}^+X^-)_{\text{H}_2\text{O}} \rightarrow s - \Delta G°, (\text{Na}^+)_{\text{H}_2\text{O}} \rightarrow s
\]

\[
\Delta H°, (X)_{\text{H}_2\text{O}} \rightarrow s = \Delta H°, (\text{Na}^+X^-)_{\text{H}_2\text{O}} \rightarrow s - \Delta H°, (\text{Na}^+)_{\text{H}_2\text{O}} \rightarrow s
\]

\[
\Delta S°, (X)_{\text{H}_2\text{O}} \rightarrow s = \Delta S°, (\text{Na}^+X^-)_{\text{H}_2\text{O}} \rightarrow s - \Delta S°(\text{Na}^+)_{\text{H}_2\text{O}} \rightarrow s
\]

Single-ion values for the transfer of sodium ion (ΔG°, Na⁺, ΔH°, Na⁺ and ΔS°, Na⁺), from water to methanol and from water to N,N'-Dimethylformamide, are those reported in the literature²¹³ and based on the Ph₄AsPh₄B convention²¹⁴.

Table 5.45 contains the different ΔG°, (X), ΔH°, (X) and ΔS°, (X) for the transfer of parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo
benzoate anions from water to methanol and water to N,N'-Dimethylformamide at 298.15 K.

**Table 5.45** Single-Ion Thermodynamic Parameters of Transfer of para-hydroxyphenylazo and chloro-Substituted para-hydroxyphenylazo Benzoate Anions from Water to Methanol and Water to N,N'-Dimethylformamide at 298.15 K. Data Based on the Ph₄AsPh₄B Convention.

<table>
<thead>
<tr>
<th>Orthogonal Ion</th>
<th>Water → MeOH</th>
<th>Water → DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN₂)B⁻</td>
<td>ΔG°, (X)</td>
<td>ΔH°, (X)</td>
</tr>
<tr>
<td>-4.47</td>
<td>1.26</td>
<td>20</td>
</tr>
<tr>
<td>meta (pOHPhN₂)B⁻</td>
<td>-11.17</td>
<td>-16.92</td>
</tr>
<tr>
<td>para (pOHPhN₂)B⁻</td>
<td>-12.13</td>
<td>-16.89</td>
</tr>
<tr>
<td>5CI-2 (pOHPhN₂)B⁻</td>
<td>-5.11</td>
<td>5.34</td>
</tr>
<tr>
<td>6CI-2 (pOHPhN₂)B⁻</td>
<td>-1.02</td>
<td>-1.31</td>
</tr>
<tr>
<td>2CI-4 (pOHPhN₂)B⁻</td>
<td>-19.91</td>
<td>-56.55</td>
</tr>
<tr>
<td>4CI-3 (pOHPhN₂)B⁻</td>
<td>-6.36</td>
<td>-18.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orthogonal Ion</th>
<th>Water → MeOH</th>
<th>Water → DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN₂)B⁻</td>
<td>17.14</td>
<td>32.54</td>
</tr>
<tr>
<td>meta (pOHPhN₂)B⁻</td>
<td>-8.90</td>
<td>4.27</td>
</tr>
<tr>
<td>para (pOHPhN₂)B⁻</td>
<td>-13.23</td>
<td>2.40</td>
</tr>
<tr>
<td>5CI-2 (pOHPhN₂)B⁻</td>
<td>13.00</td>
<td>24.49</td>
</tr>
<tr>
<td>6CI-2 (pOHPhN₂)B⁻</td>
<td>22.64</td>
<td>7.35</td>
</tr>
<tr>
<td>2CI-4 (pOHPhN₂)B⁻</td>
<td>5.61</td>
<td>14.46</td>
</tr>
<tr>
<td>4CI-3 (pOHPhN₂)B⁻</td>
<td>17.19</td>
<td>-4.11</td>
</tr>
</tbody>
</table>

* Values obtained using eqn 5.23.

b Values obtained using eqn 5.24.

c Values obtained using eqn 5.25.
It can be noticed that large variations are observed among the $\Delta G^\circ_i$ values for the different anions.

For the transfer of these anions from water to methanol, in all cases, $\Delta G^\circ_i$ values are negative indicating that these anions are better solvated in methanol than in water. However, in order to see the effect of the substituent group on the $\Delta G^\circ_i (X)$, a comparison of these data is made with similar single-ion $\Delta G^\circ_i$ values, of related anions e.g. benzoate, $\Delta G^\circ_i = 7.41$ kJ.mol$^{-1}$; p-nitrobenzoate $\Delta G^\circ_i = 4.48$ kJ.mol$^{-1}$ and p-methylbenzoate $\Delta G^\circ_i = 4.017$kJ.mol$^{-1}$. These data are also based on the Ph$\text{AsPh}_B$ convention and reported in the literature$^{213}$. As a result, it seems that the data are in line with the observation that an increase in the size of the anion will lead to more negative $\Delta G^\circ_i$ values, an effect which was attributed to the non-electrostatic contribution to the overall process of solvation$^{213}$.

However, for a better interpretation of the process of solvation of these anions, the contributions made by the transfer enthalpy, $\Delta H^\circ_i$ and entropy, $\Delta S^\circ$, to the $\Delta G^\circ$ values must be taken into consideration.

From the single-ion enthalpies and entropies of transfer of these anions from water to methanol, reported in Table 5.45, two different contributions of $\Delta H^\circ_i$ and $\Delta S^\circ_i$ lead to the negative $\Delta G^\circ_i$ values observed for the transfer of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoate anions from water to methanol. The transfer process can be:-

a) Enthalpically favourable (negative $\Delta H^\circ_i$ values) and entropically unfavourable (negative $\Delta S^\circ_i$ values). Therefore, the process is enthalpically controlled.

b) Entropically favourable (positive $\Delta S^\circ_i$ values) with $\Delta H^\circ_i$ values slightly positive or negative. Therefore, the process is entropically controlled.

The former combination (a) is observed for meta and para (para-hydroxy
phenylazo) benzoate anions. The latter (b), is typical of ortho, 5Cl-2, 6Cl-2 and 2Cl-4 (parahydroxyphenylazo) benzoate anions in transfer from water to methanol. For the latter anions, the obtained results seem to indicate that the presence of the parahydroxyphenylazo group next to the carboxylate anion results in steric restriction on the number of solvent molecules able to interact with these groups. Solvent exclusion effects are more likely to be observed in methanol (solvent molecule diameter, 3.59 Å) rather than in water (solvent molecule diameter, 2.76 Å). Consequently, an increase in entropy is expected for the transfer of these anions from water to methanol. The results shown in Table 5.45 support this interpretation.

The behaviour observed for meta and para (parahydroxyphenylazo) benzoate anions is compared to the behaviour observed for the corresponding substituted anions. In both cases, anions are enthalpy stabilised and entropy destabilised which may be partially attributed to the non-electrostatic contribution. This is expected to be larger (more negative in terms of ΔH and ΔS) in transfer from water (highly structured solvent) to methanol for the chloro-substituted anions than for the unsubstituted anions. However, it is unlikely that this contribution could result in the large differences observed among the ΔH° and ΔS° values for these anions, particularly for the 2Cl-4 (parahydroxyphenylazo) benzoate anion. The enhancement of solute-solvent interaction as a result of London dispersion forces between delocalised solutes and localised solvents have been demonstrated by Fong and Grunwald in a very interesting paper published in 1969. These forces are expected to be larger in methanol than in water. The single-ion values for the transfer of meta, para (parahydroxyphenylazo) benzoate and chloro-substituted parahydroxyphenylazo benzoate anions seem to indicate that the parahydroxyphenylazo group in meta and para positions, with respect to the carboxylate group, behave as a delocalised group. Therefore, as a result of London dispersion forces the interaction of these anions with methanol are bound to be greater than the interaction of the same anion with water. This is reflected in the relatively larger negative ΔH° and ΔS° values observed for the transfer of these ions as compared with corresponding data for the transfer of ortho and ortho substituted azobenzoate anions from water to methanol.
As far as the transfer of these anions from water to N,N'-Dimethylformamide is concerned, there are striking differences among single-ion values for the transfer of these anions from water to N,N'-Dimethylformamide. Indeed, \( \Delta G^\circ \), (X) values range from 5.6 to 21.4 kJ.mol\(^{-1}\); \( \Delta H^\circ \), values from -4 to 32.5 kJ.mol\(^{-1}\) and \( \Delta S^\circ \), values from 51.7 to -71.4 J.K\(^{-1}\).mol\(^{-1}\).

Single-ion \( \Delta G^\circ \), values from water to N,N'-Dimethylformamide are positive, indicating that these anions are better solvated in water than in N,N'-Dimethylformamide. This behaviour is somehow expected since the presence of two methyl groups in N,N'-Dimethylformamide results in a shielding effect on the positive ends of the dipole and therefore, this solvent is unlikely to be a good solvator for anions.

In chapter 3, we have reported Stokes radii of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo anions. The results indicated that these anions are better solvated in methanol than in DMF than in water (\( r_{\text{H}_2\text{O}} < r_{\text{DMF}} < r_{\text{MeOH}} \)). However, free energies of transfer of these anions from water to methanol and from water to DMF (Table 5.45) suggest that these anions are better solvated in methanol than in water but, the transfer free energy data of these anions from water to DMF indicate that water is a better solvator for the anions than DMF. Therefore, we conclude that stokes radii can not be regarded as an indication of the preferential solvation of these anions for N,N'-Dimethylformamide relative to water and hence, para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoate anions are better solvated in methanol than in water than in N,N'-Dimethylformamide.

A striking feature for these results is the compensation effect observed between \( \Delta H^\circ \), and \( \Delta S^\circ \), values. Thus an enthalpically favourable transfer is accompanied by a loss of entropy and vice versa. In fact, a linear correlation is obtained when single-ion \( \Delta H^\circ \), values are plotted vs \( \Delta S^\circ \), values for these anions. the slope of this line corresponds to the isoequilibrium temperature of 363 ± 85 K. An
intercept of $8.91 \pm 2.84 \text{kJ.mol}^{-1}$ and a correlation coefficient of 0.91 are calculated. This compensation effect is also observed for the transfer of these anions from water to methanol. In this case, a slope of $417 \pm 38 \text{K}$ and an intercept of $-7.08 \pm 1.56 \text{kJ.mol}^{-1}$ are observed. The correlation coefficient is found to be 0.98.

Figure 5.43 and 5.44 show the linear correlations observed between $\Delta H^0_\text{r} (X^\cdot)$ and $\Delta S^0_\text{r} (X^\cdot)$ for the transfer of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoate anions from water to methanol and water to N,N'-Dimethylformamide respectively.
Figure 5.43 A linear correlation suggesting a compensation effect between $\Delta H^\circ(X)$ and $\Delta S^\circ(X)$ from water to methanol.

Figure 5.44 A linear correlation suggesting a compensation effect between $\Delta H^\circ(X)$ and $\Delta S^\circ(X)$ from water to DMF.
5.2 Standard Thermodynamic Parameters of Transfer of Cyclodextrins from Water to N,N'-Dimethylformamide

In order to better understand the complexation process between cyclodextrins and haptens in water and N,N'-Dimethylformamide, solution and transfer thermodynamic properties of α, β and γ-cyclodextrins were determined in these reaction media.

5.2.1 Standard Thermodynamic Parameters of Solution of Cyclodextrins in Water and N,N'-Dimethylformamide at 298.15 K.

Solubilities of α, β and γ-cyclodextrin in N,N'-Dimethylformamide were determined by adding an excess of dextrin to the solvent. The mixture was shaken and left at 298.15 K for several days. Aliquots of the saturated solution were removed, filtered and analysed using the Hart Scientific 5021 titrator calorimeter. α, β and γ-cyclodextrin were titrated against sodium [meta (pOHPhNa)2] benzoate. The equilibrium constant and enthalpy of complexation between cyclodextrins and sodium [meta (pOHPhNa)2]benzoate are well established. Therefore, by using these data, solubilities of cyclodextrins in N,N'-Dimethylformamide were evaluated. Solubilities of α, β and γ-cyclodextrin in water are those published in the literature. In Table 5.46, solubility data of α, β and γ-cyclodextrin in water and N,N'-Dimethylformamide, at 298.15 K, are listed.

Standard free energies of solution, ΔG°, of α, β and γ-cyclodextrin in water and N,N'-Dimethylformamide were derived from their solubility data in these solvents. The process is referred:-

$$\text{CD}_{\text{solid}} \rightleftharpoons \text{CD}_{\text{soln}}$$ 5.26

The thermodynamic equilibrium constant, K, of this process may be given by:-
\[ K_s = a_{CD} \]  \hspace{1cm} 5.27

\( a_{CD} \) is the molar activity of cyclodextrin in solution. This is taken as the molar concentration of cyclodextrin in solution. Thus:

\[ a_{CD} = [CD] \]  \hspace{1cm} 5.28

where \([CD]\) is the molar concentration of cyclodextrins in solution. Therefore:

\[ K_s = [CD] \]  \hspace{1cm} 5.29

Then, the free energy of solution of cyclodextrins may be expressed by:

\[ \Delta G_s^o = -RT \ln [CD] \]  \hspace{1cm} 5.30

Details of calculations of \( \Delta G_s^o \) of \( \alpha, \beta \) and \( \gamma \)-cyclodextrin from their solubility data in water and \( N,N' \)-Dimethylformamide, at 298.15 K, are shown in Table 5.46.

Table 5.46 Solubilities and Standard Free Energies of Solution of \( \alpha, \beta \) and \( \gamma \)-Cyclodextrin in Water and \( N,N' \)-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Solubility</th>
<th>( \Delta G_s^o )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol dm(^{-3})</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>( DMF )</td>
</tr>
<tr>
<td>( \alpha )-Cyclodextrin</td>
<td>1.49x10(^{-1})</td>
</tr>
<tr>
<td>( \beta )-Cyclodextrin</td>
<td>1.63x10(^{-2})</td>
</tr>
<tr>
<td>( \gamma )-Cyclodextrin</td>
<td>1.79x10(^{-1})</td>
</tr>
</tbody>
</table>

* Data taken from reference 125.

* Data obtained by calorimetric titration.

* Data calculated using eqn 5.30

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Enthalpies of solution, $\Delta H_s$ of cyclodextrins were carried out, in water and N,N'-Dimethylformamide, using the Tronac 450 calorimeter. It must be pointed out that cyclodextrins were dried under vacuum at temperatures between 85 and 95°C for several days prior to use. Standard enthalpies of solution, $\Delta H^o_s$, were taken as an average of at least five measurements of the heat of solution of these ligands in these solvents. Details of calculation of standard enthalpies of solution of cyclodextrins in water and N,N'-Dimethylformamide are shown in Tables 5.47-5.52. A recapitulation of these data is listed in Table 5.53. The corresponding standard entropies of solution, $\Delta S^o_s$, were derived from combination between free energies and enthalpies of solution of cyclodextrins in water and N,N'-Dimethylformamide, using the equation:

$$\Delta S^o_s = (\Delta H^o_s - \Delta G^o_s)/T$$  \hspace{1cm} 5.31

Table 5.54 lists the different $\Delta S^o_s$ values of cyclodextrins in water and N,N'-Dimethylformamide at 298.15 K.

Table 5.47 Standard Enthalpy of Solution of $\alpha$-Cyclodextrin in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass g</th>
<th>$c$ mol.dm$^{-3}$</th>
<th>$\sqrt{c}$ mol$^{1/2}$.dm$^{3/2}$</th>
<th>$\Delta H_s$ kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03294</td>
<td>6.772x10$^{-4}$</td>
<td>2.60x10$^{-2}$</td>
<td>-62.78</td>
</tr>
<tr>
<td>0.05418</td>
<td>1.114x10$^{-3}$</td>
<td>3.34x10$^{-2}$</td>
<td>-64.84</td>
</tr>
<tr>
<td>0.06516</td>
<td>1.340x10$^{-3}$</td>
<td>3.66x10$^{-2}$</td>
<td>-62.82</td>
</tr>
<tr>
<td>0.05002</td>
<td>1.028x10$^{-3}$</td>
<td>3.21x10$^{-2}$</td>
<td>-63.23</td>
</tr>
<tr>
<td>0.02297</td>
<td>4.722x10$^{-4}$</td>
<td>2.17x10$^{-2}$</td>
<td>-59.78</td>
</tr>
</tbody>
</table>

Standard Enthalpy of Solution, $\Delta H^o_s = -62.69 \pm 1.39$ kJ.mol$^{-1}$
Table 5.48 Standard Enthalpy of Solution of β-Cyclodextrin in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol.dm⁻³)</th>
<th>√c (mol¹².dm⁻³²)</th>
<th>ΔH° (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03499</td>
<td>6.166x10⁻⁴</td>
<td>2.48x10⁻²</td>
<td>-75.07</td>
</tr>
<tr>
<td>0.07472</td>
<td>1.317x10⁻³</td>
<td>3.63x10⁻²</td>
<td>-75.45</td>
</tr>
<tr>
<td>0.11566</td>
<td>2.038x10⁻³</td>
<td>4.51x10⁻²</td>
<td>-76.06</td>
</tr>
<tr>
<td>0.03247</td>
<td>5.722x10⁻⁴</td>
<td>2.39x10⁻³</td>
<td>-76.23</td>
</tr>
<tr>
<td>0.09188</td>
<td>1.619x10⁻³</td>
<td>4.02x10⁻³</td>
<td>-76.52</td>
</tr>
</tbody>
</table>

Standard Enthalpy of Solution, ΔH° = -75.53 ± 0.41 kJ.mol⁻¹

Table 5.49 Standard Enthalpy of Solution of γ-Cyclodextrin in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol.dm⁻³)</th>
<th>√c (mol¹².dm⁻³²)</th>
<th>ΔH° (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02424</td>
<td>3.737x10⁻⁴</td>
<td>1.93x10⁻²</td>
<td>-91.97</td>
</tr>
<tr>
<td>0.05362</td>
<td>8.267x10⁻⁴</td>
<td>2.88x10⁻²</td>
<td>-97.49</td>
</tr>
<tr>
<td>0.04037</td>
<td>6.224x10⁻⁴</td>
<td>2.49x10⁻²</td>
<td>-95.91</td>
</tr>
<tr>
<td>0.04492</td>
<td>6.926x10⁻⁴</td>
<td>2.63x10⁻²</td>
<td>-97.11</td>
</tr>
<tr>
<td>0.06255</td>
<td>9.644x10⁻⁴</td>
<td>3.10x10⁻²</td>
<td>-97.16</td>
</tr>
<tr>
<td>0.04441</td>
<td>6.847x10⁻⁴</td>
<td>2.62x10⁻²</td>
<td>-98.22</td>
</tr>
</tbody>
</table>

Standard Enthalpy of Solution, ΔH° = -96.31 ± 1.36 kJ.mol⁻¹
Table 5.50 Standard Enthalpy of Solution of $\alpha$-Cyclodextrin in N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass $\text{g}$</th>
<th>$c$ mol dm$^{-3}$</th>
<th>$\sqrt{c}$ mol$^{1/2}$ dm$^{-3/2}$</th>
<th>$Q^a$ Joules</th>
<th>$Q^b$ Joules</th>
<th>$\Delta H_s$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03760</td>
<td>7.729x10$^{-4}$</td>
<td>2.78x10$^{-2}$</td>
<td>-4.285</td>
<td>-4.231</td>
<td>-109.47</td>
</tr>
<tr>
<td>0.04710</td>
<td>9.662x10$^{-4}$</td>
<td>3.12x10$^{-2}$</td>
<td>-5.392</td>
<td>-5.338</td>
<td>-110.25</td>
</tr>
<tr>
<td>0.02436</td>
<td>5.008x10$^{-4}$</td>
<td>2.24x10$^{-2}$</td>
<td>-2.752</td>
<td>-2.698</td>
<td>-107.74</td>
</tr>
<tr>
<td>0.07067</td>
<td>2.686x10$^{-4}$</td>
<td>5.18x10$^{-2}$</td>
<td>-7.385</td>
<td>-7.385</td>
<td>-101.66</td>
</tr>
<tr>
<td>0.02736</td>
<td>5.624x10$^{-4}$</td>
<td>2.37x10$^{-2}$</td>
<td>-3.033</td>
<td>-2.979</td>
<td>-105.91</td>
</tr>
<tr>
<td>0.03782</td>
<td>7.775x10$^{-4}$</td>
<td>2.79x10$^{-2}$</td>
<td>-4.219</td>
<td>-4.164</td>
<td>-107.13</td>
</tr>
</tbody>
</table>

Standard Enthalpy of Solution, $\Delta H^o_s = -107.03 \pm 2.80$ kJ mol$^{-1}$

*a The gross liberated heat in the calorimeter reaction vessel.

*b The gross liberated heat corrected for the heat effect due to breaking of empty ampoule in 50 ml of pure N,N'-Dimethylformamide at 298.15 K.

Table 5.51 Standard Enthalpy of Solution of $\beta$-Cyclodextrin in N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass $\text{g}$</th>
<th>$c$ mol dm$^{-3}$</th>
<th>$\sqrt{c}$ mol$^{1/2}$ dm$^{-3/2}$</th>
<th>$Q^a$ Joules</th>
<th>$Q^b$ Joules</th>
<th>$\Delta H_s$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03088</td>
<td>5.441x10$^{-4}$</td>
<td>2.33x10$^{-2}$</td>
<td>-3.469</td>
<td>-3.415</td>
<td>-125.50</td>
</tr>
<tr>
<td>0.05497</td>
<td>9.686x10$^{-4}$</td>
<td>3.11x10$^{-2}$</td>
<td>-6.145</td>
<td>-6.090</td>
<td>-125.75</td>
</tr>
<tr>
<td>0.10588</td>
<td>1.866x10$^{-3}$</td>
<td>4.32x10$^{-2}$</td>
<td>-12.016</td>
<td>-11.962</td>
<td>-128.30</td>
</tr>
<tr>
<td>0.05819</td>
<td>1.025x10$^{-3}$</td>
<td>3.20x10$^{-2}$</td>
<td>-6.489</td>
<td>-6.435</td>
<td>-125.51</td>
</tr>
<tr>
<td>0.09509</td>
<td>1.676x10$^{-3}$</td>
<td>4.09x10$^{-2}$</td>
<td>-11.011</td>
<td>-10.956</td>
<td>-130.78</td>
</tr>
<tr>
<td>0.02401</td>
<td>4.231x10$^{-4}$</td>
<td>2.06x10$^{-2}$</td>
<td>-2.541</td>
<td>-2.487</td>
<td>-117.57</td>
</tr>
</tbody>
</table>

Standard Enthalpy of Solution, $\Delta H^o_s = -125.56 \pm 4.05$ kJ mol$^{-1}$

*a The gross liberated heat in the calorimeter reaction vessel.

*b The gross liberated heat corrected for the heat effect due to breaking of empty ampoule in 50 ml of pure N,N'-Dimethylformamide at 298.15 K.
Table 5.52 Standard Enthalpy of Solution of γ-Cyclodextrin in N,N’-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>c (mol dm⁻³)</th>
<th>(\sqrt{c}) (mol⁰.⁵ dm⁻¹)</th>
<th>(Q^a) (Joules)</th>
<th>(Q^b) (Joules)</th>
<th>(\Delta H_s) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01569</td>
<td>2.419x10⁻⁴</td>
<td>1.56x10⁻³</td>
<td>-1.938</td>
<td>-1.884</td>
<td>-155.77</td>
</tr>
<tr>
<td>0.04318</td>
<td>6.657x10⁻⁴</td>
<td>2.58x10⁻³</td>
<td>-5.441</td>
<td>-5.387</td>
<td>-161.83</td>
</tr>
<tr>
<td>0.06453</td>
<td>9.949x10⁻⁴</td>
<td>3.15x10⁻³</td>
<td>-7.949</td>
<td>-7.894</td>
<td>-158.69</td>
</tr>
<tr>
<td>0.05729</td>
<td>8.833x10⁻⁴</td>
<td>2.97x10⁻³</td>
<td>-6.734</td>
<td>-6.680</td>
<td>-151.25</td>
</tr>
<tr>
<td>0.01500</td>
<td>2.313x10⁻⁴</td>
<td>1.52x10⁻³</td>
<td>-1.872</td>
<td>-1.818</td>
<td>-157.20</td>
</tr>
<tr>
<td>0.04029</td>
<td>6.212x10⁻⁴</td>
<td>2.49x10⁻³</td>
<td>-4.672</td>
<td>-4.618</td>
<td>-151.88</td>
</tr>
</tbody>
</table>

Standard Enthalpy of Solution, \(\Delta H_s\) = -156.11 ± 3.70 kJ mol⁻¹

* The gross liberated heat inside the calorimeter reaction vessel.

b The gross liberated heat corrected for the heat effect due to breaking of empty ampoule in 50 ml of pure N,N’-Dimethylformamide at 298.15 K.

