EFFECT OF SUBSTITUENTS ON THE STABILITY OF
SOME LANTHANUM PHENOLATE ION PAIRS

by

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ABSTRACT

The objects of the present work were, firstly, to investigate the effect of substituents on the stability of ion pairs of the \( \text{La}^{3+} \)-ion with some phenolate anions, and, secondly, to test the applicability of the spectrophotometric method in determining the association constants of such ion pairs. The first objective requires a knowledge of the dissociation constants of the phenols and the association constants of the respective lanthanum ion pairs.

Most of the thermodynamic dissociation constants of the weak acids used in the present work have been determined with high accuracy. However, as there was some uncertainty regarding the reliability of the published data for 3- and 5-nitro salicylaldehyde, the thermodynamic dissociation constants of these acids have been redetermined, using a modified form of the spectrophotometric method of Ernst and Menashi.

Experimental evidence for ion association in the lanthanum phenolate solutions was obtained by comparing the absorption curves recorded for two series of solutions, one of which contains the phenol only and the other, both lanthanum and the phenol. For the purpose of determining the association constants of the ion pairs studied in the present work, one new optimization and three new iteration procedures based solely on spectrophotometric measurements, were developed. By these means, the association constants of six lanthanum salicylate, three lanthanum/salicylaldehyde and four lanthanum benzoate ion pairs have been determined.

It has been found that a rough linear correlation exists between the stability of the metal complexes and that of the corresponding proton complexes; the results for the lanthanum salicylates and benzoates falling on one straight line and the results for lanthanum/salicylaldehyde ion pairs
falling on another. The plots of the logarithm of the association constants for these ion pairs, against the reciprocal of the Bjerrum distance of closest approach have been found to give very good straight lines, one for the lanthanum salicylates and benzoates and another for the lanthanum/salicylaldehyde ion pairs.

It has been shown that the lanthanum salicylates involve only the carboxylate group of the anion and that, ion-dipole interaction between the La$^{3+}$-ion and the -OH group is negligible. However, on the other hand, ion-dipole interaction between the La$^{3+}$-ion and the aldehyde group plays some part in the stabilization of the La$^{3+}$/salicylaldehyde ion pairs.
ACKNOWLEDGEMENTS

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The author wishes to express his most sincere and deep appreciation for the invaluable guidance and constant help he has received from Dr. Z.L. Ernst during the course of this work.

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SECTION 1

INTRODUCTION
A base may be defined quite generally as a nucleophilic species. It seems reasonable, therefore, to expect that the bases which have the strongest affinity for hydrogen ions, would also form the most stable complexes with a given metal ion. Since, stability constants are really measures of the standard free energy changes, it is not unreasonable to assume that some correlation should exist between the stability of a metal complex and that of the corresponding proton complex. Some workers [1,2,3] even suggested that a linear relationship should exist between the logarithm of the stability constants of the complexes (log K) which a series of closely related ligands form with a metal ion and the negative logarithm of the acid dissociation constants (pK_a) of these ligands. The general form of this correlation

$$\log K = a pK_a + b, \quad \ldots(1.1)$$

in which a and b are constants, was first used by Bjerrum [3] and by Martell and Calvin [2].

Empirical relationships of this kind have been found to hold by many workers [1 - 12]. For example, Van Uitert, Fernelius and Douglas [7] have shown that the logarithm of the stability constants of co-ordination compounds of Cu^{2+}, Ni^{2+}, and Ba^{2+} with structurally similar diketones was essentially a linear function of pK_a. Irving and Rossotti [9] also obtained good linear correlation plots for divalent metal ions with substituted oxines. These studies were extended by Irving and Da Silva [10] to the complexes formed by a number of divalent metal ions with substituted imido-diacetates. They found that in every case the plot of log K vs pK_a was approximately linear.

For an adequate discussion of such correlation plots, it is clear that data of sufficiently high precision must be used. Unfortunately many
workers do not appreciate the importance of this fact and employ data of low precision and find good correlations where they do not exist and vice-versa. For example, Larsson [11] in 1934 found a linear correlation exists for the complexes which a series of amines form with the silver ion. Brushman and Verhoek [5] also found that for the silver amine complexes, the plot of log $K_{e}$ vs $pK_{e}$ gave two straight lines. One line was obtained for the secondary amines and the other for the primary aliphatic amines and the pyridines. On the other hand, both Britten and Williams [13] and Vosberg and Cogswell [14], who also investigated the silver amines, found no such correlation.

It was Irving and Rossotti [15] who first proposed such linear relationships on the basis of the thermodynamic consideration for complexes of the type ML. Lebermann and Rabin [16] have extended the thermodynamic treatment to complexes of the type ML₂. Jones and co-workers [12] suggested that linear correlations of this type are not generally valid and that even cases in which they appear to be obeyed are fortuitous. However, this view appears to have been disproved by the extensive measurements of Perrin [17] on the complexes of the ferrous and ferric ions with amino acids and by Datta, Lebermann and Rabin [18,19] investigating the amino acid complexes of the cupric ion. These workers were able to show that, indeed, in the above cases a good linear correlation exists between the stability of the metal complex and that of the corresponding proton complex. A linear correlation plot of this type, with a correlation coefficient [20] as high as 0.998, was obtained by Ernst and Menashi [21] for a series of ferric salicylates. Similar results were obtained by Ernst and Herring [22] who investigated the effect of substituents on the stability of the complexes of the ferric ion with fifteen phenols. They found that the
correlation plot was a reasonable straight line with a slope of 0.8. The correlation coefficient [20] of the plot was 0.85. The formation of the ferric phenolates may be represented by equation (1.2).

\[ \text{Fe}^{3+} + \text{HL} \rightleftharpoons \text{FeL}^{2+} + \text{H}^+ \quad \cdots (1.2) \]

where HL is the phenol. By considering the free energy change for this reaction Ernst and Herring found

\[ \log K = \beta K_c - \left[ (\mu_{\text{FeL}^2+}^0 - \mu_{\text{HL}}^0) + (\mu_{\text{H}^+}^0 - \mu_{\text{Fe}^{3+}}^0) \right] / 2.303RT, \cdots (1.3) \]

where \( \mu^0 \) with the appropriate subscript represents the standard chemical potential.