Table 5.53 Standard Enthalpies of Solution of Cyclodextrins in Water and N,N’-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>Cyclodextrin</th>
<th>(\Delta H^\circ_s), /kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>DMF</td>
</tr>
<tr>
<td>α-Cyclodextrin</td>
<td>-62.69 ± 1.39</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>-75.53 ± 0.41</td>
</tr>
<tr>
<td>γ-Cyclodextrin</td>
<td>-96.31 ± 1.36</td>
</tr>
</tbody>
</table>

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Table 5.54 Thermodynamic Parameters of Solution of Cyclodextrins in Water and N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ΔG°, a</th>
<th>ΔH°, b</th>
<th>ΔS°, c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ.mol⁻¹</td>
<td>kJ.mol⁻¹</td>
<td>J.mol⁻¹.K⁻¹</td>
</tr>
<tr>
<td>Solvent : H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Cyclodextrin</td>
<td>4.72</td>
<td>-62.69</td>
<td>-230</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>10.21</td>
<td>-75.53</td>
<td>-290</td>
</tr>
<tr>
<td>γ-Cyclodextrin</td>
<td>4.26</td>
<td>-96.31</td>
<td>-340</td>
</tr>
<tr>
<td>Solvent : DMF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Cyclodextrin</td>
<td>6.46</td>
<td>-107.03</td>
<td>-380</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>5.95</td>
<td>-125.56</td>
<td>-440</td>
</tr>
<tr>
<td>γ-Cyclodextrin</td>
<td>5.82</td>
<td>-156.11</td>
<td>-540</td>
</tr>
</tbody>
</table>

* Data from Table 5.46.

b Data from Table 5.54.

Data obtained using eqn 5.31.
Lumry and Rajender\textsuperscript{216} shown, in a very interesting article, that the enthalpy-entropy pattern is real, very common and a consequence of the properties of liquid water as a solvent regardless of the solutes and the solute process studied. This phenomenon was also observed for \( \alpha \), \( \beta \) and \( \gamma \)-cyclodextrin in water. In fact, a plot of solution entropy against solution enthalpy data of cyclodextrins in water gives a slope, known as the compensation or isoequilibrium temperature, of \( 303 \pm 58 \) K, an intercept of \( 8.57 \pm 16.7 \) kJ.mol\(^{-1}\) and a correlation coefficient of 0.98.

Figure 5.45 shows a linear correlation between entropy and enthalpy of solution of cyclodextrins in water.

A striking feature is that this phenomenon (enthalpy-entropy pattern) has been observed for \( \alpha \), \( \beta \) and \( \gamma \)-cyclodextrin in \( N,N' \)-Dimethylformamide. Figure 5.46 shows a straight line between enthalpies and entropies of solution of cyclodextrins in \( N,N' \)-Dimethylformamide. In fact, an isoequilibrium temperature of \( 306 \pm 1 \) K, an intercept of \( 9.44 \pm 0.40 \) and a correlation coefficient of 1.00 were observed. Additionally, a plot of solution entropy data against solution enthalpy data of cyclodextrins in water and \( N,N' \)-Dimethylformamide. Figure 5.47 shows a straight line of slope \( 307 \pm 9 \) K (isoequilibrium temperature) an intercept of \( 9.87 \pm 3.5 \) kJ.mol\(^{-1}\) and a correlation coefficient of 0.998.
Figure 5.45 A Compensation Effect Between Entropy and Enthalpy of Solution of Cyclodextrins in Water.
A better interpretation of the solvation of cyclodextrins requires thermodynamic data for the transfer of these ligands water to N,N'-Dimethylformamide. Thus, these data were calculated.
5.2.2 Standard Thermodynamic Parameters of Transfer of Cyclodextrins from Water to N,N'-Dimethylformamide at 298.15 K.

Standard Thermodynamic parameters for the transfer of cyclodextrins from water to N,N'-Dimethylformamide were calculated and reported in Table 5.55. The process may be described as:

\[ \text{CD (H}_2\text{O)} \rightarrow \text{CD (DMF)} \]

where both solvents are in their pure state.

Table 5.55 Standard Thermodynamic Parameters of Transfer of Cyclodextrins from Water to N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Cyclodextrin</th>
<th>( \Delta G^{\circ} )</th>
<th>( \Delta H^{\circ} )</th>
<th>( \Delta S^{\circ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Cyclodextrin</td>
<td>1.74</td>
<td>-44.34</td>
<td>-150</td>
</tr>
<tr>
<td>( \beta )-Cyclodextrin</td>
<td>-4.26</td>
<td>-50.03</td>
<td>-150</td>
</tr>
<tr>
<td>( \gamma )-Cyclodextrin</td>
<td>1.56</td>
<td>-59.80</td>
<td>-200</td>
</tr>
</tbody>
</table>

The transfer thermodynamic data of cyclodextrin from water to N,N'-Dimethylformamide are characterised by rather small \( \Delta G^{\circ} \) values (Table 5.55). This may be attributed to the result of the compensation effect between favourable enthalpy data (\( \Delta H^{\circ} \) values are large and negative) and unfavourable entropy data (\( \Delta S^{\circ} \) values are large and negative). It must be stressed that these data do not follow the pattern usually observed in terms of enthalpy and entropy for the transfer of non-electrolytes from water to dipolar aprotic media. In fact, data for the transfer of cyclodextrins from water to N,N'-Dimethylformamide are just the opposite to those observed for the transfer of other macrocyclic ligands in their transfer from water to...
the same reaction medium. A typical example is cryptand 222. The small $\Delta G^\circ$, value observed for this ligand is the result of large and positive values for the transfer enthalpy and entropy from water to non-aqueous media. Data for the transfer of cryptands from water to dipolar aprotic solvents are shown in Table 5.56.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\Delta G^\circ$, [222] (kJ.mol$^{-1}$)</th>
<th>$\Delta H^\circ$, [222] (kJ.mol$^{-1}$)</th>
<th>$\Delta S^\circ$, [222] (J.mol$^{-1}$.K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryptand 222</td>
<td>6.69$^a$</td>
<td>59.29$^b$</td>
<td>176</td>
</tr>
</tbody>
</table>

* Data taken from ref. 217
$^b$ Data taken from ref. 218

The results shown in Table 5.55 indicate that this is not the case for cyclodextrins. As far as these ligands are concerned, cyclodextrins are enthalpically more stable in N,N'-Dimethylformamide than in water (negative $\Delta H^\circ$, values). For the latter solvent, two, eight and twelve molecules of water are known to be included respectively in the cavities of $\alpha$, $\beta$ and $\gamma$-cyclodextrin. It is not known whether N,N'-dimethylformamide is included in the cavities of cyclodextrins. However, the results in table 5.55 suggest that N,N'-Dimethylformamide may be included within the cavities of these ligands. A definite size effect is reflected in the transfer enthalpies of cyclodextrins among these two solvents. Indeed, an increase in stability (in enthalpic terms), as the size of the ligand increases, is observed. In fact, a linear relationship is observed between $\Delta H^\circ$, values in water with corresponding data in N,N'-Dimethylformamide. A slope of 1.46, an intercept of -15.36 kJ.mol$^{-1}$ and a correlation coefficient of 1.00 was calculated (Fig 5.48). The same linear
A relationship is observed in terms of $\Delta S^\circ$. The linear regression analysis gives a slope of 1.44, an intercept of -40.66 J.K$^{-1}$.mol$^{-1}$ and a correlation coefficient of 0.98 (Fig. 5.49).

Figure 5.48 A Linear Correlation between Solution Enthalpies of Cyclodextrins in Water and their Corresponding Enthalpies in DMF.

Figure 5.49 A Linear Correlation between Solution Entropies of Cyclodextrins in Water and their Corresponding values in DMF.
CHAPTER 6
TITRATION CALORIMETRY
6.1 Titration Calorimetry

The titration calorimetric technique, which was developed and extensively applied by Christensen and Izatt to measure thermodynamic quantities for reactions in solution, is a technique where one reactant is titrated into another, under conditions as nearly adiabatic as possible. The temperature of the system is measured as a function of the titrant added.

There are two types of calorimetric titrations; incremental and continuous. In the first type, the titrant is added incrementally and the temperature recorded after each addition. This requires the readjustment of the temperature to the initial temperature before each additional increment of titrant is added. It has the advantage that the overall temperature change is slight for a given incremental addition of titrant and, consequently, temperature dependent corrections, e.g., solution heat capacity change, etc., and heat leak corrections are kept small. Errors are introduced, however, in that a separate run has to be made for each data point obtained. Also, the number of data points obtained for the overall run is limited to the number of increments of titrant added.

In continuous titration calorimetry, the titrant is introduced at a constant rate during a run, and the temperature is continuously recorded. The advantage of this method is that a complete record is produced of the heat effects during a reaction, allowing one to choose any number of data points for calculation purposes. This method can only be used with calorimeters of quick response times to temperature changes. The systems which can be studied are limited to those where rapid reactions are involved.

The resulting data in the form of temperature versus volume (moles) of titrant added can be analysed to give information on types and numbers of reactions taking place in solution.
place in the reaction vessel as well as the equilibrium constant $K_c$ of the reaction. In addition, enthalpy change, $\Delta H$, and therefore entropy change, $\Delta S$ values can also be obtained from the calorimetric data. Another advantage of the titration calorimetric technique is the capability to determine $K_c$ values of systems whose study is difficult by other methods, i.e., non-aqueous systems, highly acidic or basic systems, and weak metal-ligand complexes. It can often provide sufficient information to calculate $K$ values for proton ionisation$^{222-225}$ and metal complex formation$^{226-230}$.

The successful application of the calorimetric method depends on:-

i) The equilibrium constant ($0 < \log K_c < 6$) of the reaction under study.

ii) The $\Delta H$ being concurrently large enough that a temperature change of at least $0.01^\circ C$ is generated by the reaction ($0.01^\circ C$ approaches the lower limit of temperature change necessary to generate thermograms reproducible to $0.2\%$).

Figure 6.1 shows a scheme of the main components of a titration calorimeter apparatus indicated in a block diagram.

Figure 6.1 Schematic diagram of the titration calorimeter apparatus; A, reaction vessel with temperature sensor; B, burette (constant rate or incremental); C, temperature measuring circuit; D, amplifier; E, data output (chart recorder); G, environmental control circuit.
6.2 The Hart Scientific 5021 Calorimeter

The titration calorimeter used in this study is the Hart Scientific 5021 titration calorimeter. It operates by making a precise comparison of the heats generated by a well-defined chemical process and an electrical calibration.

The Hart Scientific 5021 titration calorimeter is very similar to the Tronac 450 calorimeters (see Chapter 4, Section 4.3). The advantage of the Hart Scientific Calorimeter is that it was designed to be used as an isothermal and isoperibol calorimeter. It can also be used as a conventional solution calorimeter.

In this study, the Hart Scientific 5021 Calorimeter was used as an isoperibol titration calorimeter.

Details about calculations of heat exchange between the reaction vessel and the surrounding, temperature change and methods used for the calculations of the temperature change thought to be happening in the reaction vessel and description of the calorimeter are given in Chapter 4 Sections 4.3 and 4.5.
6.3 Thermogram Analysis

A typical thermogram obtained from a continuous titration calorimeter.

A thermogram for a titration calorimetric run is a plot of temperature or heat as moles of titrant added or time of titrant delivery. The thermogram from a single continuous titration is equivalent to that constructed from data obtained from a large number of incremental titrations.

A typical thermogram for a continuous titration run for an exothermic reaction involving only one reaction is shown in Fig 6.2 Region "a" indicates the net heat given of the reaction vessel and contents before the titration begins. The slope of the line is a function of the heat associated with side effects such as stirring, resistance heating across the thermistor, and heat leaks (heat losses by conduction, radiation, convection and evaporation). Region "b" indicates the heat rise due to the reaction taking place in the reaction vessel plus the heat effects resulting from:-

(a) the dilution of titrant and titrate,
(b) the temperature differential between the titrant and titrate, and
(c) those effects mentioned for Region "a". This region would represent the portion of the curve in which the titration continues but the reaction is complete. This does exist only for those systems in which K is too large to be determined by calorimetry.

Region "d" is generated after a titration is completed and the slope is a function of the same effects as mentioned for region "a".

Regions "a" and "d" are used to make corrections for the heat loss or gain for the reaction vessel before, during and after the titration.
6.4 Heat Measurements - Corrections

As titrant is added to the reaction vessel, the total heat produced as a function of the amount of titrant added is called the "gross heat". This involves heat due to:

1) Non-chemical energy terms
2) Temperature difference between titrant and titrate
3) Dilution of titrant and titrate
4) Heat contributed from other reactions

6.4.1 Non-chemical Energy Terms, \( Q_{nm.p} \)

Non-chemical contributions to the gross heat liberated in the reaction vessel include those energy quantities associated with stirring of the solution, heat losses between the reaction vessel and its surroundings, and resistance heating of the thermistor. This is assumed to obey Newton's Law of Cooling\(^{21}\). At any point \( P \), therefore, the non-chemical contributions can be evaluated from the following equations:

\[
q_{nm.p} = q_{nm,x} + (q_{nm,y} - q_{nm,2})(T_p - T_2)/(T_y - T_x) \quad (6.1)
\]

\[
Q_{nm,p} = \int_{x}^{p} q_{nm}.dt \quad (6.2)
\]

\( q_{nm,p} \) and \( Q_{nm,p} \) are respectively the rate of heat loss at point \( P \) and the total contribution of the non-chemical heat effects from the start of the titration (point \( x \)) to any time during the run (point \( P \)).

6.4.2 The Temperature Difference Between Titrant and Titrate, \( Q_{TCP} \)

The difference in temperature between the titrant, \( T_t \), and the titrate, \( T_x \), causes extra heat in the reaction vessel detected by the thermistor. If the quantity \( (T_x - T_t) \) is positive, there will be an endothermic heat effect as the colder titrant is
added. Conversely, there will be an exothermic heat effect if the quantity $(T_x - T)$ is negative. Therefore, the correction that must be made to the gross heat, $Q_r$, for this heat effect is:

$$Q_{r,P} = (V \cdot \rho \cdot C_p)_P (T_x - T)$$

6.3

6.4.3 The Dilutions of the Titrant and the Titrate, $Q_{d,P}$

As the titrant is added to the titrate a heat effect will occur due to chemical changes such as solvation, hydrolysis and ion-pairing. The magnitude of the heat effect changes as the relative concentrations of species present in the titrate solution. The heat effect due to dilution is given by:

$$Q_{d,P} = (\phi_{L,P} - \phi_{L,P}) n_i$$

6.4

where $\phi_{L,P}$ refers to the titrant in the titrate at point $P$, $\phi_{L,P}$ refers to the titrant and $n_i$ is the moles of titrant added.

The magnitude of the dilution heat effects must be determined either experimentally or from available Tables\textsuperscript{232-234}.

6.4.4 Heat Contributed from Side Reactions

If reactions other than the ones of interest occur in the calorimeter, their energy contributions must be corrected for the gross heat values liberated in the reaction vessel. For instance, hydrolysis of a ligand species (L) is a commonly encountered reaction and it is referred to the process:

$$L + H_2O \rightarrow HL^+ + OH^-$$

6.5

In the present work, non-chemical energy terms, $Q_{HL,P}$, were neglected. Heat
effects due to temperature difference between titrant and titrate, $Q_{t_l,p}$, was minimised and therefore neglected by immersing the burette in the thermostated bath of the calorimeter so that, both contents of burette and reaction vessel are at the same temperature when the titration starts. Heat of dilution of titrant and titrate were carried out experimentally and found to be negligible. Heat contributed from other reactions was avoided by minimising the presence of impurities in the solution. Therefore, the gross heat liberated in the reaction vessel is taken as the correct heat liberated due to the chemical reaction between cyclodextrins and sodium [parahydroxyphenylazo and chloro-substituted parahydroxyphenylazo] benzoate in water and N,N'-Dimethylformamide at 298.15 K.

The gross heat liberated in the reaction vessel, $Q_r$, is given by:-

$$Q_r = \varepsilon \Delta T_r$$

where $\varepsilon$ is the total heat capacity of the reaction vessel and $\Delta T_r$ is the temperature change taken place after one addition of titrant. The $\Delta T_r$ was calculated according to Dickinson’s method of extrapolation\textsuperscript{197,198}. 

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6.5 Electrical Calibration - Heat Capacity

In titration calorimetry, the total heat capacity of the systems must be used to determine the gross heat liberated in the reaction vessel. This can be directly measured for each system before and after each addition of titrant by electric calibration. The average of the initial and final heat capacity will then represent the total heat capacity of the reaction vessel and its contents.

This method is very accurate in determining the heat capacity of the reaction vessel and its contents, and this is the method used for evaluating all experimental data obtained from titration calorimetry.

6.6 Experimental Procedure
6.6.1 Reaction Experiment

The calorimetric titrations involved in this work were all performed using the incremental titration technique. A description of how a titration experiment was carried out is given.

An electrolyte solution (hapten, 50 ml) was pipetted into the reaction vessel and the burette loaded with the titrant. The burette and the reaction vessel contents were then immersed into the thermostated water bath (298.15 K) and left to reach thermal equilibrium. Then, the titrant was incrementally added for a given time at a fixed burette delivery rate (BDR) and the reaction thought to be occurring in the reaction vessel was monitored using a chart recorder. As the end point was approached, the volume of titrant added was reduced until an addition produced no corresponding temperature change in the reaction vessel of the calorimeter. The vessel contents were cooled to the starting temperature after each addition.
6.6.2 Electrical Calibration Experiment

An electrical calibration was carried out before and after every titrant addition. The electrical calibration run was performed over the same temperature change and under conditions as identical as possible to those of the actual reaction run. For details, see Section 4.11.1, Chapter 4.

6.6.3 Heat of Dilution

When a titrant is added to a titrate, in titration calorimetry, extra heats could be released inside the reaction vessel of the calorimeter. This is due to the dilution of the titrant and titrate inside the reaction vessel. Therefore, corrections to the gross liberated heat should be made to both titrant and titrate.

In practice, corrections of the gross liberated heat inside the reaction vessel due to the heat of dilution of the titrant were checked by adding incrementally the same amount of titrate used during a reaction experiment to 50 ml of the pure solvent in question. The corresponding temperature change was monitored with a chart recorder. For α, β and γ-cyclodextrin, their heats of dilution in water and N,N'-Dimethylformamide at 298.15 K were found to be negligible. Heats of dilution of the content of the reaction vessel (titrate=hapten) were carried out by adding incrementally a volume of the pure solvent equivalent to that of the titrant into 50 ml of the hapten solution under investigation. This was also found to be negligible. The experimental procedure followed in both runs, was the same as the experimental procedure for an actual reaction experiment as described in Section 6.6.1.
6.7 Calibration of the Calorimeter

The reproducibility of the Hart Scientific 5021 calorimeter was checked by calibrating the calorimeter. This involved the calibration of the burette and calibration of the calorimeter with a standard chemical reaction.

6.7.1 Calibration of the Burette

In order to calculate the moles of reactant added to the reaction vessel, the volume of titrant delivered by a one step movement of the burette stepper motor must be determined.

For this purpose, the burette was filled with freshly boiled deionised water and the insert assembly of the calorimeter lowered into the thermostated water bath to maintain the burette at 298.15 K. After allowing for thermal equilibrium, water was collected for a time period which was increased by 10 seconds for each successive delivery until the burette was empty. This procedure was repeated at different burette delivery rate (50, 100, 200 and 400 steps/sec). This procedure was repeated three times.

The burette delivery rates obtained at 50, 100, 200 and 400 steps/sec and at 298.15 K were $6.61 \pm 0.01 \mu l.s^{-1}$, $13.15 \pm 0.02 \mu l.s^{-1}$, $26.25 \pm 0.04 \mu l.s^{-1}$ and $53.57 \pm 0.09 \mu l.s^{-1}$ respectively. These rates are independent of the amount delivered. Figure 6.3 shows the different calibration curves of the burette at different burette delivery rates.
Figure 6.3 Burette Calibration Curves at Different Burette Delivery Rates at 298.15 K. (every point is average of three measurements)
6.7.2 Calibration of the Hart Scientific Calorimeter with Standard Chemical Reactions

Electrical calibration for the determination of the heat capacity of the calorimeter reaction vessel and its contents are usually checked against a chemical reaction where the enthalpy change is well established. This gives a measure of the accuracy and reproducibility of the calorimeter. For this purpose, the heat of protonation of THAM and the ionisation of water at 298.15 K were carried out.

i) Heat of Protonation of THAM at 298.15 K

A method of testing both, the accuracy of the burette calibration as well as the continuous and incremental titration procedures, is by carrying out an actual thermometric titration. The protonations of THAM with hydrochloric acid proposed by Wilson and Smith\textsuperscript{235} is highly recommended for this purpose. The process refers to the following reaction:

\[
\text{H}_2\text{NC} (\text{CH}_2\text{OH})_3 \text{aq} + \text{H}_3\text{O}^+ \rightarrow \text{H}_3\text{N}^+\text{C} (\text{CH}_2\text{OH})_3 \text{aq} + \text{H}_2\text{O} \text{aq} \quad 6.7
\]

The reported logK\textsubscript{w} (8.07) and ΔH (-47.49 kJ.mol\textsuperscript{-1}) values are both large enough to ensure that the interaction is stoichiometric and that the end point is sharp and easily detected\textsuperscript{236}.

An aqueous THAM solution (0.2475 mol.dm\textsuperscript{-3}) contained in the burette was incrementally titrated into 50 cm\textsuperscript{3} of 0.1 mol.dm\textsuperscript{-3} HCl. Each addition was coupled with an appropriate calibration, after which vessel contents were cooled to the starting temperature.

The increments were added at a burette delivery rate of 100 steps/sec over a 30 second interval giving an incremental volume of 0.3942 cm\textsuperscript{3}.
The heat per increment, $Q_r$, was determined over eight additions ($-4.64 \pm 0.09$ J). However, this should be corrected to the heat due to the hydrolysis of THAM in water, $Q_h$, of the incremental added volume ($0.3942$ cm$^3$) into $50$ cm$^3$ of water at 298.15K.

The enthalpy change of the protonation reaction, $\Delta H_p$, is therefore expressed as:

$$\Delta H_p = \frac{Q_p}{n}$$ \hspace{1cm} 6.8

where $n$ is the number of moles of protonated THAM, and $Q_p$ is its heat effect. $Q_p$ is thus,

$$Q_p = Q_r - Q_h - Q_d$$ \hspace{1cm} 6.9

The hydrolysis of THAM is represented by the equation:-

$$\text{THAM} + \text{H}_2\text{O} \rightarrow \text{HTHAM}^+ + \text{OH}^- \hspace{1cm} \Delta H^o_H$$ \hspace{1cm} 6.10

where $K_H$ and $\Delta H^o_H$ are the equilibrium constant and the enthalpy change due to the hydrolysis of THAM in water, respectively. Values for $\log K_H = -5.929$ and $\Delta H^o_H = -55.81$ kJ.mol$^{-1}$ were used to calculate the concentration of $\text{HTHAM}^+$ and $\text{OH}^-$ present in the titrant according to:-

$$[\text{HTHAM}^+] = [\text{OH}^-] = (K_H[\text{THAM}])^{1/2}$$ \hspace{1cm} 6.11

where $[\text{THAM}] = 0.2475$ mol.dm$^{-3}$.