Equation (1.3) predicts that a plot of \( \log K \) vs \( \beta K_c \) should yield a straight line if, for a series of closely related ligands, the term \( (\mu_{\text{FeL}^2+}^0 - \mu_{\text{HL}}^0) \) is either a constant or a linear function of \( \beta K_c \). The slope of this line will be unity in the first case but different from unity in the second. Hence, if the linear relationship holds for a given series of ligands, three cases may be distinguished,

1. Slope = 1; substitution affects the stability of the metal complex to the same extent as that of the corresponding proton complexes.

2. Slope > 1; substitution affects the stability of the metal complexes to a lesser extent than that of the corresponding proton complexes.

3. Slope < 1; substitution affects the stability of the metal complexes to a greater extent than that of the corresponding proton complexes.

Since, in this case, just as in the case of the ferric salicylates, the slope was found to be less than one, these workers concluded that on the average, substitution affects the stability of the ferric phenolate complexes to a smaller extent than that of the corresponding proton complexes.

It has been suggested that, in general, the magnitude of the slope of such correlation plots depends on a number of factors such as the
ionization potential of the metal ion [8], nuclear repulsion between the metal ion and donor atoms [24], polarisation of the ligands by the metal ion [12], tendency of the metal to form π-bonds [12] and ligand field stabilizations [25]. In most cases the slopes are different from unity, but are closer to unity for aliphatic than for aromatic ligands [12,25].

Jones, Poole, Tompkinson and Williams [12] attempted to explain the deviations from unit slope solely in terms of π-bonding effects. They concluded that with ligands whose π-orbitals can interact with suitable orbitals of the metal ion, slopes greater than unity should result if the central ion has π-acceptor properties and smaller than unity if it has π-donor properties. They also suggested that divalent ions such as Cu^{2+} and Ni^{2+} [26] acts as π-electron donors while the Fe^{3+}-ion [26,27] has the properties of a π-electron acceptor. Accordingly, for a series of closely related ligands, the slopes of the correlation plots should be smaller than unity in the former cases and greater than unity in the latter. These predictions have been found to hold good in some cases but to fail in others. Thus, Calvin and Wilson [4] showed that the slope of the correlation plots for both the cupric acetyl-acetonates and the cupric salicylaldehydes is less than unity. However, for the Ni^{2+} oxinates [9,29] and for the Ni^{2+} and Cu^{2+} imidodiacetates [1,12,26], the slope of the correlation plots is greater than unity. Also, as mentioned above, the slope of the correlation plot for both the ferric salicylates and ferric phenolates is less than one. Thus, if Williams' ideas are valid, it appears that, in some instances the Fe^{3+}-ion acts as a π-electron donor.

Since, it is difficult to assess directly the effect of π-bonding on the magnitude of the slope of such correlation plots, it appeared desirable to extend these studies to complexes in which π-bonding is
absent. For this reason, it was decided to investigate the complexes of a metal ion which is unlikely to enter into \( \pi \)-bonding with a ligand such as the phenolate anion. Accordingly, the La\(^{3+} \)-ion has been selected for it has the xenon inert gas configuration. In addition, it does not undergo hydrolysis in acid medium nor absorb light in the ultra-violet and visible regions [30]; the spectral regions within which both the undissociated and singly ionized forms of the ligands used in the present work absorb light [31,32,33,34]. Both these factors serve to simplify the interpretation of the experimental data. However, the fact that lanthanum salts precipitate at a pH of 8.25 limits the pH range within which experiments with this ion can be carried out.

Although lanthanum was first separated from the 'complex earth ceria' by Mossander [35] as early as 1838, little interest was shown for the next 80 years or so in the lanthanum chemistry apart from the development of more efficient methods of isolating lanthanum. Since, the compounds are usually the most insoluble of all the rare earth compounds, fractional recrystallisation showed itself to be very useful in obtaining pure lanthanum salts. In this way, many lanthanum compounds have been prepared including lanthanum oxalate [36,37], acetyl acetonate [38], and \( m \)-nitrobenzene sulphonate [39]. However, the separation is so difficult that until comparatively recently lanthanum chemistry has been considered a 'fruitless time-consuming venture of little theoretical significance and no practical importance' [40]. With the advent of modern separation techniques very pure lanthanum compounds have become readily available and since then, the interest in lanthanum chemistry has greatly increased. Most efficient among these separation techniques is solvent extraction and in particular the ion exchange method. The use of solvent extraction
for the separation of the rare earths was pioneered by Selwood and Appleton [41] and by Templeton and Peterson [42,43], who studied the distribution of La and Nd compounds between an aqueous and an alcoholic phase. However, the most effective tool for the resolution of the rare earths is ion exchange, a method largely pioneered by Spedding and co-workers [44,45,46]. This technique involves the selective elutriation of a mixture of rare earths absorbed on a cation-exchange resin by the use of complexing agents. Apart from being of great practical importance, these ion exchange researches have shown that of all the lanthanides, lanthanum appears to have the least tendency to form complexes [48,49,50,51].

The earliest work on the complexes of the La$^{3+}$-ion with organic ligands appears to be that of Schwarzenbach and co-workers. Using the method of pH titrations, they determined the stability constants of the complexes of the La$^{3+}$-ion with the nitrilotriacetate (N.T.A.) [52] and with the hydroxy ethyliminodiacetate (H.I.M.D.A.) [53] complexones, and found them to be of the order of $10^{10}$.

Peacock and James [54] in 1952 studied the complexes of the La$^{3+}$-ion with a number of organic ligands such as malonate, succinate, and fumarate by means of potentiometric measurements. They concluded that the La$^{3+}$-ion combines with these ligands through ion association. The association constants of these ion pairs range from $10^3$ (for lanthanum malonate) to $10^5$ (for lanthanum fumarate).

Particularly interesting, on account of their exceptional stability, are the complexes of the La$^{3+}$-ion with the amino poly-carboxylic acids, which have been the subject of extensive studies. A very good example of complexes of this type is that formed by the lanthanum ion with 1,2-diamino cyclohexane N N N N tetraacetic acid (DCTA), whose stability
constant, according to Schwarzenbach et alia [55], is $1.8 \times 10^{-16}$. Even more stable are the complexes of the $\text{La}^{3+}$-ion with di-ethylene triamino pentaacetic acid (DTPA) [56] and triethylene tetraamino hexa-N-acetic acid (TTHA) [57] whose stability constants have been found to be $9.1 \times 10^{19}$ and $1.2 \times 10^{23}$, respectively.

In 1961, Cefola et alia [58] undertook a potentiometric study of the complexes of the $\text{La}^{3+}$-ion with a number of chelating agents such as aminoacetic, malic, and salicylic acids. Of particular relevance to the present work is the lanthanum salicylate ion pair, which these authors apparently formulated as a chelate and whose stability constant they found to be $4.37 \times 10^{2}$.

The effect of substitution on the stability of the complexes of the $\text{La}^{3+}$-ion with a series of salicylaldehydes was first investigated by Postmus et alia [59]. In determining the stability constants of these complexes, the authors applied a method based upon spectrophotometric and pH measurements. Using the results of their measurements, they plotted the logarithm of the stability constants of the lanthanum complexes against the negative logarithm of the dissociation constants of the corresponding salicylaldehydes and obtained a reasonably good straight line.

Considerable amount of work has also been done on the complexes of the $\text{La}^{3+}$-ion with inorganic ligands. The earliest study of a complex of this type appears to be that of C.W. Davies [60] who estimated the association constant of the $\text{LaSO}_4^{4+}$ ion pair using conductometric measurements.

In 1948, Davies and James [61] determined, also conductimetrically, the association constant for the lanthanum ferricyanide ion pair over a wide range of concentrations and at three different temperatures. They found that their results were in accord with the predictions of the
Bjerrum theory [62], corresponding to distance of closest approach of about 7 Å and concluded that in the lanthanum ferricyanide ion pair, at least one water molecule is attached to the La$^{3+}$-ion. Virtually the same results were obtained by James and Monk [63] and by Monk [64] for the lanthanum cobalticyanide ion pair.

Mattern [65] carried out a spectrophotometric investigation of the complexes of the La$^{3+}$-ion with the carbonate, peroxide, thiosulphate, chloride, chlorate, and nitrate anions at 25°C in 1M NaClO$_4$ solution. He found that, under these experimental conditions, very weak ion pairs are formed, their association constants being less than 1.

Monk [66] measured conductimetrically the association constants for the complexes of the La$^{3+}$-ion with tri- and tetra-metaphosphates, and obtained the values $5.0 \times 10^5$ and $4.6 \times 10^6$ respectively. On the basis of the Bjerrum theory, he concluded that in these complexes the La$^{3+}$-ion is only slightly hydrated.

Panckhurst and Woolmington [67] made a spectrophotometric study of the lanthanum ferrocyanide ion pair and found it to be considerably more stable than that of the lanthanum ferricyanide ion pair.

Since, the lanthanum ion is unlikely to enter into covalent bond formation, it is reasonable to assume that all the lanthanum complexes, even the most stable ones, are formed through ion association. An intimation as to the validity of this view may be obtained by evaluating the Bjerrum distance of closest approach 'a' for the most stable complexes of the La$^{3+}$-ion, i.e. those with DCTA, DTPA, and TTHA complexones.

Let $K$ represent the association constant of a lanthanum ion pair then, according to the Bjerrum theory (loc. cit.), in dilute solutions
\[ 1/K = (1-\omega)/\omega = (4\pi N/1000)(z_{La}^{3+}z_L^3/\epsilon^2/ekT)^3Q(b), \quad \text{...(1.4)} \]
in which \( K \) is the association constant of the ion pair, \( \omega \) the degree of association of the electrolyte, \( \omega \) the concentration of the electrolyte, \( N \) the Avogadro number, \( z_{La}^{3+} \) the charge on the \( La^{3+} \)-ion, \( z_L \) the charge on the ligand, \( \epsilon \) the dielectric constant of the solvent, (in the present case, water, \( \epsilon = 78.3 \)), \( k \) the Boltzmann constant and \( e \) the electronic charge. The quantity \( Q(b) \) is defined by

\[ Q(b) = \int_{2}^{b} \exp \left( \frac{y - 4}{\epsilon^2/e^2/ekT} \right) dy, \quad \text{...(1.5)} \]

where

\[ y = \left( z_{La}^{3+}z_L^3/\epsilon^2/ekT \right), \quad \text{...(1.6)} \]

and

\[ b = \left( z_{La}^{3+}z_L^3/\epsilon^2/ekT \right), \quad \text{...(1.7)} \]
r being the distance measured from the central ion. Putting \( z_{La}^{3+} = 3 \) and solving for \( Q(b) \) we have

\[ Q(b) = K/ 74.42 z_L^3. \quad \text{...(1.8)} \]

Values of the integral \( Q(b) \) in terms of the quantity \( b \) have been calculated and are given in standard text books [68]. The value of \( b \) so obtained may then be used to find \( \omega \) for the ion pair by means of equation (1.7).