The heat contributed by the formation of water, $Q_h$, is given by:

$$Q_h = -[\text{OH}^-].V.\Delta H_H$$ \hspace{1cm} 6.12

By replacing $[\text{OH}^-]$ by its value in equation 6.12, $Q_h$ becomes...
\[ Q_\text{H} = -(K_\text{r}[\text{THAM}])^{1/2} \cdot V \cdot \Delta H_\text{H} \]

The heat of dilution resulting from the addition of 0.3942 cm\(^3\) of THAM into a volume of 50 cm\(^3\) of water was found to be negligible. Thus:

\[ \Delta H_p = \frac{(Q_r - Q_h)/V \cdot ([\text{THAM}] - [\text{HTHAM}^+] - 6.13 \text{ kJ} \cdot \text{mol}^{-1})}{\text{cm}^3} \]

The value of \( \Delta H_p = -47.54 \pm 0.98 \text{ kJ} \cdot \text{mol}^{-1} \) is in fairly good agreement with the value reported by Öjeund and Wadsø \(^2\) \(-47.49 \pm 0.04 \text{ kJ} \cdot \text{mol}^{-1}\). It should be pointed out that Öjeund and Wadsø determined their value at an ionic strength of 0.05 mol.dm\(^{-3}\). Details of calculations are shown in Table 6.1.

Table 6.1 Enthalpy of Protonation of Tris(hydroxymethyl) Aminomethane in 0.1 mol.dm\(^{-3}\) Hydrochloric Acid at 298.15K.

<table>
<thead>
<tr>
<th>V (cm(^3))</th>
<th>Q_r (J)</th>
<th>Q_H (J)</th>
<th>Q_p (J)</th>
<th>( \Delta H_p ) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3942</td>
<td>-4.4560</td>
<td>-0.0119</td>
<td>-4.4442</td>
<td>-45.65</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.7681</td>
<td>-0.0119</td>
<td>-4.7564</td>
<td>-48.86</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.7330</td>
<td>-0.0120</td>
<td>-4.7212</td>
<td>-48.50</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.6811</td>
<td>-0.0119</td>
<td>-4.6693</td>
<td>-47.97</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.5890</td>
<td>-0.0119</td>
<td>-4.5773</td>
<td>-47.02</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.7120</td>
<td>-0.0119</td>
<td>-4.7003</td>
<td>-48.28</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.5890</td>
<td>-0.0119</td>
<td>-4.5773</td>
<td>-47.02</td>
</tr>
<tr>
<td>0.3942</td>
<td>-4.5890</td>
<td>-0.0119</td>
<td>-4.5773</td>
<td>-47.02</td>
</tr>
</tbody>
</table>

Average value of \( Q_r = -4.6396 \pm 0.0958 \text{ J} \)
Average value of \( Q_p = -4.6279 \pm 0.0959 \text{ J} \)

Enthalpy of Protonation of THAM, \( \Delta H_p^o = -47.54 \pm 0.98 \text{ kJ} \cdot \text{mol}^{-1} \)
ii) Heat of Formation of Water at 298.15K.

The reaction between \( \text{HClO}_4 \) aq and \( \text{NaOH} \) aq to produce water (eq. 6.15), is considered to be a more satisfactory standard reaction\(^6\) in titration calorimetry than the protonation of Tham reaction.

\[
\text{HClO}_4 \text{ aq } + \text{NaOH aq } \rightarrow \text{NaClO}_4 + \text{H}_2\text{O} \quad \Delta H_i \quad 6.15
\]

The standard enthalpy of this reaction (\( \Delta H_i \)) is the heat of ionisation of water. In this reaction no chemical correction heats are necessary and \( \Delta H_i \) may be obtained directly from:

\[
\Delta H_i = -Q_r/[\text{HClO}_4].V \quad 6.16
\]

An aqueous solution of \( \text{HClO}_4 \) (0.3584 mol.dm\(^{-3}\)) was incrementally added to 50 cm\(^3\) of \( \text{NaOH} \) at a burette delivering rate of 50 steps/sec over a 30 seconds interval giving an incremental volume of 0.1983 cm\(^3\).

The heat per increment, \( Q_r \), was determined at 1.9945 ± 0.0163 J over 10 additions. Therefore, the standard enthalpy of ionisation of water was found to be 56.13 ± 0.46 kJ.mol\(^{-1}\). This is in good agreement with the values published by Vanderzee and Swanson\(^{239} \) (\( \Delta H = 55.80 \text{ kJ.mol}^{-1} \)), Hale et al.\(^{240} \) (\( \Delta H = 55.79 \text{ kJ.mol}^{-1} \)) and Hansen and Lewis\(^{238} \) (\( \Delta H = 55.8 \text{ kJ.mol}^{-1} \)). Details of calculations are shown in Table 6.2.
Table 6.2 Enthalpy of Formation of Water at 298.15K.

<table>
<thead>
<tr>
<th>$V$ (cm$^3$)</th>
<th>$Q_p$ (J)</th>
<th>$\Delta H_p^\circ$ (kJ.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09915</td>
<td>-1.9731</td>
<td>-55.53</td>
</tr>
<tr>
<td>0.09915</td>
<td>-2.0239</td>
<td>-56.95</td>
</tr>
<tr>
<td>0.09915</td>
<td>-1.9907</td>
<td>-56.02</td>
</tr>
<tr>
<td>0.09915</td>
<td>-1.9907</td>
<td>-56.02</td>
</tr>
<tr>
<td>0.09915</td>
<td>-1.9907</td>
<td>-56.02</td>
</tr>
<tr>
<td>0.09915</td>
<td>-2.0087</td>
<td>-56.53</td>
</tr>
<tr>
<td>0.09915</td>
<td>-1.9757</td>
<td>-55.61</td>
</tr>
<tr>
<td>0.09915</td>
<td>-2.0087</td>
<td>-56.53</td>
</tr>
<tr>
<td>0.09915</td>
<td>-1.9757</td>
<td>-55.61</td>
</tr>
<tr>
<td>0.09915</td>
<td>-2.0087</td>
<td>-56.53</td>
</tr>
</tbody>
</table>

Average value of $Q_p = -1.9945 \pm 0.0163$ J

Enthalpy of Formation of Water, $\Delta H_p^\circ = -56.13 \pm 0.46$ kJ.mol$^{-1}$
CHAPTER 7
THERMODYNAMIC PARAMETERS
OF
HAPTON-CYCLODEXTRIN COMPLEXES
IN
WATER & DMF
CHAPTER 7: CYCLODEXTRIN-HAPTEN COMPLEXES

7.1 Thermodynamic Parameters for Complexation of Cyclodextrin and Haptens

7.1.1 Generalities

A knowledge of the enthalpy and entropy terms, and their contribution to the free energy of complexation between ions and macrocyclic ligands in different reaction media, could help to elucidate some of the factors governing complex formation. The complexation parameters can also be used to obtain the corresponding parameters for the transfer of complexed ions amongst the various solvents. Furthermore, thermodynamic parameters for the complexation reaction can be of use in studying the thermodynamic parameters of extraction processes.

The determination of the stability constants, log\(K_c\), enthalpy, \(\Delta H^\circ_c\), and entropy, \(\Delta S^\circ_c\), of cyclodextrin-hapten complexes is of particular interest. This is because cyclodextrins were suggested as models to study the interaction between antibodies and antigens. The knowledge of log\(K_c\), \(\Delta H^\circ_c\) and \(\Delta S^\circ_c\) between cyclodextrins and haptens could therefore, help to give information about some of the factors governing the most important reaction in immunology which is the affinity shown by an antibody towards a hapten (antigen). Thus, thermodynamic parameters of complexation (\(\Delta G^\circ_c\), \(\Delta H^\circ_c\) and \(\Delta S^\circ_c\)), between para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoate anions and \(\alpha\), \(\beta\) and \(\gamma\)-cyclodextrins, were investigated.

7.1.2 Methods Used for Determination of Stability Constants

Stability constants provide the free energy change for complexation reaction, representing a direct measure of the extent of complexing in solution. The different methods used for the determination of stability constants of ions with microcyclic
ligands can be divided in:

i) Spectrophotometric methods: This includes UV visible and nuclear magnetic resonance spectroscopy.

ii) Electrochemical methods: This includes potentiometry, conductance measurements and polarography.

iii) Thermal methods: Among these is the calorimetric technique.

Among the spectrophotometric methods, the most commonly used is that based on NMR measurements. This method can be applied to nuclei which have non-zero spin quantum numbers.

Proton magnetic resonance (p.m.r), which was the first type of NMR used for chemical analysis, has been successfully employed for the determination of stability constants of crown ethers and metal ions. The complexation constants were evaluated from the variation of the proton chemical shifts with the ligand cation mol ratio.

Proton NMR in conjunction with $^{13}$C NMR has been also used for these purposes due to the lower magnetic sensitivity of the non-protonic nuclei with respect to that for the proton. A Fourier Transform instrument must be used to extract the spectral peaks from the background noise when $^{13}$C nuclei are involved.

This method is useful for the determination of stability constants not greater than $10^5$. The advantage of this method is that additional information such as structure and kinetic parameters can be obtained.

Among the electrochemical methods, the potentiometric technique described by Cox and Schneider has been extensively used. Direct measurement by the use of ion selective electrodes has also been used. The selectivity of an ion selective electrodes results from the ion selective membrane. When the electrode is placed in
contact with a solution containing ions to which the electrode responds, a potential
difference is developed across the ion-selective membrane. This potential, E, is a
function of the activity of the ions (a$_i$) in solution, according to the equation:

\[ E = \text{Constant} + 2.303\frac{RT}{nF}\log a_i \]  

where E is expressed in volts, R is the gas constant, T is the absolute temperature, n
is the number of electrons involved in the reaction and F is the Faraday = 96485
C.mol$^{-1}$.

This method enables the calculation of high stability constant values at very
low ionic concentration. However, in very dilute solutions, great care must be taken
to avoid the presence of impurities in solution. Kolthoff and Chantooni$^{245-247}$ used this
method for the determination of stability constants of cations with macrocyclic
ligands in different reaction media.

Another method used mainly in non-aqueous solvents is that involving
conductance measurements. In these measurements, use is made of the fact that the
mobility (hence conductivity) of the complexed ion is lower than the mobility of the
free ion$^{248-250}$.

Non-potentiometric methods of electroanalysis such as voltammetry and
related techniques, have been used with less frequency.

Voltammetry is a technique which involves the application of a varying
potential to an electrode (indicator electrode) in a sample solution. Polarography is
that type of voltametry which involves the use of an electrode (dropping mercury
electrode) whose surface is renewed as the applied potential is varied. Independently
of the way the potential changes with time, a potential value is reached at which
oxidation or reduction of the electroactive species takes place. At this point a current
flows through the indicator electrode. This current is measured and plotted versus
the applied potential.

The polarographic wave thus obtained is characterised by a half wave potential, \( E_{1/2} \), which is the potential half way up the rising portion of the polarographic wave. It is important for the polarographic analysis involving more than one species that these electroactive species are characterised by \( E_{1/2} \) values which differ between each other by more than 0.1 volts under specific conditions. Half wave potentials for the free and complexed cations are relevant in the determination of stability constants of metal ions and macrocyclic ligands. The fact that \( E_{1/2} \) for the complex is shifted to more negative potentials with an increase in the concentration of the ligand in solution provided the basis for the evaluation of stability constants in these systems\(^{251-254}\).

Among the thermal methods of analysis, calorimetry is the only technique so far used for measurements of stability constants of metal ions and macrocyclic ligands in water and in non-aqueous solvents. This method offers the advantage of providing data for the calculation of thermodynamic parameters for the complexation reaction between ions and macrocyclic ligands in different reaction media. The method is suitable to determine stability constants whose values in terms of log units are within 2 and 6. Values larger than 6 log units cannot be measured since combination of electrolyte solution and ligand leads to values close to 100 % complexation. Values less than 2, leads to very low percentage of complexation and therefore, inaccurate enthalpy data are obtained.

This method is mainly based on heat measurements carried out at different electrolyte and ligand concentration, so that different percentages of complex are formed in solution. Several authors have used this method, in particular Izatt and Christensen\(^{255-264}\) who have made significant contributions in the field of cation-macro cyclic interactions in solution.

It is well established that the complexation process involving cyclodextrins
and substrates is in most cases enthalpically controlled. Therefore, thermodynamic parameters of complexation (ΔG°, ΔH°, and ΔS°), between sodium [para hydroxyphenylazo and chloro-substituted para hydroxyphenylazo] benzoate and cyclodextrins, in water and N,N'-Dimethylformamide, was carried out at 298.15K using the calorimetric titration technique. A detailed description of this technique was given in Chapter 6.

7.1.3 Simultaneous Determination of the Equilibrium Constant and Enthalpy Change of Complexation ΔH°c of Chemical Reactions.

The selection of methods for the determination of equilibrium constants, depends on the magnitude of the equilibrium constant of the process in question. For low equilibrium constants (2 < logK < 6), however, the titration calorimetry technique is a very competitive method and it has the advantage of providing not only the equilibrium constant value but also the enthalpy change of the chemical reaction under study. This method, as described by Christensen et al, may be performed either by continuous or incremental titration procedures.

The evaluation of K-values from calorimetric data for reactions in solution involves four steps:-

1. The experimental determination of the gross heat liberated in the reaction vessel, Qr, as a function of titrant added.
2. The calculation of all correction terms for heat effects occurring in the reaction vessel other than those due to chemical reactions.
3. The evaluation of heat effects contributed from side reactions.
4. The calculation of the energy changes due to the reactions in question and the evaluation of K-values.

In general, the best values of K and ΔH are calculated by a least squares
analysis of the equation:-

\[ Q_{cp} = \Sigma \Delta H_i \Delta n_{i,p} \tag{7.2} \]

where \( Q_{cp} \) is the heat released in the reaction vessel for which K-value is to be determined. The heat is expressed as:-

\[ Q_{cp} = Q_r - Q_{hl,p} - Q_{tc,p} - Q_{dp} - \Sigma \Delta H_R \Delta n_R \tag{7.3} \]

The terms \( \Sigma \Delta H_R \Delta n_R \) refer to all reactions occurring in the reaction vessel other than the ones for which the K-value is to be determined. \( \Delta n_{i,p} \) is the number of moles of product, \( i \), formed and it is a function of the equilibrium constant for reaction \( i \). \( \Delta H_i \) is the enthalpy change of the reaction \( i \) and it is a function of \( \Delta n_{i,p} \).

For \( m \) data points of titration, the error square sum is given by:-

\[ U(K_i,\Delta H_i) = \Sigma(Q_{cp} - \Sigma(\Delta n_{i,p} \Delta H_i))^2 \tag{7.4} \]

where the subscript \( p \) is the total number of points and subscript \( i \) over all the reactions being studied.

The best values for \( K \) and \( \Delta H \) for a given run are those which minimise \( U(K_i,\Delta H_i) \), that is, those values which satisfy the following equations:-

\[ \frac{\delta U(K_i,\Delta H_i)}{\delta \Delta H_k} = \Sigma Q_{cp} \Delta n_{k,p} - \Sigma \Delta n_{k,p} \Sigma \Delta n_{i,p} \Delta H_i = 0 \tag{7.5} \]

\[ \frac{\delta U(K_i,\Delta H_i)}{\delta K_k} = \Sigma (Q_{cp} - \Sigma \Delta n_{i,p} \Delta H_i) \delta \Sigma (\Delta n_{i,p} \Delta H_i)/\delta K_k = 0 \tag{7.6} \]

where \( k = 1,\ldots,n \).

The \( n \) expressions given by equation 7.5 are all homogenous first order linear
equations in the $\Delta H_i$ values and may be easily solved if $K_i$ values, and therefore $\Delta n_i$ values are known. Equation 7.6 is a non-linear expression in $K_i$ values and must either be solved by trial and error or using iterative technique such as Raphson-Newton method.

A complete and accurate solution of equation 7.5 and 7.6 however, involves five steps:-

1. Assumption of initial $K$ values.
2. Calculation of the concentration of each species in the reaction vessel at each data point using the assumed $K$-value.
3. Calculation of the best value of $\Delta H$ corresponding to the $K$-value chosen.
4. Evaluation of the $K$ and $\Delta H$ values to establish how well these values fit the experimental data.
5. Recalculation of steps 2, 3 and 4, using new $K$-value until the best set of $K$ and $\Delta H$ values are found.
7.1.4 Calorimetric Titration Measurements of Cyclodextrin-Hapten Complexes

Analysis of Data

The calorimetric titration technique, described in chapter 6, was used to determine thermodynamic parameters of complex formation between α, β and γ-cyclodextrin (CD) and haptenic anions (X) in water and N,N'-dimethylformamide at 298.15 K. The Isoperibol Hart scientific 5021 titrator calorimeter was used for this purpose. The experimental procedure of this technique was described in the experimental part of this thesis, chapter 2.

Results of calorimetric measurements of complexation, between haptenic anions and cyclodextrins in water and N,N'-Dimethylformamide at 298.15K, are shown in Tables 7.1 - 7.25. It should be pointed out that experiments were carried out in triplicate. Only titration result of one experiment is presented.

Table 7.1 Calorimetric Titration Data for Sodium [ortho(pOHPhN₂)] Benzoate with α-Cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>X₀ (mol.dm⁻³)</th>
<th>L₀ (mol.dm⁻³)</th>
<th>Q (J)</th>
<th>V (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.266x10⁻³</td>
<td>2.165x10⁻⁴</td>
<td>-0.05745</td>
<td>0.2701</td>
</tr>
<tr>
<td>1.260x10⁻³</td>
<td>4.267x10⁻⁴</td>
<td>-0.11895</td>
<td>0.5351</td>
</tr>
<tr>
<td>1.246x10⁻³</td>
<td>8.445x10⁻⁴</td>
<td>-0.22066</td>
<td>1.0702</td>
</tr>
<tr>
<td>1.233x10⁻³</td>
<td>1.254x10⁻³</td>
<td>-0.29890</td>
<td>1.6053</td>
</tr>
<tr>
<td>1.221x10⁻³</td>
<td>1.654x10⁻³</td>
<td>-0.35367</td>
<td>2.1404</td>
</tr>
</tbody>
</table>

X₀ is the concentration of the anion in the reaction vessel.
L₀ is the concentration of the ligand (cyclodextrin).
Q is the corrected heat liberated inside the reaction vessel.
V is the volume of titrant added (cyclodextrin).
Table 7.2 Calorimetric Titration Data for Sodium [ortho (pOHPhNj)] Benzoate with γ-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol.dm⁻³)</th>
<th>$L_0$ (mol.dm⁻³)</th>
<th>Q (J)</th>
<th>V (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2473x10⁻³</td>
<td>2.187x10⁻⁴</td>
<td>-0.08100</td>
<td>0.2701</td>
</tr>
<tr>
<td>1.2406x10⁻³</td>
<td>4.350x10⁻⁴</td>
<td>-0.13623</td>
<td>0.5402</td>
</tr>
<tr>
<td>1.2340x10⁻³</td>
<td>6.491x10⁻⁴</td>
<td>-0.18686</td>
<td>0.8103</td>
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<tr>
<td>1.2275x10⁻³</td>
<td>8.608x10⁻⁴</td>
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<td>1.2148x10⁻³</td>
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<td>1.1901x10⁻³</td>
<td>2.075x10⁻³</td>
<td>-0.49062</td>
<td>2.6857</td>
</tr>
</tbody>
</table>

Table 7.3 Calorimetric Titration Data for Sodium [meta (pOHPhNj)] Benzoate with α-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol.dm⁻³)</th>
<th>$L_0$ (mol.dm⁻³)</th>
<th>Q (J)</th>
<th>V (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.630x10⁻³</td>
<td>3.856x10⁻⁴</td>
<td>-0.5983</td>
<td>0.46219</td>
</tr>
<tr>
<td>1.629x10⁻³</td>
<td>5.742x10⁻⁴</td>
<td>-0.8849</td>
<td>0.69138</td>
</tr>
<tr>
<td>1.615x10⁻³</td>
<td>7.642x10⁻⁴</td>
<td>-1.1355</td>
<td>0.92438</td>
</tr>
<tr>
<td>1.609x10⁻³</td>
<td>9.229x10⁻⁴</td>
<td>-1.3519</td>
<td>1.12069</td>
</tr>
<tr>
<td>1.600x10⁻³</td>
<td>1.136x10⁻³</td>
<td>-1.5774</td>
<td>1.38657</td>
</tr>
<tr>
<td>1.593x10⁻³</td>
<td>1.322x10⁻³</td>
<td>-1.6895</td>
<td>1.62069</td>
</tr>
<tr>
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<td>1.501x10⁻³</td>
<td>-1.8263</td>
<td>1.84876</td>
</tr>
<tr>
<td>1.580x10⁻³</td>
<td>1.673x10⁻³</td>
<td>-1.8828</td>
<td>2.06897</td>
</tr>
<tr>
<td>1.572x10⁻³</td>
<td>1.860x10⁻³</td>
<td>-1.9895</td>
<td>2.31095</td>
</tr>
<tr>
<td>1.566x10⁻³</td>
<td>2.012x10⁻³</td>
<td>-2.0284</td>
<td>2.50921</td>
</tr>
</tbody>
</table>
Table 7.4 Calorimetric Titration Data for Sodium \([meta (pOHPH_N)\] Benzoate with \(\gamma\)-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) mol.dm(^{-3})</th>
<th>(L_0) mol.dm(^{-3})</th>
<th>(Q)</th>
<th>(V) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.346x10(^{-3})</td>
<td>2.697x10(^{-4})</td>
<td>-0.3824</td>
<td>0.46219</td>
</tr>
<tr>
<td>1.340x10(^{-3})</td>
<td>3.801x10(^{-4})</td>
<td>-0.5159</td>
<td>0.65385</td>
</tr>
<tr>
<td>1.335x10(^{-3})</td>
<td>4.968x10(^{-4})</td>
<td>-0.6205</td>
<td>0.85792</td>
</tr>
<tr>
<td>1.330x10(^{-3})</td>
<td>6.079x10(^{-4})</td>
<td>-0.7084</td>
<td>1.05385</td>
</tr>
<tr>
<td>1.325x10(^{-3})</td>
<td>7.203x10(^{-4})</td>
<td>-0.7962</td>
<td>1.25365</td>
</tr>
<tr>
<td>1.320x10(^{-3})</td>
<td>8.236x10(^{-4})</td>
<td>-0.8544</td>
<td>1.43846</td>
</tr>
<tr>
<td>1.315x10(^{-3})</td>
<td>9.405x10(^{-4})</td>
<td>-0.9134</td>
<td>1.64938</td>
</tr>
<tr>
<td>1.310x10(^{-3})</td>
<td>1.044x10(^{-3})</td>
<td>-0.9418</td>
<td>1.83846</td>
</tr>
<tr>
<td>1.305x10(^{-3})</td>
<td>1.157x10(^{-3})</td>
<td>-0.9954</td>
<td>2.04511</td>
</tr>
<tr>
<td>1.295x10(^{-3})</td>
<td>1.371x10(^{-3})</td>
<td>-1.0385</td>
<td>2.44089</td>
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Table 7.5 Calorimetric Titration Data for Sodium \([meta (pOHPH_N)\] Benzoate with \(\alpha\)-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) mol.dm(^{-3})</th>
<th>(L_0) mol.dm(^{-3})</th>
<th>(Q)</th>
<th>(V) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.223x10(^{-3})</td>
<td>4.050x10(^{-4})</td>
<td>-0.3184</td>
<td>0.5351</td>
</tr>
<tr>
<td>1.210x10(^{-3})</td>
<td>8.015x10(^{-4})</td>
<td>-0.5774</td>
<td>1.0702</td>
</tr>
<tr>
<td>1.204x10(^{-3})</td>
<td>9.986x10(^{-4})</td>
<td>-0.6971</td>
<td>1.3403</td>
</tr>
<tr>
<td>1.197x10(^{-3})</td>
<td>1.194x10(^{-3})</td>
<td>-0.7866</td>
<td>1.6104</td>
</tr>
<tr>
<td>1.191x10(^{-3})</td>
<td>1.386x10(^{-3})</td>
<td>-0.8464</td>
<td>1.8805</td>
</tr>
<tr>
<td>1.185x10(^{-3})</td>
<td>1.577x10(^{-3})</td>
<td>-0.9063</td>
<td>2.1506</td>
</tr>
<tr>
<td>1.179x10(^{-3})</td>
<td>1.766x10(^{-3})</td>
<td>-0.9661</td>
<td>2.4207</td>
</tr>
<tr>
<td>1.173x10(^{-3})</td>
<td>1.953x10(^{-3})</td>
<td>-1.0259</td>
<td>2.6908</td>
</tr>
</tbody>
</table>