The results of these calculations for the three complexes are summarised in the table (1.1). It can be seen from the table that, for each of these complexes the calculations yield for \( \omega \) a value of about 0.2, which in view of the large size of the ligand molecule appears to be much too small. It must be remembered, however, that in the Bjerrum theory, the distance of closest approach is defined as the distance between the centres of two ions of opposite sign in contact, the ions being regarded
TABLE 1.1.

<table>
<thead>
<tr>
<th>LIGAND</th>
<th>K</th>
<th>$z_L$</th>
<th>$\log Q(b)$</th>
<th>b</th>
<th>a</th>
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<tbody>
<tr>
<td>DCTA</td>
<td>$1.8 \times 10^{16}$</td>
<td>-4</td>
<td>12.3</td>
<td>43.5</td>
<td>1.97 Å</td>
</tr>
<tr>
<td>DTPA</td>
<td>$9.1 \times 10^{19}$</td>
<td>-5</td>
<td>16.04</td>
<td>55.0</td>
<td>1.95 Å</td>
</tr>
<tr>
<td>TTHA</td>
<td>$1.2 \times 10^{23}$</td>
<td>-6</td>
<td>18.79</td>
<td>59.5</td>
<td>2.16 Å</td>
</tr>
</tbody>
</table>

as rigid spheres. Such a picture of an ion is certainly not a correct description of these three ligands in that they contain a number of charged and highly flexible groups. Ligands of this type have the properties of chelating agents and should be able to form with the $La^{3+}$-ion highly stable complexes, through ion association alone. It is most likely that in the course of such chelation, the $La^{3+}$-ion and the ligand molecule suffers considerable dehydration which may greatly contribute to the stability of these ion pairs. Such a dehydration effect has already been suggested by Monk in the case of the tri- and tetra-metaphosphates (loc. cit.). Further support for this conclusion may be found in the work of Betts and Dahlinger [69] who showed that the formation of the complex of the $La^{3+}$-ion with EDTA results in a large increase in entropy. Such an entropy increase can be best accounted for by assuming that in the course of the chelate formation, the ligand displaces the water molecules from the hydration sphere of the $La^{3+}$-ion.

Since, the present work is primarily concerned with the ion pairs of the $La^{3+}$-ion with some phenols, a brief account of the Bjerrum theory of ion association is perhaps desirable at this point.

An important part in the Bjerrum theory plays the quantity 'q' called the 'critical distance of separation' and defined by
\[ q = \left| z_+ z_- \right| e^2/2kT \]  \hfill (1.9)

It is equal to the distance of separation of the two ions at which the mutual potential energy of the two ions is equal to \( 2kT \) and represents the position of minimum probability of finding an ion of opposite charge on a sphere of radius \( q \) surrounding the central ion. Although the existence of ion pairs, predicted by Bjerrum, has been experimentally well established, the Bjerrum theory cannot be regarded as generally valid, at least not without suitable modifications. One defect of the Bjerrum theory is undoubtedly the inadequacy of the model of rigid spherical ions which must fail in certain cases, as for example the case of the amino polycarboxylate anions. Another objection to the Bjerrum theory is the use of the bulk value for the solvent dielectric constant, which is unjustifiable in the region close to the ion. However, in spite of its limitations, the Bjerrum theory is still very useful in the discussion of ion association.

There are several methods available for the determination of the association constants of ion pairs, of which the most widely used are conductivity, solubility, potentiometry, spectroscopy and the study of reaction rates.

The conductivity method is particularly useful in dealing with ion association in a symmetrical electrolyte, in which the ion pair will be uncharged and thus will not contribute to the total conductance of the solution. With unsymmetrical electrolytes the position is more complicated, since the ion pair is now a new, charged entity, contributing to the measured conductivity. Under suitable conditions the conductivity method is capable of providing very accurate values for the association constants of ion pairs as evidenced by the work of Davis and James (loc. cit.) with lanthanum ferricyanide.
The measurement of the solubility of a sparingly soluble salt in the presence of another electrolyte was first used by Davies [70] for the determination of ion pair formation. It was found in order for the activity coefficients to be the same in any solution of the same ionic strength, independently of the nature of the added salt, incomplete dissociation of the electrolyte had to be taken into account. Many solubility data are difficult to interpret since considerable variation often occurs in the composition of the aqueous phase and, hence, in the stoichiometric solubility product. Calcium and thallous iodates have conveniently low solubilities and have been widely studied [71,72,73] for ion pairing.

Numerous potentiometric methods have been applied to the problem of ion pair formation, the commonest being the measurement of pH, usually involving the glass electrode. Bjerrum and Schwarzenbach [113,52] were largely responsible for the early development of this method. Several workers [74,75] have extended this method to the study of incomplete dissociation in salts of weak acids and bases. The results obtained by this method are often inaccurate due to the uncertainties associated with the liquid junction potential.

The changes in the optical absorption of a solution on the addition of other ions are analysed in order to derive the extinction coefficient of an assumed new species (the ion pair) and thence, to evaluate its association constant. The optical density $D$, (in a cell of unit length), for such a system is given by

$$D = \epsilon_{\text{M}^{(n+)}_{\text{X}^{(n-m)+}}} + \epsilon_{\text{M}^{(n+)}_{\text{X}^{(n-m)+}}} + \epsilon_{\text{M}^{(n+)}_{\text{X}^{(n-m)+}}} \ldots (1.10)$$

where $\text{M}^{(n+)}$ is the metal cation, $\text{X}^{(n-m)+}$ the ligand and $\text{M}^{(n+)}_{\text{X}^{(n-m)+}}$ the ion pair, and where $\epsilon$ and square brackets denotes the extinction coefficient and
the concentration of the species, respectively. The situation is even more complicated in cases in which the ligand is formed by the dissociation of a protic acid for then, both the undissociated and the anionic form of the acid may absorb. The analysis of the absorption spectra for such a system is not simple. In fact, according to Rossotti and Rossotti [76], there appears to be no general method, reported in the literature, for the evaluation of the association constants for ion pairs from spectrophotometric data alone, when three species contribute significantly to the total absorbance. The difficulty of dealing with a system involving three or more absorbing species can be greatly simplified if a suitable wavelength can be found at which either the metal ion or one or more form of the ligand does not absorb, thereby reducing the number of unknowns [77]. Unfortunately, such a wavelength cannot always be found. Another way of overcoming the problem is to combine spectrophotometric techniques with pH measurements - the method recently employed by Postmus and co-workers (loc. cit.) in their study of ion association between the $\text{La}^{3+}$-ion and some substituted salicylaldehydes. The disadvantage of this method lies in the fact that it produces an additional source of error associated with pH measurements.