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Table 7.6 Calorimetric Titration of Sodium \([\text{meta (pOHPhN}_2\text{)}]\) Benzoate with
\(\beta\)-cyclodextrin in \(\text{N,N’-Dimethylformamide}\) at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) (mol dm(^{-3}))</th>
<th>(L_0) (mol dm(^{-3}))</th>
<th>(Q) (J)</th>
<th>(V) (cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.215x10(^{-3})</td>
<td>2.497x10(^{-4})</td>
<td>-0.21970</td>
<td>0.2701</td>
</tr>
<tr>
<td>1.209x10(^{-3})</td>
<td>4.968x10(^{-4})</td>
<td>-0.41497</td>
<td>0.5402</td>
</tr>
<tr>
<td>1.203x10(^{-3})</td>
<td>7.412x10(^{-4})</td>
<td>-0.56957</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.196x10(^{-3})</td>
<td>9.831x10(^{-4})</td>
<td>-0.67534</td>
<td>1.0804</td>
</tr>
<tr>
<td>1.190x10(^{-3})</td>
<td>1.222x10(^{-3})</td>
<td>-0.76484</td>
<td>1.3505</td>
</tr>
<tr>
<td>1.184x10(^{-3})</td>
<td>1.495x10(^{-3})</td>
<td>-0.82994</td>
<td>1.6206</td>
</tr>
<tr>
<td>1.177x10(^{-3})</td>
<td>1.694x10(^{-3})</td>
<td>-0.88282</td>
<td>1.8907</td>
</tr>
<tr>
<td>1.171x10(^{-3})</td>
<td>1.925x10(^{-3})</td>
<td>-0.92759</td>
<td>2.1608</td>
</tr>
<tr>
<td>1.165x10(^{-3})</td>
<td>2.155x10(^{-3})</td>
<td>-0.96826</td>
<td>2.4309</td>
</tr>
</tbody>
</table>

Table 7.7 Calorimetric Titration Data for Sodium \([\text{meta (pOHPhN}_2\text{)}]\) Benzoate with
\(\gamma\)-cyclodextrin in \(\text{N,N’-Dimethylformamide}\) at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) (mol dm(^{-3}))</th>
<th>(L_0) (mol dm(^{-3}))</th>
<th>(Q) (J)</th>
<th>(V) (cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1065x10(^{-3})</td>
<td>2.187x10(^{-4})</td>
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<td>0.2701</td>
</tr>
<tr>
<td>1.1006x10(^{-3})</td>
<td>4.350x10(^{-4})</td>
<td>-0.46878</td>
<td>0.5402</td>
</tr>
<tr>
<td>1.0948x10(^{-3})</td>
<td>6.491x10(^{-4})</td>
<td>-0.63166</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.0890x10(^{-3})</td>
<td>8.608x10(^{-4})</td>
<td>-0.76174</td>
<td>1.0804</td>
</tr>
<tr>
<td>1.0832x10(^{-3})</td>
<td>1.070x10(^{-3})</td>
<td>-0.85952</td>
<td>1.3505</td>
</tr>
<tr>
<td>1.0776x10(^{-3})</td>
<td>1.278x10(^{-3})</td>
<td>-0.92818</td>
<td>1.6206</td>
</tr>
<tr>
<td>1.0720x10(^{-3})</td>
<td>1.483x10(^{-3})</td>
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<td>1.8907</td>
</tr>
<tr>
<td>1.0686x10(^{-3})</td>
<td>1.686x10(^{-3})</td>
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<td>2.1608</td>
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Table 7.8 Calorimetric Titration Data for Sodium [\textit{para} (\textit{p}OHPhN\textsubscript{3})] Benzoate with \(\alpha\)-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) (mol.dm(^{-3}))</th>
<th>(L_0) (mol.dm(^{-3}))</th>
<th>(Q) (J)</th>
<th>(V) (cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.140 \times 10^{-3}</td>
<td>2.751 \times 10^{-4}</td>
<td>-0.3197</td>
<td>0.32885</td>
</tr>
<tr>
<td>1.132 \times 10^{-3}</td>
<td>5.466 \times 10^{-4}</td>
<td>-0.5966</td>
<td>0.65770</td>
</tr>
<tr>
<td>1.125 \times 10^{-3}</td>
<td>8.146 \times 10^{-4}</td>
<td>-0.8502</td>
<td>0.98655</td>
</tr>
<tr>
<td>1.118 \times 10^{-3}</td>
<td>1.079 \times 10^{-3}</td>
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<td>1.31540</td>
</tr>
<tr>
<td>1.110 \times 10^{-3}</td>
<td>1.340 \times 10^{-3}</td>
<td>-1.2037</td>
<td>1.64425</td>
</tr>
<tr>
<td>1.103 \times 10^{-3}</td>
<td>1.598 \times 10^{-3}</td>
<td>-1.3016</td>
<td>1.97310</td>
</tr>
<tr>
<td>1.097 \times 10^{-3}</td>
<td>1.853 \times 10^{-3}</td>
<td>-1.3368</td>
<td>2.30195</td>
</tr>
</tbody>
</table>

Table 7.9 Calorimetric Titration Data for Sodium [\textit{para} (\textit{p}OHPhN\textsubscript{3})] Benzoate with \(\gamma\)-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) (mol.dm(^{-3}))</th>
<th>(L_0) (mol.dm(^{-3}))</th>
<th>(Q) (J)</th>
<th>(V) (cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.058 \times 10^{-3}</td>
<td>2.697 \times 10^{-4}</td>
<td>-0.3268</td>
<td>0.46219</td>
</tr>
<tr>
<td>1.055 \times 10^{-3}</td>
<td>3.440 \times 10^{-4}</td>
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<td>0.59091</td>
</tr>
<tr>
<td>1.052 \times 10^{-3}</td>
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<td>0.75758</td>
</tr>
<tr>
<td>1.049 \times 10^{-3}</td>
<td>5.346 \times 10^{-4}</td>
<td>-0.5159</td>
<td>0.92438</td>
</tr>
<tr>
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<td>7.055 \times 10^{-4}</td>
<td>-0.5950</td>
<td>1.22727</td>
</tr>
<tr>
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<td>7.947 \times 10^{-4}</td>
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</tr>
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<td>1.50000</td>
</tr>
<tr>
<td>1.030 \times 10^{-3}</td>
<td>1.050 \times 10^{-3}</td>
<td>-0.7025</td>
<td>1.84876</td>
</tr>
<tr>
<td>1.028 \times 10^{-3}</td>
<td>1.091 \times 10^{-3}</td>
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<td>1.92424</td>
</tr>
<tr>
<td>1.021 \times 10^{-3}</td>
<td>1.301 \times 10^{-3}</td>
<td>-0.7381</td>
<td>2.31095</td>
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</tbody>
</table>
Table 7.10 Calorimetric Titration Data for Sodium [para (pOHPhNz)] Benzoate with α-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>X_0 mol dm^{-3}</th>
<th>L_0 mol dm^{-3}</th>
<th>Q J</th>
<th>V cm^{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.234x10^{-3}</td>
<td>2.007x10^{-4}</td>
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<td>0.2638</td>
</tr>
<tr>
<td>1.228x10^{-3}</td>
<td>3.994x10^{-4}</td>
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<td>0.5276</td>
</tr>
<tr>
<td>1.222x10^{-3}</td>
<td>5.960x10^{-4}</td>
<td>-0.34899</td>
<td>0.7914</td>
</tr>
<tr>
<td>1.215x10^{-3}</td>
<td>8.063x10^{-4}</td>
<td>-0.42041</td>
<td>1.0552</td>
</tr>
<tr>
<td>1.209x10^{-3}</td>
<td>9.831x10^{-4}</td>
<td>-0.47145</td>
<td>1.3190</td>
</tr>
<tr>
<td>1.203x10^{-3}</td>
<td>1.174x10^{-3}</td>
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<td>1.5828</td>
</tr>
<tr>
<td>1.197x10^{-3}</td>
<td>1.362x10^{-3}</td>
<td>-0.67174</td>
<td>1.8466</td>
</tr>
</tbody>
</table>

Table 7.11 Calorimetric Titration Data for Sodium [para (pOHPhNz)] Benzoate with β-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>X_0 mol dm^{-3}</th>
<th>L_0 mol dm^{-3}</th>
<th>Q J</th>
<th>V cm^{3}</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.5351</td>
</tr>
<tr>
<td>1.293x10^{-3}</td>
<td>7.367x10^{-4}</td>
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<td>0.8052</td>
</tr>
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<td>1.286x10^{-3}</td>
<td>9.786x10^{-4}</td>
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<td>1.0753</td>
</tr>
<tr>
<td>1.280x10^{-3}</td>
<td>1.218x10^{-4}</td>
<td>-0.76111</td>
<td>1.3454</td>
</tr>
<tr>
<td>1.273x10^{-3}</td>
<td>1.455x10^{-4}</td>
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<td>1.6155</td>
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<tr>
<td>1.266x10^{-3}</td>
<td>1.689x10^{-4}</td>
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<td>1.8856</td>
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</table>
Table 7.12 Calorimetric Titration Data for Sodium [para (pOHPhNj)] Benzoate with α-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol.dm$^{-3}$)</th>
<th>$L_0$ (mol.dm$^{-3}$)</th>
<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
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<td>1.603x10$^{-4}$</td>
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<td>0.2701</td>
</tr>
<tr>
<td>8.1846x10$^{-4}$</td>
<td>3.189x10$^{-4}$</td>
<td>-0.23246</td>
<td>0.5402</td>
</tr>
<tr>
<td>8.1411x10$^{-4}$</td>
<td>4.759x10$^{-4}$</td>
<td>-0.31401</td>
<td>0.8103</td>
</tr>
<tr>
<td>8.0940x10$^{-4}$</td>
<td>6.311x10$^{-4}$</td>
<td>-0.37924</td>
<td>1.0804</td>
</tr>
<tr>
<td>8.0554x10$^{-4}$</td>
<td>7.848x10$^{-4}$</td>
<td>-0.43225</td>
<td>1.3505</td>
</tr>
<tr>
<td>8.0133x10$^{-4}$</td>
<td>9.368x10$^{-4}$</td>
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</tr>
<tr>
<td>7.9716x10$^{-4}$</td>
<td>1.078x10$^{-3}$</td>
<td>-0.50568</td>
<td>1.8907</td>
</tr>
</tbody>
</table>

Table 7.13 Calorimetric Titration Data for Sodium [2-Chloro-4 (pOHPhNj)] Benzoate with α-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol.dm$^{-3}$)</th>
<th>$L_0$ (mol.dm$^{-3}$)</th>
<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.974x10$^{-4}$</td>
<td>2.751x10$^{-4}$</td>
<td>-0.4720</td>
<td>0.32885</td>
</tr>
<tr>
<td>9.910x10$^{-4}$</td>
<td>5.466x10$^{-4}$</td>
<td>-0.9050</td>
<td>0.65770</td>
</tr>
<tr>
<td>9.846x10$^{-4}$</td>
<td>8.146x10$^{-4}$</td>
<td>-1.2606</td>
<td>0.98655</td>
</tr>
<tr>
<td>9.783x10$^{-4}$</td>
<td>1.079x10$^{-3}$</td>
<td>-1.4774</td>
<td>1.31540</td>
</tr>
<tr>
<td>9.720x10$^{-4}$</td>
<td>1.340x10$^{-3}$</td>
<td>-1.6037</td>
<td>1.64425</td>
</tr>
<tr>
<td>9.659x10$^{-4}$</td>
<td>1.598x10$^{-3}$</td>
<td>-1.6761</td>
<td>1.97310</td>
</tr>
</tbody>
</table>
Table 7.14 Calorimetric Titration Data for Sodium [2-Chloro-4 (pOHPhN\textsubscript{3})] Benzoate with \(\gamma\)-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) mol.dm(^{-3})</th>
<th>(L_0) mol.dm(^{-3})</th>
<th>(Q) J</th>
<th>(V) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.296x10(^{-3})</td>
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<td>-0.5176</td>
<td>0.46219</td>
</tr>
<tr>
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<td>5.346x10(^{-4})</td>
<td>-0.8422</td>
<td>0.92438</td>
</tr>
<tr>
<td>1.273x10(^{-3})</td>
<td>7.947x10(^{-4})</td>
<td>-1.0159</td>
<td>1.38657</td>
</tr>
<tr>
<td>1.261x10(^{-3})</td>
<td>1.050x10(^{-3})</td>
<td>-1.1330</td>
<td>1.84876</td>
</tr>
<tr>
<td>1.250x10(^{-3})</td>
<td>1.301x10(^{-3})</td>
<td>-1.2025</td>
<td>2.31095</td>
</tr>
<tr>
<td>1.246x10(^{-3})</td>
<td>1.400x10(^{-3})</td>
<td>-1.2247</td>
<td>2.49583</td>
</tr>
</tbody>
</table>

Table 7.15 Calorimetric Titration Data for Sodium [2-Chloro-4 (pOHPhN\textsubscript{3})] Benzoate with \(\alpha\)-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) mol.dm(^{-3})</th>
<th>(L_0) mol.dm(^{-3})</th>
<th>(Q) J</th>
<th>(V) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.248x10(^{-3})</td>
<td>2.055x10(^{-4})</td>
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</tr>
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<td>4.088x10(^{-4})</td>
<td>-0.18585</td>
<td>0.5402</td>
</tr>
<tr>
<td>1.235x10(^{-3})</td>
<td>6.100x10(^{-4})</td>
<td>-0.26409</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.228x10(^{-3})</td>
<td>8.090x10(^{-4})</td>
<td>-0.33844</td>
<td>1.0804</td>
</tr>
<tr>
<td>1.222x10(^{-3})</td>
<td>1.006x10(^{-3})</td>
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<td>1.3505</td>
</tr>
<tr>
<td>1.216x10(^{-3})</td>
<td>1.201x10(^{-3})</td>
<td>-0.46564</td>
<td>1.6206</td>
</tr>
<tr>
<td>1.209x10(^{-3})</td>
<td>1.394x10(^{-3})</td>
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<td>1.8907</td>
</tr>
<tr>
<td>1.203x10(^{-3})</td>
<td>1.585x10(^{-3})</td>
<td>-0.55367</td>
<td>2.1608</td>
</tr>
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Table 7.16 Calorimetric Titration Data for Sodium [2-Chloro-4 (pOHPhN)] Benzoate with β-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol dm$^{-3}$)</th>
<th>$L_0$ (mol dm$^{-3}$)</th>
<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.310x10$^{-3}$</td>
<td>2.497x10$^{-4}$</td>
<td>-0.1453</td>
<td>0.2701</td>
</tr>
<tr>
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<td>4.968x10$^{-4}$</td>
<td>-0.2677</td>
<td>0.5402</td>
</tr>
<tr>
<td>1.296x10$^{-3}$</td>
<td>7.412x10$^{-4}$</td>
<td>-0.3727</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.289x10$^{-3}$</td>
<td>9.831x10$^{-4}$</td>
<td>-0.4543</td>
<td>1.0804</td>
</tr>
<tr>
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<td>1.222x10$^{-3}$</td>
<td>-0.5238</td>
<td>1.3505</td>
</tr>
<tr>
<td>1.276x10$^{-3}$</td>
<td>1.459x10$^{-3}$</td>
<td>-0.5870</td>
<td>1.6206</td>
</tr>
<tr>
<td>1.269x10$^{-3}$</td>
<td>1.694x10$^{-3}$</td>
<td>-0.6405</td>
<td>1.8907</td>
</tr>
<tr>
<td>1.262x10$^{-3}$</td>
<td>1.925x10$^{-3}$</td>
<td>-0.6826</td>
<td>2.1608</td>
</tr>
</tbody>
</table>

Table 7.17 Calorimetric Titration Data for Sodium [2-Chloro-4 (pOHPhN)] Benzoate with γ-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol dm$^{-3}$)</th>
<th>$L_0$ (mol dm$^{-3}$)</th>
<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.302x10$^{-3}$</td>
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<td>0.2701</td>
</tr>
<tr>
<td>1.295x10$^{-3}$</td>
<td>4.350x10$^{-4}$</td>
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<td>0.5402</td>
</tr>
<tr>
<td>1.288x10$^{-3}$</td>
<td>6.491x10$^{-4}$</td>
<td>-0.3679</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.281x10$^{-3}$</td>
<td>8.608x10$^{-4}$</td>
<td>-0.4612</td>
<td>1.0804</td>
</tr>
<tr>
<td>1.275x10$^{-3}$</td>
<td>1.070x10$^{-3}$</td>
<td>-0.5473</td>
<td>1.3505</td>
</tr>
<tr>
<td>1.268x10$^{-3}$</td>
<td>1.278x10$^{-3}$</td>
<td>-0.6197</td>
<td>1.6206</td>
</tr>
<tr>
<td>1.261x10$^{-3}$</td>
<td>1.483x10$^{-3}$</td>
<td>-0.6761</td>
<td>1.8907</td>
</tr>
<tr>
<td>1.255x10$^{-3}$</td>
<td>1.686x10$^{-3}$</td>
<td>-0.7204</td>
<td>2.1608</td>
</tr>
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</table>
Table 7.18 Calorimetric Titration Data for Sodium [4-Chloro-3 \((pOHPhN)\)] Benzoate with \(\gamma\)-cyclodextrin in Water at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) mol.dm(^{-3})</th>
<th>(L_0) mol.dm(^{-3})</th>
<th>(Q) J</th>
<th>(V) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0651x10(^{-3})</td>
<td>1.542x10(^{-4})</td>
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<td>0.2638</td>
</tr>
<tr>
<td>1.0595x10(^{-3})</td>
<td>3.068x10(^{-4})</td>
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<td>0.5276</td>
</tr>
<tr>
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<td>4.578x10(^{-4})</td>
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<td>0.7914</td>
</tr>
<tr>
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</tr>
<tr>
<td>1.0445x10(^{-3})</td>
<td>7.551x10(^{-4})</td>
<td>-0.92747</td>
<td>1.2535</td>
</tr>
<tr>
<td>1.0418x10(^{-3})</td>
<td>7.925x10(^{-4})</td>
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<td>1.3861</td>
</tr>
<tr>
<td>1.0391x10(^{-3})</td>
<td>8.661x10(^{-4})</td>
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<td>1.5187</td>
</tr>
<tr>
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<td>-0.40794</td>
<td>0.3254</td>
</tr>
<tr>
<td>1.0516x10(^{-3})</td>
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</tr>
<tr>
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<td>3.837x10(^{-4})</td>
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<td>0.6617</td>
</tr>
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</table>

Table 7.19 Calorimetric Titration Data for Sodium [4-Chloro-3 \((pOHPhN)\)] Benzoate with \(\alpha\)-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>(X_0) mol.dm(^{-3})</th>
<th>(L_0) mol.dm(^{-3})</th>
<th>(Q) J</th>
<th>(V) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.216x10(^{-3})</td>
<td>4.050x10(^{-4})</td>
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</tr>
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</tr>
<tr>
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<td>8.053x10(^{-4})</td>
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<td>1.0753</td>
</tr>
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</table>
Table 7.20 Calorimetric Titration Data for Sodium [4-Chloro-3 (pOHPhN)] Benzoate with β-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
<th>$X_0$ (mol dm$^{-3}$)</th>
<th>$L_0$ (mol dm$^{-3}$)</th>
<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.245x10$^{-3}$</td>
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<td>0.2701</td>
</tr>
<tr>
<td>1.239x10$^{-3}$</td>
<td>4.350x10$^{-4}$</td>
<td>-0.38643</td>
<td>0.5402</td>
</tr>
<tr>
<td>1.232x10$^{-3}$</td>
<td>6.491x10$^{-4}$</td>
<td>-0.52894</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.226x10$^{-3}$</td>
<td>3.608x10$^{-4}$</td>
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<td>1.0804</td>
</tr>
<tr>
<td>1.219x10$^{-3}$</td>
<td>1.070x10$^{-3}$</td>
<td>-0.74355</td>
<td>1.3505</td>
</tr>
<tr>
<td>1.213x10$^{-3}$</td>
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<td>1.6206</td>
</tr>
<tr>
<td>1.206x10$^{-3}$</td>
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<td>-0.86731</td>
<td>1.8907</td>
</tr>
<tr>
<td>1.200x10$^{-3}$</td>
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<td>2.1608</td>
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</table>

Table 7.21 Calorimetric Titration Data for Sodium [4-Chloro-3 (pOHPhN$_2$)] Benzoate with β-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
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<th>$V$ (cm$^3$)</th>
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</tr>
<tr>
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<td>-0.35765</td>
<td>0.5402</td>
</tr>
<tr>
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<td>7.412x10$^{-4}$</td>
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<td>0.8103</td>
</tr>
<tr>
<td>1.242x10$^{-3}$</td>
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<td>1.3505</td>
</tr>
<tr>
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<td>-0.83801</td>
<td>1.6206</td>
</tr>
<tr>
<td>1.223x10$^{-3}$</td>
<td>1.694x10$^{-3}$</td>
<td>-0.91010</td>
<td>1.8907</td>
</tr>
<tr>
<td>1.216x10$^{-3}$</td>
<td>1.925x10$^{-3}$</td>
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Table 7.22 Calorimetric Titration Data for Sodium [4-Chloro-3 (pOHPhNg)] Benzoate with γ-cyclodextrin in N,N’-Dimethylformamide at 298.15K.

<table>
<thead>
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<th>$X_0$ (mol.dm$^{-3}$)</th>
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<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
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<tbody>
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</tr>
<tr>
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<td>0.5402</td>
</tr>
<tr>
<td>1.232x10$^{-3}$</td>
<td>6.491x10$^{-3}$</td>
<td>-0.49961</td>
<td>0.8103</td>
</tr>
<tr>
<td>1.226x10$^{-3}$</td>
<td>8.608x10$^{-3}$</td>
<td>-0.62450</td>
<td>1.0804</td>
</tr>
<tr>
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</tr>
<tr>
<td>1.213x10$^{-3}$</td>
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<td>1.6206</td>
</tr>
<tr>
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<td>1.483x10$^{-3}$</td>
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<td>1.8907</td>
</tr>
<tr>
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Table 7.23 Calorimetric Titration Data for Sodium Benzoate with α-cyclodextrin in N,N’-Dimethylformamide at 298.15K.

<table>
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<tr>
<th>$X_0$ (mol.dm$^{-3}$)</th>
<th>$L_0$ (mol.dm$^{-3}$)</th>
<th>$Q$ (J)</th>
<th>$V$ (cm$^3$)</th>
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<tbody>
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</tr>
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</tr>
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</tr>
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<td>1.0804</td>
</tr>
<tr>
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<td>1.060x10$^{-3}$</td>
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<td>1.3505</td>
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<tr>
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</tr>
<tr>
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<td>1.8907</td>
</tr>
<tr>
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<td>2.1608</td>
</tr>
<tr>
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<tr>
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<td>2.7010</td>
</tr>
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</table>
Table 7.24 Calorimetric Titration Data for Sodium Benzoate with 
\( \beta \)-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
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<tr>
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<th>( L_0 )</th>
<th>( Q )</th>
<th>( V )</th>
</tr>
</thead>
<tbody>
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<td>mol.dm(^{-3})</td>
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<td>cm(^3)</td>
</tr>
<tr>
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<td>0.2701</td>
</tr>
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<td>1.0804</td>
</tr>
<tr>
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<td>-1.19148</td>
<td>1.3505</td>
</tr>
<tr>
<td>1.629\times10^{-3}</td>
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<td>1.6206</td>
</tr>
<tr>
<td>1.621\times10^{-3}</td>
<td>1.600\times10^{-3}</td>
<td>-1.38244</td>
<td>1.8907</td>
</tr>
<tr>
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<tr>
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<td>2.4309</td>
</tr>
<tr>
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<td>-1.54268</td>
<td>2.7010</td>
</tr>
</tbody>
</table>

Table 7.25 Calorimetric Titration Data for Sodium Benzoate with 
\( \gamma \)-cyclodextrin in N,N'-Dimethylformamide at 298.15K.