The measurement of reaction rates provides a useful method for estimating the degree of dissociation of salts in solution. When an ion of a strong electrolyte takes part in a reaction with a neutral molecule, the reaction velocity is usually more closely proportional to the concentration of the ion than to its activity [78]. Thus, when the ion is present as a salt which is incompletely dissociated, the reaction velocity may be used as a measure of its true concentration. The method, of course, can only be used in cases in which the rate of reaction is sufficiently slow that it may be conveniently measured. When this is
possible, the association constants found by this method are in general agreement with those derived by other techniques.

Of the methods described above, the spectrophotometric procedure appears to be the most promising and that, for the following reasons -

1. Modern spectrophotometers are capable of measuring optical density with high precision; moreover, optical density measurements made at very low concentration are relatively as accurate as those made at higher concentration [79].

2. It dispenses with pH measurements.

3. In many cases a wavelength can be found at which one or more species do not absorb.

Since no general method for the determination of association constants of ion pairs by purely spectrophotometric measurements has been reported in the literature (loc. cit.), it is clear that a new approach to this problem is necessary. In this connexion it appeared desirable to explore, in the present work, the applicability of the spectrophotometric method to the quantitative study of ion association as widely as possible.
SECTION II

EXPERIMENTAL
PART 1

MATERIALS

Unless otherwise stated, standard analytical procedures were carried out as described by Vogel [80]. All glassware used was either of Grade 'A' standard or of carefully calibrated Grade 'B' standard. All reagents were of 'AnalaR' grade - with the exception of the benzoic acids, phenols, sodium perchlorate, and lanthanum oxide.

Purification of the Benzoic Acids and Phenols.

The benzoic acids and phenols - with the exception of salicylaldehyde itself which is a liquid at room temperature - were purified by decolourising with activated charcoal (where necessary), and repeated recrystallisation from conductivity water with subsequent drying in vacuo over P_2O_5. Special care was taken to remove all traces of the 5-nitro-isomer from 3-nitro salicylaldehyde. This involved dissolving the impure sample of 3-nitro salicylaldehyde in NaOH solution, from which the 5-nitro isomer crystallised out on standing [81]. The purity of each benzoic acid or phenol was tested by melting point determination and by comparing the absorption curves for solutions of the ligand with those reported in the literature. The following table (2.1) gives the origin of the sample, the colour, and the observed and literature values of the melting points of the benzoic acids and phenols, used in the course of the present work.

Purification of Salicylaldehyde.

Salicylaldehyde (Eastman Chemicals) was purified by the copper acetate method [86]. The purified material was a very pale yellow liquid which after 3-4 days turned cherry pink, even though it was stored in stoppered bottles in the dark. No colour change, however, was observed
<table>
<thead>
<tr>
<th>Compound</th>
<th>Origin of Sample</th>
<th>Colour and Nature of Compound</th>
<th>Melting Point Value °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic Acid</td>
<td>B.D.H.</td>
<td>White needles</td>
<td>159.5</td>
<td>[82]</td>
</tr>
<tr>
<td>3-Methyl-Salicylic Acid</td>
<td>B.D.H.</td>
<td>White needles</td>
<td>161.75</td>
<td>[82]</td>
</tr>
<tr>
<td>5-Chloro-Salicylic Acid</td>
<td>Eastman Chemicals</td>
<td>White needles</td>
<td>172.25</td>
<td>[82]</td>
</tr>
<tr>
<td>5-Bromo-Salicylic Acid</td>
<td>Eastman Chemicals</td>
<td>White needles</td>
<td>168.5</td>
<td>[82]</td>
</tr>
<tr>
<td>5-Nitro-Salicylic Acid</td>
<td>Eastman Chemicals</td>
<td>White needles</td>
<td>231.75</td>
<td>[82]</td>
</tr>
<tr>
<td>3-Nitro-Salicylic Acid</td>
<td>B.D.H.</td>
<td>Bright yellow needles</td>
<td>145.0</td>
<td>[82]</td>
</tr>
<tr>
<td>3-Nitro-Salicylaldehyde</td>
<td>Eastman Chemicals</td>
<td>Tan needles</td>
<td>109.25</td>
<td>[83]</td>
</tr>
<tr>
<td>5-Nitro-Salicylaldehyde</td>
<td>Eastman Chemicals</td>
<td>Bright yellow needles</td>
<td>126.0</td>
<td>[85]</td>
</tr>
<tr>
<td>4-Hydroxy-Benzaldehyde</td>
<td>B.D.H.</td>
<td>White needles</td>
<td>116.25</td>
<td>[83]</td>
</tr>
<tr>
<td>4-Nitro-Benzoic Acid</td>
<td>Obtained by hydrolysis of 'AnalaR' 4-nitro Benzoyl Chloride</td>
<td>Pale yellow needles</td>
<td>241.5</td>
<td>[83]</td>
</tr>
<tr>
<td>3-Bromo-Benzoic Acid</td>
<td>Eastman Chemicals</td>
<td>White needles</td>
<td>155.5</td>
<td>[83]</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>B.D.H.</td>
<td>White plates</td>
<td>121.8</td>
<td>[83]</td>
</tr>
<tr>
<td>4-Hydroxy-Benzoic Acid</td>
<td>Hopkin and Williams</td>
<td>White needles</td>
<td>215.25</td>
<td>[84]</td>
</tr>
</tbody>
</table>
when the purified material was kept under nitrogen. The purity of the material was tested by measuring the refractive index and the absorption curves for solutions of the ligand. Good agreement between observed and literature values was found [87,88,89,90].

**Sodium Perchlorate**

Sodium perchlorate was purified by repeated recrystallisation from conductivity water, and the resultant crystals were dried at 130°C and allowed to cool in a desiccator over phosphorus pentoxide.

**Perchloric Acid**

Standard perchloric acid solutions were prepared from a 70-72% perchloric acid solution and standardised against both borax and sodium carbonate. The borax used for this purpose was purified by recrystallisation from conductivity water, as described by Manov, Dehollis and Acree [91].

**Sodium Hydroxide**

Standard solutions of sodium hydroxide were prepared by transferring a filtered 50% sodium hydroxide into a nickel-bottle [92] (fitted with a soda-lime guard tube) containing a requisite amount of carbon dioxide-free conductivity water. The resulting solution was standardised with potassium hydrogen phthalate and standard perchloric acid.

**Lanthanum Perchlorate**

A stock solution of lanthanum perchlorate was made up by dissolving 99.5% lanthanum oxide (Johnson and Matthey) in a dilute perchloric acid solution [93]. The resulting solution was analysed for lanthanum by titration with E.D.T.A. in the presence of xylenol orange as the indicator [94]. The E.D.T.A. used for this purpose was purified by recrystallisation from conductivity water in the manner described by Blaedel and Knight [95]. The E.D.T.A. solution was standardised [96] against spectroscopically pure zinc (Johnson and Matthey). The concentration of free perchloric acid
in the lanthanum perchlorate stock solution was found by passing an aliquot of the solution through a cation-exchange resin (Zeocarb 225) in the hydrogen form and titrating the eluant with a standard CO$_2$-free sodium hydroxide solution using methyl red as the indicator.
PART II

SPECTROPHOTOMETRIC MEASUREMENTS.

The Instrument.

All spectrophotometric measurements were made by means of a Unicam S.P. 500 spectrophotometer. The instrument consists of a deuterium lamp, for the range 200 - 320 μm, and a tungsten lamp, for the 320 - 1000 μm region, a monochromator with a 30° quartz prism, and interchangeable blue and red photocells. The photocell output current is measured by balancing the drop across a load resistance of 2000 megohms with a slide wire potentiometer calibrated in both percentage transmission and optical density. The sensitivity control varies the electrical sensitivity by approximately 10 to 1, allowing the user to set the slit width and operate at predetermined band widths. A switch is also provided which increases the scale sensitivity by a factor of 10, permitting greater accuracy of reading when the optical density is above unity. The instrument is equipped with a thermostated cell holder, in which the cells are kept at 25 ± 0.1°C.

The wavelength scale of the instrument was calibrated initially by means of the hydrogen lines at 6563° and 4861°. It was then checked every time optical density measurements were made using a holmium glass filter which absorbs very strongly at 3609°. The optical density scale was calibrated using an aqueous solution of potassium chromate [97] in 0.05 M KOH, which was found to be a suitable standard. Measurements were made occasionally at a number of wavelengths to check the optical density calibration.

Optical Density Measurements

Before any optical measurements were made the spectrophotometer
was always switched on for at least one hour to allow the machine to become electronically stable. In all spectrophotometric measurements matched silica cells were used; these were of 1, 2 or 4 cm. path length, depending on the nature of the experiment. One cell always contained the solvent, and the other the solution whose optical density was to be measured. The cells were placed in exactly the same position every time measurements were made. The cells were calibrated, every time optical density measurements were made, with solvent in both cells. The measured optical densities were then corrected for these small cell differences. In measurements where sodium hydroxide was employed, the cell containing the solution was washed with water, followed by alcohol, acetone and ether. The dry cell was quickly filled with the solution containing sodium hydroxide and stoppered.

In the measurement of optical density for calculation purposes, duplicate solutions were used in all cases. The concentrations of the absorbing species were adjusted, in such a way so as to give optical density readings in the preferred range 0.2 - 0.8. For measurements made at a fixed wavelength, the specified wavelength was always approached from one direction. This was done to prevent 'backlash'. The slit width was then set and all measurements at that wavelength were made using the same slit width.

Prior to any optical density measurements the experimental solutions were kept in a thermostat at 25°C for at least one hour. After the solutions had attained thermal equilibrium, they were transferred to optical cells and the latter placed in the thermostated cell holder; there they were allowed to stand until the temperature of the solutions in the optical cells reached 25°C. This usually took only a few minutes. The temperature
of the solutions in the optical cells was measured by means of a thermistor bridge. The optical density was then recorded as an average of at least three successive readings, which agreed to within $\pm 0.2\%$. 
PART III

PROCEDURE USED TO OBTAIN EXPERIMENTAL EVIDENCE FOR ION PAIR FORMATION.

In the present work experimental evidence for ion association was obtained by applying the following procedure: Two series of solutions, (referred to as series A and series B), were obtained by mixing fixed amounts of a standard La(ClO$_4$)$_3$ solution and a standard solution of the ligand, with varying amounts of either a standard HClO$_4$ or a standard NaOH solution. In some cases, the requisite amount of HClO$_4$ was very small; so that to minimize the experimental error sodium hydroxide was also added.