<table>
<thead>
<tr>
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<th>( L_0 )</th>
<th>( Q )</th>
<th>( V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol.dm(^{-3})</td>
<td>mol.dm(^{-3})</td>
<td>J cm(^3)</td>
<td>cm(^3)</td>
</tr>
<tr>
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<td>0.2701</td>
</tr>
<tr>
<td>1.3336\times10^{-3}</td>
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<td>0.5402</td>
</tr>
<tr>
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</tr>
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</tr>
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</tr>
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</tr>
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</tr>
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</tr>
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<td>1.529\times10^{-3}</td>
<td>-1.17960</td>
<td>2.7010</td>
</tr>
</tbody>
</table>
In most cases the cyclodextrin-ions complexes are believed to be of the 1:1 type, but the formation of 1:2 and 2:1 compounds has also been observed. However, for cyclodextrin-hapten complexes, a 1:1 complex formation was observed. This was checked by titrating the hapten solution, in both water and N,N'-Dimethylformamide, with solutions of cyclodextrins which contains the same number of moles as the hapten in solution. It was noticed that the addition of an excess of cyclodextrins evolved no heat. Therefore, it was assumed that cyclodextrin-hapten complexes, in water and N,N'-Dimethylformamide, are of 1:1 complexes. Then, for an anion (X) and a ligand (L) the process involved could be represented by the equation:

\[ X_{\text{soln}} + L_{\text{soln}} \rightleftharpoons X\cdot L_{\text{soln}} \]  \hspace{1cm} (7.6)

The thermodynamic equilibrium constant, \( K_c \), may be expressed as:

\[ K_c = \frac{a_{X\cdot L}}{a_X \cdot a_L} \]  \hspace{1cm} (7.7)

where \( a_X \), \( a_L \) and \( a_{X\cdot L} \) are the molar activities of the anion, the ligand and the complexed anion species respectively. Thus, \( K_c \) may written as:

\[ K_c = \frac{[X\cdot L] \cdot Y_L}{[X] \cdot Y_X \cdot [L] \cdot Y_L} \]  \hspace{1cm} (7.8)

\([X]\) and \([L]\) and \([X\cdot L]\) are the molar concentration of the anion, the cyclodextrin and the formed complex at the equilibrium. \( Y_{X\cdot L} \), \( Y_X \) are the mean molar activity coefficients of the species \( X\cdot L \) and \( X \) respectively; \( Y_L \) the activity coefficient of the ligand is equal to 1. Assuming that \( X_0 \) and \( L_0 \) are the initial concentration of the anion and the ligand species in solution, then, at the equilibrium, the material balance of the system can be written as:

\[ X_0 = [X] + [X\cdot L] \]  \hspace{1cm} (7.9)

\[ L_0 = [L] + [X\cdot L] \]  \hspace{1cm} (7.10)
By replacing \([X]\) and \([L]\) by their values in eqn 7.8, \(K_c\) becomes:

\[
K_c = [X:L] \cdot \gamma_{xL}/(X_o - [X:L])(L_o - [X:L]) \cdot \gamma_x.
\]  

7.11

\(\gamma_m\) and \(\gamma_{xL}\) can be determined using the Debye-Huckel equation in its extended form. Equation 7.11 leads to a quadratic equation of the form:

\[
[X:L]^2 - (X_o + L_o + (\gamma_{xL}/\gamma_x)/K_c)[X:L] + X_oL_o = 0
\]

7.12

Solving for \([X:L]\),

\[
[X:L] = -(X_o + L_o + (\gamma_{xL}/\gamma_x)/K_c) \pm \sqrt{(X_o + L_o + (\gamma_{xL}/\gamma_x)/K_c)^2 + 4X_oL_o})/2
\]

7.13

If we know \(K_c\), then we can calculate the enthalpy of complexation, \(\Delta H^\circ_c\). This is given by:

\[
\Delta H^\circ_c = Q_r/([X:L].V)
\]

7.14

\(Q_r\) is the correct heat released inside the calorimetric vessel after addition of a volume \(V\) of cyclodextrin to the hapten solution. The term \([M*L].V\) represent the number of moles of the complex in the reaction vessel of the calorimeter.

\(K_c\) depends on the number of moles of the complex, \(n_{xL}\). Also \(\Delta H^\circ_c\) is \(n_{xL}\) dependent. Therefore, an iterative calculation procedure is needed. For this purpose, a computer program, based on the method presented in section 7.1.3 and the method proposed by Karlsson and Kullberg, was devised to allow simultaneous calculation of the stability constant and the enthalpy of complexation. The program, written in Fortran77, is shown in appendix C.

Analysis of the calorimetric titration data yielded the stability constants (\(\log K_c\)) and corresponding enthalpy of complexation (\(\Delta H^\circ_c\)). Free energies of
complexation ($\Delta G^0$) were derived from the complex stability constants ($K_c$) using the relation:

$$\Delta G^0_c = -RT \ln K_c$$  \hspace{1cm} 7.15

Entropies of complexation ($\Delta S^0$) were obtained from combinations between free energies and enthalpies of complexation data.

Table 7.26 and 7.27 contain the different thermodynamic parameters of complexation ($\log K_c$, $\Delta H^0$, $\Delta G^0$, and $\Delta S^0$) between $\alpha$, $\beta$ and $\gamma$-cyclodextrin and haptenic anions in water and N,N'-Dimethylformamide at 298.15 K.
Table 7.26 Thermodynamic Parameters of Cyclodextrin-Hapten Complexes in Water at 298.15 K.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Ligand: α-CD</th>
<th>logK&lt;sub&gt;e&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;e&lt;/sub&gt;</th>
<th>ΔH°&lt;sub&gt;e&lt;/sub&gt;</th>
<th>ΔS°&lt;sub&gt;e&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta (pOHPhN₂)B⁻</td>
<td>3.72±0.03</td>
<td>-21.23</td>
<td>-33.35±1.89</td>
<td>-40.6</td>
<td></td>
</tr>
<tr>
<td>para (pOHPhN₂)B⁻</td>
<td>3.63±0.04</td>
<td>-20.72</td>
<td>-29.13±0.43</td>
<td>-28.2</td>
<td></td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN₂)B⁻</td>
<td>4.14±0.06</td>
<td>-22.63</td>
<td>-36.96±0.39</td>
<td>-44.7</td>
<td></td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anion</th>
<th>Ligand: γ-CD</th>
<th>logK&lt;sub&gt;e&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;e&lt;/sub&gt;</th>
<th>ΔH°&lt;sub&gt;e&lt;/sub&gt;</th>
<th>ΔS°&lt;sub&gt;e&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta (pOHPhN₂)B⁻</td>
<td>3.94±0.05</td>
<td>-22.49</td>
<td>-25.18±0.25</td>
<td>-9.0</td>
<td></td>
</tr>
<tr>
<td>para (pOHPhN₂)B⁻</td>
<td>4.13±0.09</td>
<td>-23.57</td>
<td>-20.44±1.08</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>5Cl-2 (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Cl-2 (pOHPhN₂)B⁻</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Cl-4 (pOHPhN₂)B⁻</td>
<td>4.30±0.17</td>
<td>-24.55</td>
<td>-28.04±0.77</td>
<td>-11.7</td>
<td></td>
</tr>
<tr>
<td>4Cl-3 (pOHPhN₂)B⁻</td>
<td>4.16±0.02</td>
<td>-23.75</td>
<td>-34.84±1.17</td>
<td>-37.2</td>
<td></td>
</tr>
</tbody>
</table>
Table 7.27 Thermodynamic Parameters of Cyclodextrin-Hapten Complexes in \(\text{N},\text{N}'\)-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Anion</th>
<th>(\log K_c)</th>
<th>(\Delta G^\circ) (^{\text{kJ.mol}^{-1}})</th>
<th>(\Delta H^\circ) (^{\text{kJ.mol}^{-1}})</th>
<th>(\Delta S^\circ) (^{\text{J.K}^{-1}.\text{mol}^{-1}})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ligand: (\alpha)-CD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.20±0.04</td>
<td>-18.27</td>
<td>-9.29±0.08</td>
<td>30.1</td>
</tr>
<tr>
<td>meta ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.47±0.03</td>
<td>-19.81</td>
<td>-21.37±0.23</td>
<td>-5.2</td>
</tr>
<tr>
<td>para ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.77±0.12</td>
<td>-21.52</td>
<td>-15.53±0.93</td>
<td>20.8</td>
</tr>
<tr>
<td>5CI-2 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6CI-2 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2CI-4 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.32±0.18</td>
<td>-18.95</td>
<td>-14.49±1.22</td>
<td>14.9</td>
</tr>
<tr>
<td>4CI-3 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.71±0.04</td>
<td>-21.18</td>
<td>-19.27±1.10</td>
<td>6.4</td>
</tr>
<tr>
<td><strong>Ligand: (\beta)-CD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>4.01±0.03</td>
<td>-22.89</td>
<td>-17.47±0.03</td>
<td>18.2</td>
</tr>
<tr>
<td>para ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>4.04±0.09</td>
<td>-23.06</td>
<td>-17.17±0.79</td>
<td>19.7</td>
</tr>
<tr>
<td>5CI-2 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6CI-2 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2CI-4 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.64±0.05</td>
<td>-20.78</td>
<td>-12.94±0.35</td>
<td>26.3</td>
</tr>
<tr>
<td>4CI-3 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.51±0.14</td>
<td>-20.04</td>
<td>-20.05±0.60</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Ligand: (\gamma)-CD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.28±0.06</td>
<td>-18.72</td>
<td>-10.24±0.74</td>
<td>28.4</td>
</tr>
<tr>
<td>meta ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>4.04±0.01</td>
<td>-23.06</td>
<td>-22.05±0.20</td>
<td>3.4</td>
</tr>
<tr>
<td>para ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>4.15±0.05</td>
<td>-23.69</td>
<td>-15.56±2.20</td>
<td>27.3</td>
</tr>
<tr>
<td>5CI-2 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6CI-2 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>no complexation was observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2CI-4 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.63±0.07</td>
<td>-20.72</td>
<td>-14.82±0.45</td>
<td>19.8</td>
</tr>
<tr>
<td>4CI-3 ((p\text{OHPhN}_2)\text{B}^-)</td>
<td>3.88±0.02</td>
<td>-22.15</td>
<td>-18.73±0.50</td>
<td>11.5</td>
</tr>
</tbody>
</table>
7.2 Discussion of Thermodynamic Parameters of Complexation of Cyclodextrin and Haptenic Anions

The thermodynamic parameters of complexation between cyclodextrins and haptenic anions, in water and N,N’-Dimethylformamide, are listed in Tables 7.26 and 7.27. It is shown that only three anions [meta, para and \(2\text{Cl}-4\) (pOHPhN\(_2\))B\(^-\)] were found to form 1:1 complexes with \(\alpha\)-cyclodextrin in water. In addition, the \(4\text{Cl}-3\) (pOHPhN\(_2\))B\(^-\) anion was also found to form a 1:1 complex with \(\gamma\)-cyclodextrin in this solvent. The relatively low solubility of \(\beta\)-cyclodextrin in water prevented us from detecting whether or not complexation of \(\beta\)-cyclodextrin and these anions takes place in water.

As far as N,N’-Dimethylformamide is concerned, five out of seven anions [ortho, meta, para, \(2\text{Cl}-4\) and \(4\text{Cl}-3\) (pOHPhN\(_2\))B\(^-\)] considered are able to form 1:1 complexes with \(\alpha\) and \(\gamma\)-cyclodextrin. Among these five anions, only ortho (pOHPhN\(_2\))B\(^-\) anion did not complex with \(\beta\)-cyclodextrin in this solvent.

The anions, \(5\text{Cl}-2\) and \(6\text{Cl}-2\) (pOHPhN\(_2\))B\(^-\), showed no sign of complexation with \(\alpha\), \(\beta\) and \(\gamma\)-cyclodextrin neither in water nor in N,N’-Dimethylformamide.

In attempt to explain the lack of complexation observed between certain anions and cyclodextrin in these solvents, the solvation properties of these anions are considered. These properties are best reflected in their transfer free energies, \(\Delta G^0\), from water to N,N’-Dimethylformamide (Table 5.45, chapter 5). The data indicate that (pOHPhN\(_2\))B\(^-\) anions are better solvated in water than in N,N’-Dimethylformamide in the order:

\[
6\text{Cl}-2 > 4\text{Cl}-3 = \text{ortho} > \text{para} > 5\text{Cl}-2 > \text{meta} > 2\text{Cl}-4
\]

If competition between ligand and solvent for the anion is likely to play a significant role in the complexation process involving cyclodextrins, it would not be
surprising to find that anions which are well solvated in water are not able to complex with cyclodextrins in this solvent. However, the solvation of the anion does not appear to be the only factor which contributes to the lack of complexation of some anions and cyclodextrins in water. This is illustrated by considering the 5CI2 (pOHPhN2)B⁻ anion. This anion is less solvated than a number of other anions in this series for which complexation occurs. However, complexation of 5CI-2 (pOHPhN2)B⁻ with α, β and γ-cyclodextrin does not take place either in water or in N,N'-Dimethylformamide.

Examination of these results in water shows (Table 7.26) that unlike meta, para and 2CI-4 (pOHPhN2)B⁻, complexation between ortho and substituted ortho (pOHPhN2)B⁻ anions and α and γ-cyclodextrin does not occur in water. These observations lead to the suggestion that the pOHPhN2 group must be the active site for complexation between these anions and cyclodextrins. This suggestion is strongly supported by the results obtained from computer calculations using a COSMIC package. The structural conformation which corresponds to the minimum energy (higher stability) for the formation of inclusion complexes is that shown in Figures 7.1-7.3. These findings suggest that steric effects which may not be attributed only to the position but also to the state of solvation of the substituent groups in the guest species are likely to be responsible for the lack of complexation of α and γ-cyclodextrin in water.

Unlike γ-cyclodextrin, complexation of 4CI-3 (pOHPhN2)B⁻ anion and α-cyclodextrin does not take place. This can hardly be explained on the basis of steric effects due to the presence of the chlorine atom next to the pOHPhN2 group since this effect should also be observed with γ-cyclodextrin. However, one can guess either that the complexation is very weak and was not detected or the presence of the chlorine group in the para position and the pOHPhN2 group in the meta position might disturb the interaction between the α-cyclodextrin and this anion in water.
Figure 7.1 Inclusion Complexation Model between Cyclodextrin and \textit{para} (pOHPhN$_2$)B$^-$ Anion.
Figure 7.2 Inclusion Complexation Model between Cyclodextrin and $2Cl-4(pOHPhN_2)B^-$ Anion.
Figure 7.3 Inclusion Complexation Model between Cyclodextrin and meta \( \text{pOHPhN}_2 \)B\(^-\) Anion.
7.2.1 Stability Constants, LogK

Stability constant data, reported as logK, enthalpies, ΔH°, free energies, ΔG°, and entropies of complexation, ΔS°, for para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoate anions and cyclodextrins in water and N,N′-Dimethylformamide at 298.15 K are listed in Tables 7.26 and 7.27. The standard deviation of the data are also included in these Tables. No significant differences are found among logK values for these anions and cyclodextrins in these solvents. The average values of logK were found to be 3.83 ± 0.27 and 3.49 ± 0.25 (α-cyclodextrin) against values of 4.13 ± 0.15 and 3.80 ± 0.35 (γ-cyclodextrin) in water and N,N′-Dimethylformamide respectively. With β-cyclodextrin in N,N′-Dimethylformamide, the average logK value is 3.80 ± 0.26. From these data, it can be concluded that:

i) Stability constants in water and N,N′-Dimethylformamide are slightly higher for anions complexed with γ-cyclodextrin.

ii) The ligands (α, β and γ-cyclodextrin) do not show any specificity for these anions.

iii) The reaction media does not seem to have any significant effect on the stability constant data. Obviously, these statements can be extended to the free energies of complexation, ΔG°.

7.2.1 Free Energy, Enthalpy and Entropy of Complexation - Compensation Effect

The free energies of complexation of these haptenic anions and cyclodextrins are similar (Table 7.26-7.27). This could be the result of:

a) An equal value for the enthalpic and entropic contributions for the different
complexes and ligands.

b) A compensation effect between enthalpy and entropy data.

The obtained standard enthalpies and entropies for the complexation of cyclodextrins with these anions in water and N,N'-Dimethylformamide (Tables 7.26 - 7.27) shows that a compensation effect takes place. In fact, plotted $\Delta H^\circ$ versus $\Delta S^\circ$ data, in water, gives a straight line of intercept $-23.52 \pm 0.62 \text{kJ.mol}^{-1}$, a slope (the compensation temperature) of $305 \pm 30 \text{K}$ and a correlation coefficient of 0.99. Also, another straight line was observed between $\Delta H^\circ$ and $\Delta S^\circ$ for the complexation of para-hydroxyphenylazo and chloro-substituted para-hydroxyphenylazo benzoate anions with cyclodextrins in N,N'-Dimethylformamide. A compensation temperature of $307 \pm 46 \text{K}$, an intercept of $-21.22 \pm 0.87 \text{kJ.mol}^{-1}$ and a correlation coefficient of 0.89 were calculated. Figures 7.4 and 7.5 show the different linear correlation obtained between $\Delta H^\circ$ and $\Delta S^\circ$ for the complexation of $\alpha$, $\beta$ and $\gamma$-cyclodextrin with haptens in water and N,N'-Dimethylformamide respectively.

Furthermore, except for $p(p\text{OHPhN}_2)B\alpha$-CD (DMF) and $p(p\text{OHPhN}_2)B\gamma$-CD (H$_2$O), two distinctive patterns are observed in terms of entropy. Unlike water, the complexation process between these anions and cyclodextrins is entropically favourable. For both solvents, this process is enthalpically controlled.
Figure 7.4 Compensation Effect between Entropy and Enthalpy of Complexation of Haptenic Anions and Cyclodextrins in Water

Figure 7.5 Compensation Effect between Entropy and Enthalpy of Complexation of Haptenic Anions and Cyclodextrins in DMF
7.2.3 Effect of Ligand and Anion on the Complexation Process

In the complexation process involving ions and macrocyclic ligands, a significant role must be played by the solvation state of the anion and the ligand. On this basis, a good solvating medium for the anion or indeed the ligand is unlikely to be a good solvating medium for complexation. In order to apply this criterion for the interpretation of the enthalpy and entropy data of complexation of these anions with cyclodextrins, in water and N,N'-Dimethylformamide, their transfer data ($\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$) are considered.

i) effect of ligand on the complexation process

The effect of the ligand on the complexation process is reflected in the two different patterns shown by the thermodynamic parameters of complexation in water and in N,N'-Dimethylformamide:-

a) In water, $\Delta H^\circ$ and $\Delta S^\circ$ values are ligand dependent. Thus for a given anion, the following differences in terms of enthalpies or entropies of complexation are found.

$$\Delta H^\circ, X_{aCD} - \Delta H^\circ, X_{\gamma CD} = -8.6 \text{ kJ.mol}^{-1}$$  
7.16

$$\Delta S^\circ, X_{aCD} - \Delta S^\circ, X_{\gamma CD} = -34.8 \text{ JK}^{-1}.\text{mol}^{-1}$$  
7.17

These results, suggest that independently of the anion, substitution of the ligand (a-CD for y-CD) results in an almost constant variation in the enthalpies and entropies of complexation which may be attributed to the release of solvent (water) from the ligand cavity during the complexation process.

b) In N,N'-Dimethylformamide, no significant differences are observed between the $\Delta H^\circ$ and $\Delta S^\circ$ values for a given anion and the various cyclodextrins. Upon these findings, it can be suggested that the cavity of the ligand is unlikely to provide the site of complexation for these anions in this solvent. Indeed, these results support the
interpretation that the larger stability observed for cyclodextrins in N,N'-
Dimethylformamide with respect to water (ΔH° and ΔS°, Table 5.55) must be
attributed to the inclusion of solvent molecules in the cavity of the ligand. Therefore,
unless the energy requirements to remove the solvent from the cavity are met, the
formation of inclusion complexes (axial) with these anions in this solvent is unlikely
to take place.

ii) effect of the anion upon complexation with cyclodextrins

The stability (in enthalpic terms) of these anions, is greater in water than in
N,N'-Dimethylformamide (ΔH°, values are positive, Table 5.45). These data are
referred to the transfer of the whole anion. To facilitate the discussion, the structure
of the para hydroxyphenylazo benzoate anion is divided in its constituent parts:-

i) the para hydroxyphenylazo group and
ii) the benzoate or substituted benzoate group.

The solvation of these groups in water and in N,N'-Dimethylformamide is
particularly relevant to this discussion. We have demonstrated in chapter 5 that the
pOHPN₂ group in meta and para positions, with respect to the carboxylate group,
behave as a delocalised group. The importance of London dispersion forces between
delocalised solutes and localised solvents have been discussed by Fong and
Greenwald. These forces are expected to be greater in N,N'-Dimethylformamide
than in water. In water, the benzoate group is better solvated than the pOHPN₂
group, whereas the opposite is true for N,N'-Dimethylformamide. Indeed, it is the
introduction of the pOHPN₂ group which makes the pOHPN₂B'Na+ electrolyte
soluble in N,N'-Dimethylformamide. Sodium benzoate is only slightly soluble in this
solvent. Therefore, the solvation of the constituent parts of these anions seem to
play a significant role in the process of complexation. Consequently, it can not be
assumed that the formation of inclusion complexes (axial) involving the pOHPN₂
group in water will necessary occur in N,N'-Dimethylformamide.
7.2.4 Interpretation of the Complexation Process in DMF

In order to interpret the enthalpy and entropy data in N,N'-Dimethylformamide, we visualise the complexation process as the transfer of these anions from N,N'-Dimethylformamide to a rich alcoholic medium (the cyclodextrins molecules constituted of an interior cavity and two open ends; the open ends surrounded on one side by primary hydroxyl groups and on the other by secondary hydroxyl groups) in which these anions are known to interact strongly. In chapter 5, we have shown that among the three solvents considered (H₂O, MeOH and DMF), methanol is the best and N,N'-Dimethylformamide the poorest solvator for these anions. Therefore, it is reasonable to assume that para-hydroxyphenylazo benzoate anions poorly solvated in N,N'-Dimethylformamide (particularly the carboxylate group) are likely to interact with the hydroxyl groups of the cyclodextrins. Comparison between the complexation data (ΔH°c and ΔS°c) for meta and para para-hydroxyphenylazo benzoate anions and cyclodextrins with transfer data (ΔH°t and ΔS°t) for these anions from N,N'-Dimethylformamide to methanol (Table 7.28) support this interpretation. In fact, a remarkable agreement is found between these two sets of data. We consider that it is most unlikely that the chlorine atom (in the chloro-substituted anions) could be an active site of interaction with cyclodextrin. Therefore, for the purpose of this interpretation, 2Cl⁻-4 and 4Cl⁻-3 (pOHPhN₂)B⁻ are related to para and meta (pOHPhN₂)B⁻ anions, respectively. Again this interpretation is supported by the results given in Table 7.26 and Table 7.27. Agreement between complexation and transfer data is not found for ortho (pOHPhN₂)B⁻ anion and cyclodextrins for which heats of complexation are relatively small. This must be attributed to a reduction in the number of active sites in the guest molecule able to interact with the hydroxyl groups of the ligand in N,N'-Dimethylformamide. This effect is even more pronounced for 5Cl⁻-2 and 6Cl⁻-2 (pOHPhN₂) benzoate anions. These two anions are unable to interact with cyclodextrins in N,N'-Dimethylformamide. It can be argued that the proximity between the carboxylate and pOHPhN₂ groups in ortho (pOHPhN₂)B⁻ or chloro-substituted anions inhibits (partially or totally) interaction with the hydroxyl groups of the ligand which (unlike
methanol) are likely to be in relatively fixed positions within the structure of the ligand.

Table 7.28 Thermodynamic Parameters of Transfer of ortho, meta and para parahydroxyphenylazo Benzoate Anions from DMF to Methanol at 298.15 K.

<table>
<thead>
<tr>
<th>Anion</th>
<th>$\Delta G^\circ_i$</th>
<th>$\Delta H^\circ_i$</th>
<th>$\Delta S^\circ_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (pOHPhN$_2$)B$^-$</td>
<td>-21.62</td>
<td>-31.27</td>
<td>-32.0</td>
</tr>
<tr>
<td>meta (pOHPhN$_2$)B$^-$</td>
<td>-20.07</td>
<td>-21.18</td>
<td>-3.7</td>
</tr>
<tr>
<td>para (pOHPhN$_2$)B$^-$</td>
<td>-25.36</td>
<td>-19.30</td>
<td>20.8</td>
</tr>
</tbody>
</table>

* Single-ion values for the transfer of ortho, meta and para (pOHPhN$_2$)B$^-$ anions from DMF to methanol. Data based on Ph$_4$AsPh$_3$B convention.
7.2.5 Conclusions Regarding Complexation Data

It can be concluded that, the thermodynamic data suggest that:-

a) In water, the complexation between cyclodextrins and these anions takes place through the inclusion of the $p$OHPhN$_2$ group in the cavity of the ligand and an axial type complex results. The proposed type of interaction is illustrated in Figures 7.6.

b) In N,N'-Dimethylformamide, the cavity of the ligand is not available for complexation as a result of the strong interaction between the ligand and the solvent. Therefore, complexation of these anions and cyclodextrins takes place at the hydroxyl groups located at the open ends of the ligand cavity and an equatorial or lid type complex results. The proposed interaction type is illustrated in Figure 7.7.

These conclusions were further confirmed by carrying out UV spectrophotometric studies in solutions containing the free and complexed anion in water and in N,N'-Dimethylformamide. A remarkable shift in the wavelength of the anion-α-cyclodextrin solution with respect to that of the free anion was observed in water. This could be attributed to a change in the cromophore as a result of hydrogen bonding between the azo group of the anion and the hydroxyl groups of the cyclodextrin when the phenyl group is enclosed in the ligand cavity. No shift in wavelength was observed in N,N'-Dimethylformamide for the complexed anion with respect to the free anion. Figures 7.8-7.28 show the different spectra for complexed and free anion solutions obtained in water and N,N'-Dimethylformamide.
Figure 7.6 Inclusion Complexation Model of Haptenic Anions and Cyclodextrins in Water

Figure 7.7 Equatorial Complexation Model of Haptenic Anions and Cyclodextrins in DMF
Figure 7.8 — Spectrum of meta \((p\text{OHPhN}_2)\text{NaB}\) with \(\alpha\)-Cyclodextrin in Water

- Spectrum of meta \((p\text{OHPhN}_2)\text{NaB}\) in water

Figure 7.9 — Spectrum of para \((p\text{OHPhN}_2)\text{NaB}\) with \(\alpha\)-Cyclodextrin in Water

- Spectrum of para \((p\text{OHPhN}_2)\text{NaB}\) in Water
Figure 7.10 -- Spectrum of $2Cl-4 (pOHPnN_2)NaB$ with $\alpha$-Cyclodextrin in Water

- Spectrum of $2Cl-4 (pOHPnN_2)NaB$ in water

Figure 7.11 -- Spectrum of meta $(pOHPnN_2)NaB$ with $\gamma$-Cyclodextrin in Water

- Spectrum of meta $(pOHPnN_2)NaB$ in Water
Figure 7.12 -- Spectrum of $para \ (p\text{OHPhN}_2)\text{NaB}$ with $\gamma$-Cyclodextrin in Water
- Spectrum of $para \ (p\text{OHPhN}_2)\text{NaB}$ in Water

Figure 7.13 -- Spectrum of $2Cl-4 \ (p\text{OHPhN}_2)\text{NaB}$ with $\gamma$-Cyclodextrin in Water
- Spectrum of $2Cl-4 \ (p\text{OHPhN}_2)\text{NaB}$ in Water
Figure 7.14 -- Spectrum of $4Cl-3\,(pOHPhN_2)NaB$ with $\gamma$-Cyclodextrin in Water

- Spectrum of $4Cl-3\,(pOHPhN_2)NaB$ in Water

Figure 7.15 -- Spectrum of ortho $\,(pOHPhN_2)NaB$ with $\alpha$-Cyclodextrin in DMF

- Spectrum of ortho $\,(pOHPhN_2)NaB$ in Water
Figure 7.16 -- Spectrum of *meta* (pOHPhN$_2$)$_2$NaB with $\alpha$-Cyclodextrin in DMF  
- Spectrum of *meta* (pOHPhN$_2$)$_2$NaB in DMF

Figure 7.17 -- Spectrum of *para* (pOHPhN$_2$)$_2$NaB with $\alpha$-Cyclodextrin in DMF  
- Spectrum of *para* (pOHPhN$_2$)$_2$NaB in DMF
Figure 7.18 -- Spectrum of $2\text{Cl-4}\ (p\text{OHPhN}_2)\text{NaB}$ with $\alpha$-Cyclodextrin in DMF

- Spectrum of $2\text{Cl-4}\ (p\text{OHPhN}_2)\text{NaB}$ in DMF

Figure 7.19 -- Spectrum of $4\text{Cl-3}\ (p\text{OHPhN}_2)\text{NaB}$ with $\alpha$-Cyclodextrin in DMF

- Spectrum of $4\text{Cl-3}\ (p\text{OHPhN}_2)\text{NaB}$ in DMF
Figure 7.20 — Spectrum of meta \((pOHP\text{PhN}_2)\text{NaB}\) with β-Cyclodextrin in DMF

- Spectrum of meta \((pOHP\text{PhN}_2)\text{NaB}\) in DMF

Figure 7.21 — Spectrum of para \((pOHP\text{PhN}_2)\text{NaB}\) with β-Cyclodextrin in DMF

- Spectrum of para \((pOHP\text{PhN}_2)\text{NaB}\) in DMF
Figure 7.22 -- Spectrum of $2Cl$-$4\ (pOHPhN)NaB$ with $\beta$-Cyclodextrin in DMF

- Spectrum of $2Cl$-$4\ (pOHPhN)NaB$ in DMF

Figure 7.23 -- Spectrum of $4Cl$-$3\ (pOHPhN)NaB$ with $\beta$-Cyclodextrin in DMF

- Spectrum of $4Cl$-$3\ (pOHPhN)NaB$ in DMF

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Figure 7.24 -- Spectrum of ortho \((pOHPn)_2NaB\) with \(\gamma\)-Cyclodextrin in DMF
- Spectrum of ortho \((pOHPn)_2NaB\) in DMF

Figure 7.25 -- Spectrum of meta \((pOHPn)_2NaB\) with \(\gamma\)-Cyclodextrin in DMF
- Spectrum of meta \((pOHPn)_2NaB\) in DMF
Figure 7.26 -- Spectrum of para \((pOHPhN_2)NaB\) with \(\gamma\)-Cyclodextrin in DMF
- Spectrum of para \((pOHPhN_2)NaB\) in DMF

Figure 7.27 -- Spectrum of 2CI-4 \((pOHPhN_2)NaB\) with \(\gamma\)-Cyclodextrin in DMF
- Spectrum of 2CI-4 \((pOHPhN_2)NaB\) in DMF
Figure 7.28 -- Spectrum of 4Cl-3 (pOHPnN)NaB with γ-Cyclodextrin in DMF

- Spectrum of 4Cl-3 (pOHPnN)NaB in DMF
7.3 Thermodynamic Parameters of Transfer of Anion-Cyclodextrin Complexes

Availability of transfer data for guest anion $X^-$, the cyclodextrin ligands (CD) and data for the complexation of anions with $\alpha$ and $\gamma$-cyclodextrin in water and in N,N'-Dimethylformamide permit the calculation of single-ion transfer parameters ($\Delta P^\circ_i = \Delta G^\circ_i$, $\Delta H^\circ_i$, and $\Delta S^\circ_i$) of the anion cyclodextrin complexes ($X^-CD$) from water to N,N'-Dimethylformamide. For this purpose, the thermodynamic cycle is used to obtain transfer data for anion-cyclodextrin complex ions.

$$\Delta P^\circ_i [X^-CD]_{H_2O} \rightarrow_{DMF} = \Delta P^\circ_i [X^-CD]_{DMF} - \Delta P^\circ_i [X^-CD]_{H_2O} \quad 7.18$$

Alternatively, free energies, enthalpies and entropies of transfer of ion-macrocyclic ligand complexes may be obtained indirectly through a thermodynamic cycle as represented by:

$$X^- (H_2O) + CD (H_2O) \xrightarrow{\Delta P^\circ_i} X^-CD (H_2O)$$

$$\Delta P^\circ_i [X^-] \quad \Delta P^\circ_i [CD] \quad \Delta P^\circ_i [X^-CD]$$

$$X^- (DMF) + CD (DMF) \xrightarrow{\Delta P^\circ_i} X^-CD (DMF)$$

The thermodynamic cycle was introduced by Abraham and Namori\(^{271}\). They obtained $\Delta H^\circ_i [M^{2+222}]$ in transfer from water to methanol\(^{271}\) directly as well as via the cycle. Values obtained by the two methods were compared, and good agreement between the two sets of data was found. Schneider and co-workers\(^{343,344,272,274}\) used extensively the thermodynamic cycle to relate differences in stability constants of metal-ion cryptates between two solvents, and free energy of transfer of that cryptate.
The data listed in Table 7.29 are the first reported in the transfer of cyclodextrin complexes from water to any non-aqueous solvent. The data are based on the Ph₃AsPh₃B convention. It must be emphasised that relative transfer data for anions are not dependent on any extrathermodynamic convention.

7.3.1 Transfer Free Energy

Examination of ΔG° values in water and in N,N'-Dimethylformamide (Table 7.29) leads to the suggestion that:

\[ \Delta G^\circ (H_2O) = \Delta G^\circ (DMF) \] 7.19

Therefore, taking into account eqn. 7.19 and the thermodynamic cycle, it emerges that:

\[ \Delta G^\circ_{\text{X-CD}}(\text{H}_2\text{O}) \rightarrow_{\text{DMF}} = -\Delta G^\circ_{\text{X-DMF}} + \Delta G^\circ_{\text{DMF}} + \Delta G^\circ_{\text{H}_2\text{O}} + \Delta G^\circ_{\text{H}_2\text{O}} \rightarrow_{\text{DMF}} \] 7.20

The ΔG° values given in Table 7.29 support this interpretation. An illustrative example is given by inserting in the thermodynamic cycle, transfer free energy data for the meta para-hydroxyphenylazo benzoate anion and α-cyclodextrin (Table 7.28) and complexation data for the same anion and ligand in water and in N,N'-Dimethylformamide (Table 7.29).

\[
\begin{align*}
m(p\text{OHPhN}_2)\text{B}^- (\text{H}_2\text{O}) + \alpha-\text{CD (H}_2\text{O}) & \quad -21.23 \quad m(p\text{OHPhN}_2)\text{B}^-\alpha\text{CD (H}_2\text{O}) \\
8.90 & \quad 1.74 & \quad 12.06 \quad (7.21)
m(p\text{OHPhN}_2)\text{B}^- (\text{DMF}) + \alpha-\text{CD (DMF)} & \quad -19.81 \quad m(p\text{OHPhN}_2)\text{B}^-\alpha\text{CD (DMF)}
\end{align*}
\]

As far as solvation is concerned, ΔG° is the most significant thermodynamic parameter. Therefore, we conclude that no significant change in solvation occurs in both, the ligand and the anions upon complexation in this solvent system.
7.3.2 Transfer Enthalpy and Entropy Data

The $\Delta G^\circ_i$ values result from the contribution of $\Delta H^\circ_i$ and $\Delta S^\circ_i$ values. Therefore, a similar example to that given in terms of $\Delta G^\circ_i$ is now presented in terms of $\Delta H^\circ_i$ (kJ.mol$^{-1}$).

\[
\begin{align*}
\text{m}([p\text{OHPhN}_2]B^- (\text{H}_2\text{O}) &+ \alpha-\text{CD (H}_2\text{O}) \rightarrow & \text{m}([p\text{OHPhN}_2]B^-\alpha\text{CD (H}_2\text{O}) \\
4.28 &-44.34 & -33.35 \\
\text{m}([p\text{OHPhN}_2]B^- (\text{DMF}) + \alpha-\text{CD (DMF)} &\rightarrow & \text{m}([p\text{OHPhN}_2]B^-\alpha\text{CD (DMF)} \\
-21.37 & & -28.08
\end{align*}
\]

and in terms of $\Delta S^\circ_i$ (J.K$^{-1}$.mol$^{-1}$)

\[
\begin{align*}
\text{m}([p\text{OHPhN}_2]B^- (\text{H}_2\text{O}) &+ \alpha-\text{CD (H}_2\text{O}) \rightarrow & \text{m}([p\text{OHPhN}_2]B^-\alpha\text{CD (H}_2\text{O}) \\
-15.5 &-155.9 & -40.6 \\
\text{m}([p\text{OHPhN}_2]B^- (\text{DMF}) + \alpha-\text{CD (DMF)} &\rightarrow & \text{m}([p\text{OHPhN}_2]B^-\alpha\text{CD (DMF)} \\
-5.2 & & -136.0
\end{align*}
\]

Enthalpy and entropy data for the transfer of the anion-cyclodextrin complexes are largely influenced by corresponding data for the transfer of the ligand, $\Delta H^\circ_i$ values being largely compensated by $\Delta S^\circ_i$ values as a result of rearrangements taken place during the transfer process. It is remarkable to find that the same enthalpic and entropic contributions are observed for meta and para $(p\text{OHPhN}_2)B^-\text{CD}$ anions. These data reflect that these two anions are likely to have the same groups exposed to solvation in the axial (water) or equatorial (DMF) complexes.
Table 7.29 Single-ion free energies, enthalpies and entropies of transfer of anion cyclodextrin complexes from water to N,N'-Dimethylformamide at 298.15 K.

<table>
<thead>
<tr>
<th>Complexed Anion (CDX^-)</th>
<th>( \Delta G^\circ ) (X^-)</th>
<th>( \Delta G^\circ ) (CD)</th>
<th>( \Delta G^\circ ),</th>
<th>( \Delta G^\circ ),</th>
<th>( \Delta G^\circ ),</th>
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<td>kJ.mol(^{-1})</td>
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<tr>
<td>H(_2)O \rightarrow DMF</td>
<td>H(_2)O \rightarrow DMF</td>
<td>DMF</td>
<td>H(_2)O \rightarrow DMF</td>
<td>DMF</td>
<td>H(_2)O \rightarrow DMF</td>
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<tr>
<td><strong>meta (pOHPhN(_2))B(\alpha)CD</strong></td>
<td>8.90</td>
<td>1.74</td>
<td>-19.81</td>
<td>-21.23</td>
<td>12.06</td>
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<tr>
<td><strong>para (pOHPhN(_2))B(\alpha)CD</strong></td>
<td>13.23</td>
<td>1.74</td>
<td>-21.52</td>
<td>-20.72</td>
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<td><strong>2Cl(_4) (pOHPhN(_2))B(\alpha)CD</strong></td>
<td>5.61</td>
<td>1.74</td>
<td>-18.95</td>
<td>-23.63</td>
<td>12.03</td>
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<td><strong>meta (pOHPhN(_2))B(\gamma)CD</strong></td>
<td>8.90</td>
<td>1.56</td>
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<td>-22.49</td>
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<td><strong>para (pOHPhN(_2))B(\gamma)CD</strong></td>
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<td>-20.72</td>
<td>-24.55</td>
<td>11.00</td>
</tr>
<tr>
<td><strong>4Cl(_3) (pOHPhN(_2))B(\gamma)CD</strong></td>
<td>17.19</td>
<td>1.56</td>
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<td>-23.75</td>
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<tr>
<th>Complexed Anion (CDX^-)</th>
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<th>( \Delta H^\circ ) (CD)</th>
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<th>( \Delta H^\circ ),</th>
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<td>H(_2)O \rightarrow DMF</td>
<td>DMF</td>
<td>H(_2)O \rightarrow DMF</td>
<td>DMF</td>
<td>H(_2)O \rightarrow DMF</td>
</tr>
<tr>
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<td>4.28</td>
<td>-44.34</td>
<td>-21.37</td>
<td>-33.35</td>
<td>-28.08</td>
</tr>
<tr>
<td><strong>para (pOHPhN(_2))B(\alpha)CD</strong></td>
<td>2.40</td>
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<td><strong>2Cl(_4) (pOHPhN(_2))B(\alpha)CD</strong></td>
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<td>-15.56</td>
<td>-20.44</td>
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<th>( \Delta S^\circ ) (CD)</th>
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<th>( \Delta S^\circ ),</th>
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<td>H(_2)O \rightarrow DMF</td>
<td>DMF</td>
<td>H(_2)O \rightarrow DMF</td>
</tr>
<tr>
<td><strong>meta (pOHPhN(_2))B(\alpha)CD</strong></td>
<td>-15.5</td>
<td>-155.9</td>
<td>-5.2</td>
<td>-40.6</td>
<td>-136.0</td>
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<td>20.8</td>
<td>-28.2</td>
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<td>-205.8</td>
<td>11.5</td>
<td>-37.2</td>
<td>-228.5</td>
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* Data from Table 5.42; † Data from Table 5.56; ‡ Data from Tables 7.26 and 7.27.
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APPENDICES
Appendix A

This appendix contains two computer programs. The first was devised to calculate molar conductance data $\Lambda$ from experimental measurements of specific conductivity $\kappa$. The program requires data on the specific conductivity of the pure solvent at the operating temperature and volume of electrolyte solution one addition. Another advantage of the program is it prepares a data file $(\Lambda, c)$ for the second program, which uses the Shedlovsky equation for strong electrolytes. The second program calculates preliminary values of the association constant $(K_a)$ and the molar conductance at infinite dilution $(\Lambda^0)$. These values of $K_a$ and $\Lambda^0$ are very useful in their recalculation using a modern equation of conductance (e.g. Fuoss-Hsia equation). The programs are written in FORTRAN 77 Language and can be compiled on IBM computers or compatibles.
PROGRAM WORK OUT CONCENTRATION AND MOLAR CONDUCTANCE

REAL L(20), C(20), FULEMP(20,20), SOLINI(20)
REAL VOLUME(20), CU(20), MOLCON(20), ROOTCO(20)
REAL CORMOL(20), LS(20)
REAL STOCKS, SPECON, DENSU, CELCON
CHARACTER*25 NAME1, NAME2, FILE1, FILE2, FILE3, FILE4

WRITE(*,8)
8  FORMAT(1X,'THIS PROGRAM HELPS TO DETERMINE THE CONCENTRATION
&WHICH CORRESPONDS TO EACH READING OF THE SPECIFIC CONDUCTANCE')
WRITE(*,11)
11 FORMAT( 1X,'CONSEQUENTLY CORRECTED MOLAR CONDUCTANCE AND SQUARE
&ROOT OF CONCENTRATION ARE DETERMINED AND READY TO PLOT.' )

WRITE(*,'(" ENTER NAME OF THE SOLUTE ")')
READ(*,'(A)') NAME1
WRITE(*,'(" ENTER NAME OF THE SOLVENT ")')
READ(*,'(A)') NAME2
WRITE(*,'(" ENTER NAME OF THE FILE CONTAINING THE WEIGHT OF
&THE SYRINGE WHEN IT IS LOADED AND THEN EMPTIED")')
READ(*,'(A)') FILE1
WRITE(*,'(" ENTER THE NAME OF THE FILE OF RESULTS")')
READ(*,'(A)') FILE2
WRITE(*,'(" ENTER NAME OF FILE CONTAINING SPECIFIC CON")')
READ(*,'(A)') FILE3
WRITE(*,'(" ENTER NAME OF CONCENTRATION,MOLAR CONDUCTANCE")')
WRITE(*,'(" FILE. THIS FILE WILL BE USEFUL IN CALCULATING")')
WRITE(*,'(" ^0 AND Ka IN ASSOCIAT.FOR PROGRAM. IT SAVES ")')
WRITE(*,'(" YOU TO GIVE DATA FROM KEYBOARD. ")')
READ(*,'(A)') FILE4
OPEN(8,FILE=FILE4)
OPEN(7,FILE=FILE3)
OPEN(5,FILE=FILE1)
OPEN(6,FILE=FILE2)

WRITE(*,'(" ENTER DENSITY OF THE SOLVENT AT THE OPERATING
&TEMPERATURE")')
READ(*,*) DENSU
WRITE(*,'(" ENTER CONCENTRATION OF THE STOCK SOLUTION")')
READ(*,*) STOCKS
WRITE(*,'(" ENTER SPECIFIC CONDUCTANCE OF THE SOLVENT")')
READ(*,*) SPECON
WRITE(*,'(" ENTER THE CELL CONSTANT AT THE OPERATING TEMPERATURE
&RE")')
READ(*,*) CELCON
WRITE(*,'(" ENTER NUMBER OF DATAPAIRS THAT EXIST IN THE FILE")')
READ(*,*) N
WRITE(*,'(" IF DATA ARE READ FROM A FILE TYPE(50) ELSE(51)")')
READ(*,*) IDATA
IF(IDATA.EQ.50) THEN
  DO 7,J=1,N
  READ(5,*)FULEMP(I,J),J=1,2)
CONTINUE
DO 9, I=1,N
READ(7,*) LS(I)
9  CONTINUE
ELSE
WRITE(*,'(" ENTER DATAPAIRS FROM KEYBOARD")')
WRITE(*,'(" ENTER SPECIFIC CONDUCTANCE L(I)")')
DO 50, I=1,N
39 READ(*,*) LS(I)
WRITE(*,'(" HAVE YOU MADE A MISTAKE ")')
WRITE(*,'(" IF YES TYPE 5 ELSE TYPE 6")')
READ(*,*) IMISTK
IF(IMISTK.EQ.6) THEN
GOTO 50
ELSE
GOTO 39
ENDIF
50 CONTINUE
WRITE(*,'(" ENTER LSYRINGE,ESYRINGE DATAPAIRS")')
DO 55, I=1,N
45 READ(*,*) (FULEMP(I,J), J=1,2)
WRITE(*,'(" HAVE YOU MADE A MISTAKE ")')
WRITE(*,'(" IF YES TYPE (1) NO TYPE (2)")')
READ(*,*) IMIST
IF(IMIST.EQ.1) THEN
GOTO 45
ELSE
GOTO 55
ENDIF
55 CONTINUE
ENDIF
DO 60, I=1, N
SOLINJ(I)=FULEMP(1,1)-FULEMP(I,2)
VOLUME(I)=SOLINJ(I)*DENSIT
60 CONTINUE
DO 82, I=1, N
SUM=0.0
DO 83, M=1, I
SUM=SUM+VOLUME(M)
83 CONTINUE
CU(I)=SUM
82 CONTINUE
DO 87, I=1, N
L(I)=LS(I)-SPECON
87 CONTINUE
WRITE(*,'(" WHEN YOU CARRIED OUT THE CONDUCTIVITY MEASUREMENT +STRENGTHEN THE SOLUTION OR DILUTE IT?. IF YOU HAVE +STRENGTHEN TYPE(1), IF YOU DILUTED TYPE(2).")")
READ(*,*) ISTREN
IF(ISTREN.EQ.1) THEN
DO 76, I=1, N
286
C(I)=CU(I)*STOCKS/(100+CU(I))
ROOTCO(I)=C(I)**0.5
MOLCON(I)=1000*L(I)/C(I)
CORMOL(I)=MOLCON(I)*CELCON
76 CONTINUE
ELSE
DO 112,1=1,N
C(I)=STOCKS*100/(100+CU(I))
ROOTCO(I)=C(I)**0.5
MOLCON(I)=1000*L(I)/C(I)
CORMOL(I)=MOLCON(I)*CELCON
112 CONTINUE
ENDIF
WRITE(6,('*'))
WRITE(6,('(FILENAME IS : ',A)') NAME1
WRITE(6,('FILEDATA IS : ',A)') FILE1
WRITE(6,('FILERESULT IS : ',A)') FILE2
WRITE(6,('SOLVENT USED : ',A)') NAME2
WRITE(6,(''))
WRITE(6,85) STOCKS
85 FORMAT(1X,'CONCENTRATION OF THE STOCK SOLUTION',F10.7,2X,'mol/l &')
WRITE(6,(''))
WRITE(6,89) SPECON
89 FORMAT(1X,'SPECIFIC CONDUCTIVITY OF THE SOLVENT',E11.3,3X,'mohs')
WRITE(6,(''))
WRITE(6,('DENSITY OF THE SOLVENT : ',1X,F8.4)) DENSIT
WRITE(6,(''))
WRITE(6,('CELL CONSTANT : ',1X,F7.3)) CELCON
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,93)
93 FORMAT(4X,'1 8X,L,SYRINGE',4X,'ESYRINGE',2X,'SOLINJEC',2X, &'VOLUME',4X,'CUMVOLUME'./ & 3X,'---',8X,'--------',4X,'--------',2X,'--------',2X, &'--------',4X,'--------'/)
DO 101,1=1,N
WRITE(6,100),FULEMP(I,1),FULEMP(I,2),SOLINJ(D,V0LUME(I),CU(I)
100 FORMAT(4X,I2,8X,F7.4,7X,F7.4,2X,F7.4,4X,F7.4,4X,F7.4,2X,F7.4,/)
101 CONTINUE
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,(''))
WRITE(6,93)
105 FORMAT(2X,'--------------------------------------------------------