To each mixture, a calculated amount of a standard NaClO$_4$ solution and a requisite amount of water were added, so that, in each series, the stoichiometric concentration $T_M$ of La(ClO$_4$)$_3$, the stoichiometric concentration $T_L$ of the ligand, and the ionic strength $I$ of the final solutions were maintained constant. Throughout the present work the concentration of lanthanum was kept at $T_M = 1 \times 10^{-2}$ mole/l., and the ionic strength at $I = 0.1$. It should be pointed out, however, that in order to observe the lower pH convergence limit in a few cases, e.g. the lanthanum salicylates, it was found necessary to use solutions whose ionic strength was slightly greater than 0.1. In order to keep the optical density within the optimum region of 0.2 - 0.8, the concentration of the ligand was varied from case to case in the range $2.5 \times 10^{-4} - 1 \times 10^{-5}$ mole/l. The stoichiometric concentration of La(ClO$_4$)$_3$ was thus always 40 - 1000 times greater; this large excess of La$^{3+}$-ions being used to minimize the formation of ion pairs containing more than one ligand per metal ion.

The solutions of series B were prepared in exactly the same way except that the La(ClO$_4$)$_3$ was replaced by NaClO$_4$ - the amount of which
was adjusted so as to keep the ionic strength of the solutions constant at $I = 0.1$. Thus, to each solution of series A, there corresponds a solution of series B at exactly the same stoichiometric concentration of HClO$_4$ (and/or NaOH). The hydrogen ion concentration of the solutions, in both series A and B, was varied in a pH range which depended on the nature of the ligand.

To obtain evidence for the occurrence of ion association between the La$^{3+}$-ion and a given ligand, the absorption curves of the two series of solutions were recorded as a function of pH. The absorption curves of all the solutions of series A were then compared with those of the corresponding solutions of series B. In all cases studied in the present work significant differences between the two types of absorption curves were observed, the magnitude of which depended on the pH of the solutions and the wavelength, (see for example figure 4.1). These differences were interpreted as evidence for ion association.
SECTION III

SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANTS OF 3- AND 5-
NITRO-SALICYLALDEHYDES.
The determination of the association constants for the ion pairs to be studied in the present work requires a knowledge of the dissociation constant of the respective organic acids. The thermodynamic dissociation constants of most of these acids have already been determined with high precision by other workers,[31,98,99,100,101,102,103]. The values obtained are listed in table (3.1). There was, however, some doubt as to the reliability of the values of the dissociation constants for the 3- and 5-nitro-salicylaldehydes. These have been determined by Postmus, Magnusson and Craig [59] using a procedure involving both spectrophotometric and pH measurements. Since, this method involves two sources of error, it was decided to redetermine these quantities spectrophotometrically. For this purpose, a modified form of the procedure reported by Ernst and co-workers [98,105] was used. The theoretical basis of this method is explained below.

Spectrophotometric methods of measuring acid dissociation constants have been extensively used in recent years [97,103,104]. As already mentioned, the main advantages of this method lie in the fact that optical density measurements made at very low concentration are relatively as accurate as those made at higher concentrations, and that even for very small dissociation constants, quite reliable results can be obtained under favourable conditions. Thus, for example, Ernst and Menashi [31] have shown that dissociation constants as small as $10^{-15}$ can be measured spectrophotometrically with sufficiently high precision ($\pm 2\%$).
**TABLE 3.1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dissociation Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic acid</td>
<td>$1.064 \times 10^{-3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>3-Methyl Salicylic acid</td>
<td>$1.135 \times 10^{-3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>5-Chloro Salicylic acid</td>
<td>$2.23 \times 10^{-3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>5-Bromo Salicylic acid</td>
<td>$2.20 \times 10^{-3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>5-Nitro Salicylic acid</td>
<td>$7.57 \times 10^{-3}$</td>
<td>[99]</td>
</tr>
<tr>
<td>3-Nitro Salicylic acid</td>
<td>$13.4 \times 10^{-3}$</td>
<td>[99]</td>
</tr>
<tr>
<td>Salicylaldehyde</td>
<td>$4.23 \times 10^{-9}$</td>
<td>[100]</td>
</tr>
<tr>
<td>4-Hydroxy Benzaldehyde</td>
<td>$2.43 \times 10^{-8}$</td>
<td>[100]</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$6.295 \times 10^{-5}$</td>
<td>[101]</td>
</tr>
<tr>
<td>4-Nitro Benzoic acid</td>
<td>$3.61 \times 10^{-4}$</td>
<td>[102]</td>
</tr>
<tr>
<td>3-Bromo Benzoic acid</td>
<td>$1.553 \times 10^{-4}$</td>
<td>[102]</td>
</tr>
<tr>
<td>4-Hydroxy Benzoic acid</td>
<td>$2.692 \times 10^{-5}$</td>
<td>[32]</td>
</tr>
<tr>
<td>3-Nitro Salicylaldehyde</td>
<td>$5.870 \times 10^{-6}$</td>
<td>present work</td>
</tr>
<tr>
<td>5-Nitro Salicylaldehyde</td>
<td>$4.676 \times 10^{-6}$</td>
<td>present work</td>
</tr>
</tbody>
</table>

**THEORETICAL**

The thermodynamic dissociation constant of a weak acid of the type $HL$ is defined by

$$K_1 = h \left[ L^- \right] f_1^2 / \left[ HL \right], \quad \ldots (3.1)$$

where $f_1$ is the activity coefficient of the singly charged species, $h = \left[ H^+ \right]$, and all the other symbols have the usual significance.

The optical density of a solution of a weak monobasic acid of
concentration \( T_L \), obeying the Lambert Beer law, can be shown to be given by

\[
D = \left( D_0 \frac{hf^2_1}{K_1} + D_1 \right) / (K_1 + hf^2_1). \tag{3.2}
\]

In the above equation the quantities \( D_0 \) and \( D_1 \) are defined by

\[
D_0 = e_{HL} T_L, \tag{3.3}
\]

\[
D_1 = e_{L^-} T_L, \tag{3.4}
\]

in which \( e_{HL} \) and \( e_{L^-} \) are the molar extinction coefficients of the undissociated and dissociated forms of the acid, respectively, and \( L \) the optical path length.