&-------------------

WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,109)

109 FORMAT(4X,'1 ',4X,'SPECCICO',4X,'CONCENTRATION',2X,'MOLCOND',
&2X,'SQRT(conc)',2X,'CORMOLCOND'
& 4X,'-----',4X,'--------',4X,'-----------',2X,'------',
&2X,'--------',2X,'--------')
DO 116,1=1,N
WRITE(6,117)L(I),C(I),MOLCON(I),ROOTCO(I),CORMOL(I)
117 FORMAT(4X,I2,3X,E11,3,4X,E8,2,2X,F10,3,2X,E9,2,2X,F10,3,/) 
116 CONTINUE
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,'(" ")')
WRITE(6,122)

122 FORMAT(2X,'--------------------------------------------------------

&-------------------')
DO 170,1=1,N
WRITE(8,*) C(I) CORMOL(I)
170 CONTINUE
CLOSE(8)
CLOSE(7)
CLOSE(6)
CLOSE(5)
STOP
END
PROGRAM ASSOCIATION CONSTANT AND LIMITING CONDUCTANCE

REAL ACL(20,20), ZC(20), FZ(20), DOD(20), FS(20)
REAL FST(20), SND(20), FSF(20), FSE(20)
REAL LC0, INTERC, LC1, Ka, LC01, NETA, PKa
CHARACTER*25 FILE1, FILE2, NAME1, NAME2

WRITE(*,'(" THIS PROGRAM HELPS TO DETERMINE THE ASSOCIATION")')
&)
WRITE(*,'(" CONSTANT Ka AND THE LIMITING CONDUCTANCE ^o FOR")')
&)
WRITE(*,'(" MODERATELY STRONG ELECTROLYTES( acids, bases and +ion-pairing of salts")")')
WRITE(*,'(" THEREFORE DATAPAIRS OF MOLAR CONDUCTANCE AND "")')
WRITE(*,'(" CONCENTRATION, OPERATING TEMPERATURE, DIELECTRIC +CONSTANT AND VISCOSITY OF THE SOLVENT AND NUMBER OF DATAPAIRS +ARE REQUIRED.")")
WRITE(*,'(" ")')
WRITE(*,'(" ")')
WRITE(*,'(" ENTER THE NAME OF THE OUTPUT DATA FILE")')
READ(*,'(A)') FILE2
OPEN(6,FILE=FILE2)
WRITE(*,'(" ENTER THE NAME OF THE SOLVENT")')
READ(*,'(A)') NAME1
WRITE(*,'(" ENTER THE NAME OF THE SOLUTE")')
READ(*,'(A)') NAME2
WRITE(*,'(" ENTER THE NUMBER OF DATA THAT EXIST IN THE FILE")')
&)
READ(*,*) N
WRITE(*,'(" ENTER THE OPERATING TEMPERATURE T")')
READ(*,*) T
WRITE(*,'(" ENTER THE DIELECTRIC CONSTANT OF THE SOLVENT")')
READ(*,*) D
WRITE(*,'(" ENTER THE VISCOSITY OF THE SOLVENT NETA")')
READ(*,*) NETA
WRITE(*,'(" IF DATA ARE READ FROM A FILE TYPE(1) ELSE(2)")")
READ(*,*) IDATA
IF(IDATA.EQ.1) THEN
WRITE(*,'(" ENTER THE NAME OF THE INPUT DATA FILE")')
WRITE(*,'(" OF CONCENTRATION AND MOLAR CONDUCTANCE.")')
READ(*,'(A)') FILE1
OPEN(5,FILE=FILE1)
DO 3,I=1,N
READ(5,*)(ACL(I,J),J=1,2)
3 CONTINUE
ELSE
WRITE(*,'(" ENTER CONCENTRATION, MOLAR CONDUCTANCE DATA")')
DO 4, I=1,N
READ(*,*)(ACL(I,J),J=1,2)
4 CONTINUE
WRITE(*,'(" HAVE YOU MADE A MISTAKE ?")')
WRITE(*,'(" IF YES TYPE(1) NO TYPE(2)")')
READ(*,*) IMIST

289
IF(IMIST.EQ.1) THEN
  GOTO 46
ELSE
  GOTO 4
ENDIF

4 CONTINUE
ENDIF
WRITE(*,'(" ENTER AN APPROXIMATE VALUE OF THE LIMITING CONDUCTANCE \alpha")')
READ(*,*) LCO1
ALPHA = 8.18*10**5/(D*T)**1.5
BETA = 82/(NETA*(D*T)**0.5)
B = 1812163.716/(D*T)**1.5
LCO = LCO1
59 SONSAG=ALPHA*LCO+BETA
DO 5,I=1,N
  ZC(I)= ONSAG*((LCO**(-1.5))*((ACL(I,1)*ACL(I,2))**0.5)
  FZ(I)=1+ZC(I)
  DOD(I)=FZ(I)*ACL(I,1)/LCO
  FS(I)=10**(-B*(ACL(I,1)*DOD(I))**0.5)
  FST(I)=ACL(I,1)*(ACL(I,2)*FS(I)*FZ(I))**2
  SND(I)=FS(I)*ACL(I,2)
CONTINUE
CALL SLACLI(N,FST,SND,SL0PE2,INTERC,CORCOE,SYP,SSLO,SINTE)
SL0PE3=SL0PE2
SINTER=INTERC
COF=CORCOE
SYAX=SYP
SSLOPE=SSLO
STINTE=SINTE
LC1=SINTER
IF(ABS(LCO-LC1).LT.1E-2) THEN
  Ka=-1/(SL0PE3*LC1)
  SLC1=INTERC
  SKa=SQRT((1/SSL0PE**2)+(1/SLC1**2))
GOTO 78
ELSE
  LCO=LC1
GOTO 59
ENDIF

78 WRITE(*,'(" PROGRAM TERMINATED ")')
WRITE(*,'(" WISHING YOU GOOD RESULTS ")')
WRITE(6,'(" NAME OF FILE DATA IS :",A)') FILE1
WRITE(6,'(" ")')
WRITE(6,'(" NAME OF FILE RESULT IS :",A)') FILE2
WRITE(6,'(" ")')
WRITE(6,'(" SOLUTE USED IS :",A)') NAME2
WRITE(6,'(" ")')
WRITE(6,'(" SOLVENT USED IS :",A)') NAME1
WRITE(6,'(" ")')

290
WRITE(6,'(" ONSAGER CONSTANT ALPHA =",1X,F7.4")') ALPHA
WRITE(6,'(" ONSAGER CONSTANT BETA =",1X,F7.4")') BETA
WRITE(6,'(" DIELECTRIC CONSTANT D =",1X,F7.4")') D
WRITE(6,'(" OPERATING TEMPERATURE T =",1X,F6.2")') T
WRITE(6,'(" SOLVENT VISCOSITY NETA =",1X,F8.5")') NETA
WRITE(6,'("")')
89  FORMAT(1X,'LIMIT CONDUCTANCE no IS :',F8.4,1X,'mohs')
WRITE(6,91) COF
91  FORMAT(1X,'CORRELATION COEFFICIENT IS :',1X,F7.4,1X)
WRITE(6,93) SLOPE3
93  FORMAT(1X,'SLOPE OF THE NEW PLOT IS :',1X,F12.7,1X)
WRITE(6,'(" ASSOCIATION CONSTANT IS :",1X,E10.4,1X)') Ka
WRITE(6,'(" STANDARD DEVIATION OF Yaxis :",1X,F12.5,1X)') SYAX
WRITE(6,127) SSLOPE
127  FORMAT(1X,'STANDARD DEVIATION OF SLOPE',1X,F12.5,1X)
WRITE(6,129) STINTE
129  FORMAT(1X,'STANDARD DEVIATION OF INTERCEPT',1X,F12.5,1X)
WRITE(6,201) SKa
201  FORMAT(1X,'STANDARD DEVIATION OF Ka-value :',1X,F12.0,1X)
WRITE(6,99) +CTANCE'
99  FORMAT(1X,'I ',4X,'CONCENTRATION',8X,'ZC',8X,'F(ZC)',6X,'MCONDU
+CTANCE'/
+'''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''
DO 130, I=1,N
WRITE(6,229) I, DOD(I), FS(I), FST(I), SND(I)
229 FORMAT(1X,I2,4X,F7.4,8X,F7.4,9X,F10.7,4X,F10.5,/
130 CONTINUE
WRITE(6,(" "))
WRITE(6,(" "))
WRITE(6,(" --------------------------------------------------
+------------------
" Y)
CLOSE(6)
CLOSE(5)
STOP
END
SUBROUTINE SLACLI(K,X,Y,SLOPE,INTERS,COCOEF,SY,SSL,SINT)
DIMENSION X(20), Y(20), V(20), Z(20), W(20)
REAL INTERS
S1=0
S2=0
S3=0
S4=0
S5=0
V1=0
W1=0
DO 150, I=1,K
S1=X(I) + S1
S2=Y(I) + S2
S3=X(I)*Y(I) + S3
S4=X(I)*X(I) + S4
S5=Y(I)*Y(I) + S5
150 CONTINUE
XMEAN=S1/K
SLOPE=(S3-S1*S2/K)/(S4-S1*S1/K)
COCOEF=(K*S3-S1*S2)/SQRT((K*S4-S1*S1)*(K*S5-S2*S2))
INTERS=(S2*SLOPE*S1)/K
DO 160, I=1, K
Z(I)=SLOPE*X(I)+INTERS
V(I)=(Z(I)-Y(I))**2
W(I)=(X(I)-XMEAN)**2
160 CONTINUE
DO 170, I=1, K
V1=V(I)+V1
W1=W(I)+W1
170 CONTINUE
SY=SQRT(V1/(K-2))
SSL=SY/(SQRT(W1))
SINT=SY*SQR(S4/(K*W1))
RETURN
END
Appendix B

Two computer programs for determination of heat of solution (\(\Delta H\)) using the LKB 8700 precision calorimeters are included in this appendix. The programs are based on the Regnault-Pfaudler method and Dickinson method of extrapolation. Both programs are written in FORTRAN 77 Language and can be compiled on IBM computers.
PROGRAM REGNAULT-PFAUDLER METHOD

DIMENSION R(IOO), X(IOO), T(IOO), Z(IOO)
INTEGER A5, P, P1, F2, P3, P4, Q, Q13, Q14
REAL MM, MW, NM, K
CHARACTER F2*25, F3*25, F4*55
OPEN(6,FILE='RESULT')
OPEN(5,FILE='RESIST')
OPEN(7,FILE='TIME')
WRITE(*,7)
7 FORMAT(1X,'ENTER DATE UP TO 10 CHARACTERS')
READ(*,'(A)') F2
WRITE(*,10)
10 FORMAT(1X,'ENTER PROCESS NAME')
READ(*,'(A)') F4
WRITE(*,13)
13 FORMAT(1X,'ENTER THERMISTOR CONSTANT A')
READ(*,*) A
WRITE(*,16)
16 FORMAT(1X,'ENTER THERMISTOR CONSTANT B')
READ(*,*) B
WRITE(*,19)
19 FORMAT(1X,'ENTER AMOUNT OF SOLUTE IN MILLIGRAMS')
READ(*,*) MM
WRITE(*,22)
22 FORMAT(1X,'ENTER MOLECULAR WEIGHT OF SOLUTE USED')
READ(*,*) MW
WRITE(*,25)
25 FORMAT(1X,'ENTER RUN NUMBER')
READ(*,'(A)') F3
WRITE(*,28)
28 FORMAT(1X,'IF YOU RUN A CALIBRATION TYPE(1) ELSE TYPE(2)')
READ(*,*) A5
IF(A5.EQ.1) THEN
WRITE(*,32)
32 FORMAT(1X,'ENTER ENERGY OF CALIBRATION EC')
READ(*,*) EC
ELSE
WRITE(*,36)
36 FORMAT(1X,'ENTER ENERGY OF CALIBRATION EC')
READ(*,*) EC
ELSE WRITE(*,39)
39 FORMAT(1X,'ENTER EQUIVALENCE ENERGY EPSILON')
READ(*,*) EPS
ENDIF
WRITE(*,43)
43 FORMAT(1X,'ENTER DATAPAIRS NUMBER J')
READ(*,*) J
WRITE(*,46)
46 FORMAT(1X,'IF DATA READ FROM A FILE TYPE(50)')
WRITE(*,48)
48 FORMAT(1X,'IF DATA READ FROM KEYBOARD TYPE(51)')

293
READ(*,*) IDATA
IF(IDATA.EQ.50) THEN
READ(5,*)(R(I),I=1,J)
READ(7,*)(X(I),I=1,J)
ELSE
WRITE(*,54)
54 FORMAT(1X,'ENTER RESISTANCE R(Ohm) AND TIME X(Min)')
DO 1,I = 1,J
115 READ(*,*) R(I), X(I)
WRITE(*,58)
58 FORMAT(1X,'NO MISTAKES TYPE(65) ELSE TYPE(66)')
READ(*,*) IMIST
IF(IMIST.EQ.65) THEN
GOTO 1
ELSE
GOTO 115
ENDIF
1 CONTINUE
ENDIF
DO 3,I = 1,J
T(I) = B/(LOG(R(I))-A)
Z(I) = T(I) - T(1)
3 CONTINUE
C = T(1)
WRITE(*,76)
76 FORMAT(1X,'ENTER VALUE OF INITIAL TIME U')
READ(*,*) U
WRITE(*,79)
79 FORMAT(1X,'ENTER VALUE OF FINAL TIME V')
READ(*,*) V
I = 0
20 I = I + 1
IF((X(I)-U).LT.0) THEN
GOTO 20
ELSEIF((X(I)-U).GT.0) THEN
I = I - 1
N = I
N1 = I
Q = I
P = I
P1 = I
ELSE
I = I
N = I
N1 = I
Q = I
P = I
P1 = I
ENDIF
CALL RAFIC(N, Q, P, G3, R3, S1, S2, S3, S4, S5, C, Z, X, T)
G1 = G3
R1 = R3
W1 = S1
W2 = S2
W3 = S3
W4 = S4
W5 = S5
O3 = W1/N + C
I = 0

DO 30 I = I + 1
IF(X(I).LT.V) THEN
    GOTO 30
ELSE
    N = J - I + 1
    N2 = J - I + 1
    Q = 1
    P2 = I
    P = J
ENDIF
CALL RARIC(N, Q, P, G4, R4, S1, S2, S3, S4, S5, C, Z, X, T)
G2 = G4
R2 = R4
Q1 = S1
Q2 = S2
Q3 = S3
Q4 = S4
Q5 = S5
O4 = Q1/N2 + C
K = (G1 - G2)/(O4 - O3)
K = K
N3 = N1
Q13 = 1
P3 = P1
CALL FRANZ(K, N3, Q13, P3, A1, B1, S6, S7, S8, S9, C, Z, X, T)
U1 = A1
U3 = B1 + C
N4 = N2
Q14 = P2
P4 = J
CALL FRANZ(K, N4, Q14, P4, E6, E7, E1, E2, E3, E4, C, Z, X, T)
U2 = E6
U4 = E7 + C
Y = 0.5
C1 = EXP(-(U*K))*U1 + U3
C2 = EXP(-(U+Y)*K))*U1 + U3
C3 = EXP(-(V*K))*U2 + U4
V1 = (C2 - C+C1 -C)/2*Y+(Z(P3+1)+C2-C)/2*(X(P3+1)-(U+Y))
DO 6,1 = P3+2, P4-1
V1 = (Z(I)+Z(I-1))/2*(X(I)-X(I-1)) + V1
6 CONTINUE
V1 = (C3 - C + Z(P4-1))/2*(V-X(P4-1)) + V1
U5 = (G1 + K*(O3 - C -1/(V-U)*V1))*(V-U)
U6 = (G2 + K*(O4 - C -1/(V-U)*V1))*(V-U)
U7 = C3 - C1 - U5
U8 = C3 - C1 - U6
C1 = C1 - 273.15
C3 = C3 - 273.15
EPSIL = EC / U8
IF(A5.EQ.1) THEN
EPS = EPSIL
ELSE
EPS = EPS
ENDIF
NM = MM / MW
WRITE(*,166)
166 FORMAT(1X,'IF CALIBRATION TYPE (167) ELSE TYPE (168)')
READ(*,*) ICALIB
IF(ICALIB.EQ.168) THEN
WRITE(*,170)
170 FORMAT(1X,'IF ENDOXERMIC TYPE(5) ELSE TYPE(6)')
READ(*,*) IENDO
IF(IENDO.EQ.5) THEN
DH = (-1)*((EPS*U8)/(4.184*NM))*1000
DHJ = (DH*4.184)/1000
ELSE
DH = (-1)*((EPS*U8)/(4.184*NM))*1000
DHJ = (DH*4.184)/1000
ENDIF
ELSE
GOTO 183
ENDIF
183 WRITE(6,'("DATE :",A)') F2
WRITE(6,'("PROCESS NAME :",A)') F4
WRITE(6,'("RUN NUMBER :",A)') F3
IF(A5.EQ.1) THEN
WRITE(6,188)
188 FORMAT(18X,'***********************')
WRITE(6,190)
190 FORMAT(18X,'* CALIBRATION *')
WRITE(6,192)
192 FORMAT(18X,'***********************')
ELSE
WRITE(6,195)
195 FORMAT(18X,'***********************')
WRITE(6,197)
197 FORMAT(18X,'* EXPERIMENT *')
WRITE(6,199)
199 FORMAT(18X,'***********************')
ENDIF
WRITE(6,202) A
202 FORMAT("THERMISTOR CONSTANT A :",F12.9)
WRITE(6,204) B
204 FORMAT("THERMISTOR CONSTANT B :",F11.6)
WRITE(6,206) J
206 FORMAT('DATAPAIRS NUMBER J :',I2)
WRITE(6,208) U
208 FORMAT('INITIAL TIME U :',F5.2)
WRITE(6,210) V
210 FORMAT('FINAL TIME V :',F5.2)
WRITE(6,'('THE THERMAL LEAKAGE CONSTANT K :',F12.9')') K
WRITE(6,214) R1
214 FORMAT('CORRECTION TERM OF INITIAL RESISTANCE Ri :',F11.7)
WRITE(6,216) R2
216 FORMAT('CORRECTION TERM OF FINAL RESISTANCE Rf :',F11.7)
WRITE(6,218) O3
218 FORMAT('MEAN TEMPERATURE OF FOREPERIOD Tmi :',F10.6)
WRITE(6,220) O4
220 FORMAT('MEAN TEMPERATURE OF AFTERPERIOD Tmf :',F10.6)
WRITE(6,222) U3
222 FORMAT('INITIAL TEMPERATURE Tool :',F10.6)
WRITE(6,224) U4
224 FORMAT('FINAL TEMPERATURE Toolf :',F10.6)
WRITE(6,226) C1
226 FORMAT('THE CORRECTED INITIAL TEMPERATURE Ti :',F10.6)
WRITE(6,228) C3
228 FORMAT('THE CORRECTED FINAL TEMPERATURE Tf :',F10.6)
WRITE(6,'('INITIAL CORRECTION TERM dTi :',F12.9')') U5
WRITE(6,'('FINAL CORRECTION TERM dTf :',F12.9')') U6
WRITE(6,'('THE CORRECTED TEMPERATURE CHANGE DT :',F9.6')') U8
WRITE(6,'('CALORIMETER EQUIVALENCE ENERGY EPS :',F7.3')') EPS
WRITE(6,'('ENERGY OF CALIBRATION EC :',F8.5,1X,'CAL')') EC
WRITE(6,'('AMOUNT OF SOLUTE :',F10.6,1X,'MILLIGRAMS')') MM
WRITE(6,'('MOLECULAR WEIGHT :',F7.3')') MW
IF(A5.EQ.2) THEN
WRITE(6,'('ENTHALPY CHANGE :',F7.0,1X,'KJ/MOL')') DH
WRITE(6,'('ENTHALPY CHANGE :',F8.3,1X,'KJ/MOL')') DHJ
ELSE
GOTO 241
ENDIF
241 WRITE(*,'('DO YOU WANT TO CHANGE U AND V Y(37) N(38)'')')
READ(*,*) ICOM
IF(ICOM.EQ.37) THEN
GOTO 75
ELSE
GOTO 242
ENDIF
242 WRITE(*,'('IT IS OVER'')')
WRITE(6,251)
251 FORMAT('RESISTANCE',8X,'TEMPERATURE',8X,'TIME')
DO 254,1 = 1, J
WRITE(6,252) R(I), T(I), X(I)
254 CONTINUE
WRITE(*,'(" IT IS DONE",A")')
CLOSE(6)
CLOSE(5)
CLOSE(7)
STOP
END
SUBROUTINE RAFIC(J,K,L,D6,D7,D1,D2,D3,D4,D5,C,Z,X,T)
DIMENSION T(100), X(100), Z(100)
D1 = 0
D2 = 0
D3 = 0
D4 = 0
D5 = 0
DO 21, I = K, L
Z(I) = T(I) - C
21 CONTINUE
DO 7, I = K, L
D1 = Z(I) + D1
D2 = X(I) + D2
D3 = Z(I)*X(I) + D3
D4 = X(I)**2 + D4
D5 = Z(I)**2 + D5
7 CONTINUE
D6 = (D3-D2*D1)/D4
IF((D5-D1**2/J).LE.0) THEN
D7 = 0
ELSE
D7 = D6*SQRT((D4-D2**2/J)/(D5-D1**2/J))
ENDIF
RETURN
END
SUBROUTINE FRANZ(K2,J,K1,L,Y6,Y7,Y1,Y2,Y3,Y4,C,Z,X,T)
DIMENSION T(100), X(100), Z(100)
REAL K2
Y1 = 0
Y2 = 0
Y3 = 0
Y4 = 0
DO 22, I = K1, L
Z(I) = T(I) - C
22 CONTINUE
DO 8, I = K1, L
Y1 = EXP(-(X(I)*K2)) + Y1
Y2 = EXP(-(X(I)*K2)**2) + Y2
Y3 = Z(I)*EXP(-(X(I)*K2)) + Y3
Y4 = Z(I) + Y4
8 CONTINUE
Y6 = (Y3-Y1*Y4/J)/(Y2-Y1**2/J)
Y7 = Y4/J - Y6*Y1/J
RETURN
END

298
PROGRAM DICKINSON METHOD OF EXTRAPOLATION

DIMENSION R(IOO), X(IOO), T(IOO), Z(IOO)
INTEGER P, P1, P2, P5, Q, Q5, A5
REAL K, MM, MW
CHARACTER F2*25, F3*25, F4*55
OPEN(6,FILE='RESULT')
OPEN(5,FILE='RESIST')
OPEN(7,FILE='TIME')
WRITE(*,9)
9 FORMAT(1X,'ENTER DATE UP TO 10 CHARACTERS')
READ(*,'(A)') F2
WRITE(*,12)
12 FORMAT(1X,'ENTER PROCESS NAME')
READ(*,'(A)') F4
WRITE(*,15)
15 FORMAT(1X,'ENTER THERMISTOR CONSTANT A')
READ(*,*) A
WRITE(*,18)
18 FORMAT(1X,'ENTER THERMISTOR CONSTANT B')
READ(*,*) B
WRITE(*,21)
21 FORMAT(1X,'ENTER AMOUNT OF SOLUTE IN MILLIGRAMS')
READ(*,*) MM
WRITE(*,24)
24 FORMAT(1X,'ENTER MOLECULAR WEIGHT OF THE SOLUTE')
READ(*,*) MW
WRITE(*,27)
27 FORMAT(1X,'ENTER RUN NUMBER')
READ(*,'(A)') F3
WRITE(*,30)
30 FORMAT(1X,'IF YOU RUN A CALIBRATION TYPE(1) ELSE TYPE(2)')
READ(*,*) A5
IF(A5.EQ.1) THEN
WRITE(*,34)
34 FORMAT(1X,'ENTER ENERGY OF CALIBRATION')
READ(*,*) EC
ELSE
WRITE(*,38)
38 FORMAT(1X,'ENTER ENERGY OF CALIBRATION')
READ(*,*) EC
ELSE
WRITE(*,41)
41 FORMAT(1X,'ENTER EQUIVALENCE ENERGY EPSILON')
READ(*,*) EPS
ENDIF
WRITE(*,45)
45 FORMAT(1X,'ENTER DATAPAIRS NUMBER J')
READ(*,*) J
WRITE(*,48)
48 FORMAT(1X,'IF DATA READ FROM A FILE TYPE 50')
WRITE(*,50)
50 FORMAT(1X,'IF DATA READ FROM THE KEYBOARD TYPE 51')
READ(*,*) IDATA
IF(IDATA.EQ.50) THEN
  READ(5,*) (R(I), I=1, J)
  READ(7,*) (X(I), I=1, J)
ELSE
  WRITE(*,57)
  57 FORMAT(1X,'ENTER RESISTANCE R(Ohm) AND TIME X(min)'
  DO 68, I = 1, J
  59 READ(*,*) R(I), X(I)
  WRITE(*,61)
  61 FORMAT(1X,'NO MISTAKES TYPE(65) ELSE TYPE(66)'
  IF(IMIST.EQ.65) THEN
    GOTO 68
  ELSE
    GOTO 59
  ENDIF
  68 CONTINUE
ENDIF
DO 73, I = 1, J
  T(I) = B/(LOG(R(I))-A)
  Z(I) = T(I) - T(1)
  73 CONTINUE
WRITE(*,75)
  75 FORMAT(1X,'ENTER INITIAL REACTION TIME U'
  READ(*,*) U
  WRITE(*,78)
  78 FORMAT(1X,'ENTER FINAL REACTION TIME V'
  READ(*,*) V
  I = 0
  81 I = I + 1
  IF(X(I).LT.U) THEN
    GOTO 81
  ELSEIF(X(I).GT.U) THEN
    I = I - 1
  ELSE
    I = I
  ENDIF
  N = I
  N1 = I
  Q = I
  P = I
  P1 = I
  CALL RAFIC(N,Q,P,G3,R3,S1,S2,S3,S4,S5,Z,X,T)
  G1 = G3
  R1 = R3
  W1 = S1
  W2 = S2
  W3 = S3
  W4 = S4
  W5 = S5
  300
T3 = W1/N + T(1)
I = 0

104  I = I + 1
IF(X(I).LT.V) THEN
  GOTO 104
ELSE
  I = I
ENDIF
N5 = J - 1 + 1
N2 = J - 1 + 1
Q5 = I
P2 = I
P5 = J
CALL RAFIC(N5,Q5,P5,G4,R4,S1,S2,S3,S4,S5,Z,X,T)
G2 = G4
R2 = R4
T4 = S1/N2 + T(1)
K = (G1 - G2)/(T4 - T3)
CALL FRANZ(K,N1,Q,P1,A1,B1,S6,S7,S8,S9,Z,X,T)
U1 = A1
U3 = B1 + T(1)
CALL FRANZ(K,N2,P2,P5,E6,E7,E1,E2,E3,E4,Z,X,T)
U2 = E6
U4 = E7 + T(1)
WRITE(*,'(" CALIBRATION TYPE(1),ELSE TYPE(2)")')
READ(*,*) IREACT
IF(IREACT.EQ.2) THEN
  Y = 0.2
  X3 = U + Y
ELSE
  X3 = U
ENDIF
T5 =U1*(EXP(-(K*X3))) + U3
T6 =U2*(EXP(-(K*X3))) + U4
U8 = T6 - T5
WRITE(*,'(" CALIBRATION TYPE(1),ELSE TYPE(2)")')
READ(*,*) ICALIB
IF(ICALIB.EQ.2) THEN
  WRITE(*,141)
ENDIF
141  FORMAT(1X,,'IF ENDOThERMIC TYPE(5),ELSE TYPE(6)')
READ(*,*) IENDEX
IF(IENDEX.EQ.5) THEN
  DH=(-1*EPS*U8*1000*MW)/(4.184*MM)
ELSE
  DH=(-1*EPS*U8*1000*MW)/(4.184*MM)
ENDIF
ELSE
  EPSIL = EC/U8
  EPS = EPSIL
ENDIF
WRITE(6,"("DATE :,",A") F2
WRITE(6,'("PROCES NAME :",A)') F4
WRITE(6,'("RUN NUMBER :",A)') F3
IF(A5.EQ.1) THEN
  WRITE(6,156)
  FORMAT(18X,'***********************')
  WRITE(6,158)
  FORMAT(18X,'* CALIBRATION *')
  WRITE(6,160)
  FORMAT(18X,'***********************')
ELSE
  WRITE(6,163)
  FORMAT(18X,'***********************')
  WRITE(6,165)
  FORMAT(18X,'* EXPERIMENT *')
  WRITE(6,167)
  FORMAT(18X,'***********************')
ENDIF
WRITE(6,170) A
FORMAT('THERMISTOR CONSTANT A :',F12.9)
WRITE(6,172) B
FORMAT('THERMISTOR CONSTANT B :',F11.6)
WRITE(6,174) J
FORMAT('DATAPAIRS NUMBER J :',I2)
WRITE(6,176) U
FORMAT('INITIAL REACTION TIME U :',F5.2)
WRITE(6,178) V
FORMAT('FINAL REACTION TIME V :',F5.2)
WRITE(6,181) K
FORMAT('THE THERMAL LEAKAGE CONSTANT K :',F12.9)
WRITE(6,183) R1
WRITE(6,185) T3
FORMAT('CORRECTION TERM OF INITIAL RESISTANCE Ri :',F11.7)
WRITE(6,187) R2
WRITE(6,189) T4
FORMAT('CORRECTION TERM OF FINAL RESISTANCE Rf :',F11.7)
WRITE(6,191) T5
FORMAT('MEAN TEMPERATURE OF FOREPERIOD Tmi :',F10.6)
WRITE(6,193) T6
FORMAT('MEAN TEMPERATURE OF AFTERPERIOD Tmf :',F10.6)
WRITE(6,195) T7
FORMAT('INITIAL TEMPERATURE Tool :',F10.6)
WRITE(6,197) T8
FORMAT('FINAL TEMPERATURE Toof :',F10.6)
WRITE(6,199) T9
FORMAT('TEMPERATURE CHANGE CORRECTED DT :',F9.5)
WRITE(6,'("energy of calibration energy EPS :",F7.3)') EPS
WRITE(6,'("ENERGY OF CALIBRATION EC :",F8.5,1X,"J")') EC
WRITE(6,196) EC/4.184
WRITE(6,202) DHM.184/1000
WRITE(6,'("AMOUNT OF SOLUTE :",F10.6,1X,"MILLIGRAMS")') MM
WRITE(6,'("MOLECULAR WEIGHT OF SOLUTE :",F7.3)') MW
IF(A5.EQ.2) THEN
WRITE(6,'("ENTHALPY CHANGE DH :",F8.1,1X,"Cal/mol")') DH
WRITE(6,208) DH
WRITE(6,210) DH*4.184/1000

202 FORMAT(’ENTHALPY CHANGE DH :’,1X,F6.2,1X,’Kjoules/mol’)
ELSE
GOTO 206
ENDIF
206 WRITE(*,’(’’ DO YOU WANT TO CHANGE U AND V Y(37) N(38)’’))
READ(*,*) ICHANG
IF(ICHANG.EQ.37) THEN
GOTO 74
ELSE
GOTO 213
ENDIF
213 WRITE(*,’(’’ IT IS OVER’’,A)’’)
WRITE(6,215)
215 FORMAT(6X,’RESISTANCE’,7X,’TEMPERATURE’,7X,’TIME’)
WRITE(6,217)
217 FORMAT(6X,’---’,7X,’-----’,6X,’---’)
DO 221, I = 1, J
WRITE(6,220) R(I), T(I), X(I)
220 FORMAT(7X,F7.2,9X,F10.6,8X,F5.2)
221 CONTINUE
WRITE(*,’(’’ IT IS DONE’’,A)’’)
CLOSE(6)
CLOSE(5)
CLOSE(7)
STOP
END
SUBROUTINE RAHC(J,K,L,D6,D7,D1,D2,D3,D4,D5,Z,X,T)
DIMENSION T(IOO), X(IOO), Z(IOO)
D1 = 0
D2 = 0
D3 = 0
D4 = 0
D5 = 0
DO 241, I = K, L
D1 = Z(I) + D1
D2 = X(I) + D2
D3 = Z(I)*X(I) + D3
D4 = X(I)**2 + D4
D5 = Z(I)**2 + D5
241 CONTINUE
D6 = (D3 - D2*D1/J)/(D4 - D2**2/J)
IF((D5 - D1**2/J).LE.0) THEN
D7 = 0
ELSE
D7 = D6*SQR((D4 - D2**2/J)/(D5 - D1**2/J))
ENDIF
RETURN
END
SUBROUTINE FRANZ(K2,J,K1,L,Y6,Y7,Y1,Y2,Y3,Y4,Z,X,T)
DIMENSION T(IOO), X(IOO), Z(IOO)
D1 = 0
D2 = 0
D3 = 0
D4 = 0
D5 = 0
DO 241, I = K1, L
D1 = Z(I) + D1
D2 = X(I) + D2
D3 = Z(I)*X(I) + D3
D4 = X(I)**2 + D4
D5 = Z(I)**2 + D5
241 CONTINUE
D6 = (D3 - D2*D1/J)/(D4 - D2**2/J)
IF((D5 - D1**2/J).LE.0) THEN
D7 = 0
ELSE
D7 = D6*SQR((D4 - D2**2/J)/(D5 - D1**2/J))
ENDIF
RETURN
END
SUBROUTINE FRANZ(K2,J,K1,L,Y6,Y7,Y1,Y2,Y3,Y4,Z,X,T)
DIMENSION T(IOO), X(IOO), Z(IOO)
REAL K2
Y1 = 0
Y2 = 0
Y3 = 0
Y4 = 0
DO 262,1 = K1, L
  Y1 = EXP(-(X(I)*K2)) + Y1
  Y2 = EXP(-(X(I)*K2))**2 + Y2
  Y3 = Z(I)*EXP(-(X(I)*K2)) + Y3
  Y4 = Z(I) + Y4
262  CONTINUE
  Y6 = (Y3 - Y1*Y4/I)/(Y2 - Y1**2/I)
  Y7 = Y4/I - Y6*Y1/I
RETURN
END
Appendix C

This appendix contains three programs written in Fortran 77 Language. The first is used to calculate the free energy of solution of electrolytes from solubility data. The second is a linear regression analysis used to determine mean value, standard deviation, intercept, slope and the correlation coefficient. The third is a program which determines simultaneously the stability constant and the enthalpy of complexation of a given process from calorimetric titration data.
PROGRAM  CALCULATION OF FREE ENERGY OF SOLUTION
REAL  Ksp, Ka
CHARACTER  SOLV*20, SOLU*50
OPEN(6,FILE='FILERES')
WRITE(*,30)
30  FORMAT(2X,'ENTER SOLVENT NAME')
READ(*,'(A)') SOLV
WRITE(*,32)
32  FORMAT(2X,'ENTER SOLUTE NAME')
READ(*,'(A)') SOLU
WRITE(*,1)
1   FORMAT(2X,'ENTER SOLUBILITY DATA IN Mol/l')
READ(*,*) S
WRITE(*,2)
2   FORMAT(2X,'ENTER OPERATING TEMPERATURE IN KELVIN')
READ(*,*) T
WRITE(*,3)
3   FORMAT(2X,'ENTER DIELECTRIC CONSTANT Dc OF THE SOLVENT')
READ(*,*) Dc
WRITE(*,4)
4   FORMAT(2X,'ENTER THE ION-SIZE PARAMETER A0 IN ANGSTROMS')
READ(*,*) A0
WRITE(*,5)
5   FORMAT(2X,'ENTER ION ASSOCIATION CONSTANT Ka')
READ(*,*) Ka
A = (1.825*(10**6))/((Dc*T)**1.5)
B = 50.29/(Dc*T)**0.5
C11 = 0.1*S
28  F1 = EXP((-2.303*A*(C11**0.5))/(1+A0*B*(C11**0.5)))
C12 = ((SQRT(1 + 4*S*Ka*F1*F1)) - 1)/(2*Ka*F1*F1)
IF(ABS(C12-C11).LE.1E-7) THEN
C11 = C11
Ci = C12
F = F1
ELSE
C11 = C12
GOTO 28
ENDIF
Cip = S - Ci
Ksp = (C1*F)*2
pKs = -LOG10(Ksp)
DG = -1.987*T*LOG(Ksp)
WRITE(6,18)
18  FORMAT('PROCESS :  FREE ENERGY OF SOLUTION FROM SOLUBILITY')
WRITE(6,'("SOLVENT ":",1X,A") SOLV
WRITE(6,'("SOLUTE ":",1X,A") SOLU
WRITE(6,'("OPERATING TEMPERATURE T ":",1X,F7.3,1X,"K")') T
WRITE(6,'("CONSTANT A =":",1X,F12.8")') A
WRITE(6,'("CONSTANT B =":",1X,F12.8")') B
WRITE(6,'("DIELECTRIC CONSTANT Dc ":",1X,F5.2")') Dc
WRITE(6,'("ION-SIZE PARAMETER A0 ":",1X,F5.2,1X,"ANG")') A0
WRITE(6,'("ASSOCIATION CONSTANT Ka :",1X,E15.8)') Ka
WRITE(6,'("MEAN IONIC ACTIVITY F :",1X,F12.8)') F
WRITE(6,'("SOLUBILITY S :",1X,F12.8,1X,"Mol/L")') S
WRITE(6,'("ION CONCENTRATION Ci :",1X,F12.8,1X,"Mol/L")') Ci
WRITE(6,'("CONCENTRATION C1 :",1X,F12.8,1X,"Mol/L")') C1
WRITE(6,10) Ksp
10 FORMAT('SOLUBILITY PRODUCT CONSTANT Ksp :",1X,E15.8)
WRITE(6,'("pKs = ",1X,F5.2)') pKs
WRITE(6,'("FREE ENERGY DG :",1X,F15.8,1X,"Cal/mol")') DG
WRITE(6,11) Cip
11 FORMAT('CONCENTRATION OF ION-PAIR Cip :",1X,F12.8,1X,"Mol/L")
CLOSE(6)
STOP
END
PROGRAM LINEAR REGRESSION ANALYSIS

DIMENSION X(IOO), Y(IOO), Z(IOO), V(IOO), W(IOO)

OPEN(6, FILE='RESULT2')

WRITE(*, '(" THIS PROGRAM HELPS TO DETERMINE THE STANDARD")')
WRITE(*, '(" DEVIATION, THE MEAN VALUE, THE CORRELATION ")')
WRITE(*, '(" COEFFICIENT, THE SLOPE AND THE INTERCEPT IN")')
WRITE(*, '(" CASE OF TWO VARIABLES AS WELL AS ONE.")')
WRITE(*, '(" IF ONE VARIABLE TYPE (1), ELSE TYPE (2.")')
READ(*, *) K
IF(K.EQ.1) THEN
WRITE(*, '(" ENTER N, NUMBER OF XDATA")')
READ(*, *) N
WRITE(*, '(" ENTER XDATA")')
9 DO 3, I = 1, N
READ(*, *) X(I)
WRITE(*, '(" HAVE YOU MADE A MISTAKE? YES(1), NO(1)")')
READ(*, *) IDATA
IF(IDATA.EQ.10) THEN
GOTO 9
ELSE
GOTO 3
ENDIF
3 CONTINUE
51 = 0
52 = 0
DO 4, I = 1, N
51 = X(I) + S1
52 = X(I)**2 + S2
4 CONTINUE
XMEAN = S1/N
XSTND = SQRT((S2-(S1**S1/N))/N)
WRITE(6, '('"XDATA")')
WRITE(6, '('"-----")')
DO 19, I = 1, N
WRITE(6, 18) X(I)
18 FORMAT('" ",F15.8)
19 CONTINUE
WRITE(6, 5) XMEAN
5 FORMAT(1X, 'THE MEAN VALUE OF X IS:', 2X, F15.8, /)
WRITE(6, 6) XSTND
6 FORMAT(1X, 'STANDARD DEVIATION OF X IS:', 2X, F15.8)
ELSE
WRITE(*, '(" ENTER NUMBER OF ELEMENTS PER ARRAY")')
READ(*, *) N
WRITE(*, '(" ENTER XDATA AND YDATA AS (XXX YYY)")')
DO 7, I = 1, N
14 READ(*, *) X(I), Y(I)
WRITE(*, '(" HAVE YOU MADE A MISTAKE? YES(12), NO(13)")')
READ(*, *) IMIST
IF(IMIST.EQ.12) THEN
GOTO 14
ELSE
GOTO 7
ENDIF
7 CONTINUE
SX = 0
SX2 = 0
SY = 0
SY2 = 0
SXY = 0
V1=0
W1=0
DO 15, I=1, N
SX = X(I) + SX
SY = Y(I) + SY
SXY = X(I)*Y(I) + SXY
SX2 = X(I)**2 + SX2
SY2 = Y(I)**2 + SY2
15 CONTINUE
XMEAN = SX/N
YMEAN = SY/N
XSTND = SQRT((SX2-SX*SX/N)/N)
YSTND = SQRT((SY2-SY*SY/N)/N)
SLOPE = (SXY - SX*SY/N)/(SX2 - SX*SX/N)
AINTER = (SY - SLOPE*SX)/N
COCOEF = (N*SXY-SX*SY)/SQRT((N*SX2-SX*SX)*(N*SY2-SY*SY))
Yx = YSTND*SQRT((1 - COCOEF*COCOEF))
DO 160, I=1, N
Z(I)=SLOPE*X(I) + AINTER
V(I)=(Z(I)-Y(I))**2
W(I)=(X(I)-XMEAN)**2
160 CONTINUE
DO 170, I=1, N
V1=V(I)+V1
W1=W(I)+W1
170 CONTINUE
SY=SQRT(V1/(N-2))
SSL=SY/(SQRT(W1))
SINT=SY*SQRT(SX2/(N*W1))
WRITE(6,'(" XDATA YDATA")')
WRITE(6,'(" "")')
DO 16, I=1, N
WRITE(6,17) X(I), Y(I)
16 CONTINUE
WRITE(6,17) "MEAN VALUE OF XDATA IS: ",XMEAN
WRITE(6,17) "MEAN VALUE OF YDATA IS: ",YMEAN
WRITE(6,17) "STANDARD DEVIATION OF X-val IS: ",XSTND
WRITE(6,17) "STANDARD DEVIATION OF Y-val IS: ",YSTND
WRITE(6,17) "SLOPE IS: ",SLOPE
WRITE(6,17) "COR. COEFFICIENT IS: ",COCOEF
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WRITE(6,('"INTERCEPT IS:" ,F15.8,')) AINTER
WRITE(6,('"STANDARD DEVIATION OF Yx:" ,F8.5,')) Yx
WRITE(6,('"STANDARD DEVIATION OF THE INTERCEPT:" ,F9.5,')) SINT
WRITE(6,('""'))
WRITE(6,('"STANDARD DEVIATION OF THE SLOPE:" ,F9.5,')) SSL
WRITE(6,('"STANDARD DEVIATION OF Y:" ,F9.5,')) SY
ENDIF
WRITE(*,('" IT IS DONE"'))
CLOSE(6)
STOP
END
PROGRAM SIMULTANEOUS DETERMINATION OF STABILITY CONSTANT AND ENTHALPY OF COMPLEXATION
CHARACTER*75 F, F1, F2
REAL X(100,40)
REAL M, K1, K2, K3, M0, L0, K
WRITE(*,'(" This program helps to calculate LOG(K) and")')
WRITE(*,'(" enthalpy of complexation.")')
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Data required are debye-huckel constant A,B")')
WRITE(*,'(" ion-size paramters for the free and complexed")')
WRITE(*,'(" cation for D.H equation, s1 and s2")')
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Enter name of the file result.")')
READ(*,'(A)') F
WRITE(*,'(" Enter name of the data file.")')
READ(*,'(A)') F1
WRITE(*,'(" Input the logk, Sigma filename ----> "')
READ(*,'(A)') F2
OPEN(6, FILE=F, STATUS="NEW")
OPEN(7, FILE=F2, STATUS="NEW")
WRITE(*,'(" Enter number of data")')
READ(*,*) N
WRITE(*,'("")')
WRITE(*,'(" Enter Debye-Huckel constants A and B.")')
READ(*,*) A, B
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Enter ion-size parameters before and after")')
WRITE(*,'(" complexation, S1 and S2 in angstrom.")')
READ(*,*) S1, S2
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Enter initial volume of solution in ml.")')
READ(*,*) V
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Enter the minimum value of LOG(k), K1.")')
WRITE(*,'(" Enter the maximum value of LOG(k), K2.")')
READ(*,*) K1, K2
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Enter increment value of LOG(K), K3.")')
READ(*,*) K3
WRITE(*,'("")')
WRITE(*,'("")')
WRITE(*,'(" Enter precision limit which should be the")')
WRITE(*,'(" difference between two successive iteration.")')
READ(*,*) T

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WRITE(*,'(" Enter the metal solution concentration MO."))
WRITE(*,'(" the ligand concentration LO in mol/L."))
WRITE(*,'(" the heat of reaction, Q in calories."))
WRITE(*,'(" and volume injected in each run, Vinj in ml."))
WRITE(*,'(" Data should be organised as a matrix like "))
WRITE(*,'(" MO, LO, Q, Vinj "))
WRITE(*,'(" "))
WRITE(*,'(" Data can be read from keyboard or a data file")')
WRITE(*,'(" If data are read from the keyboard type in 1")')
WRITE(*,'(" If data are read from a file type in 2")')
WRITE(*,'(" ")')
READ(*,*) IDATA
IF(IDATA.EQ.1) THEN
   DO 48 I=1, N
      READ(*,*)(X(I,J),J=1,4)
   48 CONTINUE
ELSE
   OPEN(5,FILE=F1)
   DO 3, I=1, N
      READ(5,*)(X(I,J),J=1,4)
   3 CONTINUE
   CLOSE(5)
ENDIF
WRITE(*,'(" ")')
K=0
K=K+K1
100 DO 52 I=1, N
   G=1
   H=1
   Z=0
   M=Z
   VAR1=(X(I,1)+X(I,2)+G/(H*(10**K)))
   VAR2=(VAR1+VAR2)**2-4*X(I,1)*X(I,2)**.5
   Z=(VAR1-VAR2)/2
   G=10**((-A*X(I,1)**.5)/1+S2*B**Z**.5)
   H=10**((-A*X(I,1,1)**.5)/1+S1*B*(X(I,1,Z)**.5))
   IF(ABS(Z-M).GE.T) THEN
      GOTO 54
   ELSE
      X(I,5)=Z
      X(I,6)=G
      X(I,7)=H
      R=1000/(X(1,3)+X(I,4)*X(I,5))
      X(I,8)=R
   ENDIF
52 CONTINUE
H1=0
DO 56, I=1, N
H9=H1+X(I,8)
H1=H9
56 CONTINUE
H2=H1/N
Y1=0
DO 58, I=1, N
Y2=(H2-X(I,8))**2+Y1
Y1=Y2
SIGMA=(Y1/(N-1))**.5
58 CONTINUE
WRITE(6,80) K, H2, SIGMA
80 FORMAT(1X,'LOG(k)=',F4.2,1X,'Av. Del H=',F7.0,1X,'Sigm=',F12.5)
WRITE(7,81) H2, K
81 FORMAT(5X,F15.5,',',F15.5)
WRITE(6,'(')
WRITE(6,87) X(I,3), X(I,5), X(I,6), X(I,7), X(I,8)
87 FORMAT(lX,'Q=',F12.5,lX,'Z=',F12.7,lX,'G=',F12.7,'H=',F12.7,1X,
+ 'Del H=',F7.0,/) 
85 CONTINUE
WRITE(6,'(')
WRITE(6,'(')
IF (K.GE.K2) THEN
GOTO 104
ELSE
WRITE(6,'(')
WRITE(6,'(')
K=K
K=K+K3
GOTO 100
ENDIF
104 WRITE(*,'(" Calculation stopped")')
WRITE(*,'(" BYE, BYE, BYE,...")')
CLOSE(6)
CLOSE(7)
STOP
END

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