Equation (3.2) may be rearranged to yield

\[
K_1 / (K_1 + hf^2_1) = (D - D_0) / (D_1 - D_0). \tag{3.5}
\]

The concentration of the anion \( L^- \), corresponding to any given value of \( h \) is

\[
[L^-] = \frac{K_1 T_L}{(K_1 + hf^2_1)}. \tag{3.6}
\]

By combining equations (3.5) and (3.6) we find

\[
[L^-] = \frac{(D - D_0) T_L}{(D_1 - D_0)}. \tag{3.7}
\]

Let \( a \) and \( b \) represent the stoichiometric concentration of \( HClO_4 \) and \( NaOH \), respectively, then the electroneutrality condition takes here the form

\[
h = (a - b) + [L^-], \tag{3.8}
\]

or, in view of equation (3.7)

\[
h = (a - b) + (D - D_0) T_L / (D_1 - D_0). \tag{3.9}
\]

By combining the last equation (3.9) with equation (3.2) and rearranging we find

\[
(a-b) + (D-D_0) T_L / (D_1-D_0) = K_1 (D_1-D)/ f^2_1 (D - D_0). \tag{3.10}
\]

Thus a plot of \( y_1 = (a-b) + (D-D_0) T_L / (D_1-D_0) \) against \( (D_1-D) / f^2_1 (D - D_0) \) should yield a straight line passing through the origin, with a slope equal to \( K_1 \).
Accordingly, the determination of $K_1$ requires the measurement of the optical densities of solutions of the nitro-salicylaldehydes, under conditions of varying pH.

RESULTS AND DISCUSSION

SELECTION OF WAVELENGTH

To find the most suitable wavelength, the absorption curves for solutions of the two salicylaldehydes were recorded at various pH values. The results are presented in figures (3.1) and (3.2), from which it can be seen that the spectra consist of two distinct bands, and that the absorption curves intersect at a well defined isosbestic points. In both cases, the band corresponding to the presence of the undissociated species occurs at shorter wavelengths than that of the ionized species. It can be seen that in both cases the effect of changing the pH is most pronounced at the wavelength corresponding to the absorption band of the anion. Accordingly, optical density measurements were carried out at these wavelengths, that is, at $\lambda = 425$ mμ for 3-nitro salicylaldehyde and at $\lambda = 405$ mμ for 5-nitro salicylaldehyde.

MEASUREMENT OF $D_0$ AND $D$

The procedure based upon equation (3.10) requires a knowledge of $D_0$ and $D_1$ at the selected wavelength. The quantity $D_0$ was found by measuring the optical density of solutions of the two salicylaldehydes which were 0.001, 0.005, 0.01, 0.05, and 0.10 M in perchloric acid. The results of these measurements, which were carried out at the selected wavelength show that as the concentration of HClO$_4$ was increased, at first a decrease in the optical density of the solutions took place but over the range 0.01 - 0.10 M HClO$_4$, no further variation in $D$ was observed.
FIGURE 3.1  ABSORPTION CURVES OF 3-NITRO SALICYLALDEHYDE IN AQUEOUS SOLUTION.

\[ T_L = 4.653 \times 10^5 \text{ mole/l.} \]
\[ l = 2 \text{ cm.} \]
1. 0.10M HClO₄
2. \( h^0 = 1.444 \times 10^4 \text{ mole/l.} \)
3. \( h^0 = 3.289 \times 10^5 \text{ mole/l.} \)
4. 0.10M NaOH.
FIGURE 3.2  ABSORPTION CURVES OF 5-NITRO SALICYLALDEHYDE IN AQUEOUS SOLUTION.

\[ T_L = 1.074 \times 10^4 \text{ mole/l.} \]
\[ l = 1 \text{ cm.} \]

1. 0.10 M HClO₄
2. \( h^0 = 5.101 \times 10^{-5} \text{ mole/l.} \)
3. \( h^0 = 1.424 \times 10^{-5} \text{ mole/l.} \)
4. \( h^0 = 3.621 \times 10^{-6} \text{ mole/l.} \)
5. 0.010 M NaOH.
Accordingly, the optical density of the solutions which were 0.1 M in HClO₄ were adopted for D₀.

For the purpose of determining the quantity D₁, solutions of the salicylaldehyde were prepared which were 0.01, 0.05, and 0.10 M in NaOH. The optical density of all these solutions over this concentration range of NaOH was found to have the same value, which was therefore identified as D₁. The values of D₀ and D₁ for 3-nitro salicylaldehyde are given in table (3.2) and for 5-nitro salicylaldehyde in table (3.3).

**MEASUREMENT OF THE DISSOCIATION CONSTANTS OF 3- AND 5-NITRO SALICYLALDEHYDES.**

For the determination of the dissociation constants of 3- and 5-nitro salicylaldehydes, varying amounts of either a standard HClO₄ or a standard NaOH solution were added to a fixed amount of a standard solution of the salicylaldehyde. To each mixture, a calculated amount of a standard NaClO₄ and a requisite amount of water were added, so that the stoichiometric concentration Tₐ of the acid, and the ionic strength I of the final solutions were maintained constant. In order for the pH variation of optical density to be as large as possible, solutions of the salicylaldehydes were used whose pH values were of the same order of magnitude as the corresponding value of pK₁. Thus, for both salicylaldehydes the pH of the solutions ranged from about 4.5 - 5.5. In general, the effect of CO₂ on solutions of pH~5 is negligible. Nevertheless, to minimize this effect, boiled-out water was used throughout and all experimental work was carried out in an atmosphere of nitrogen.

The ionic strength of the experimental solutions is given by

\[ I = \frac{1}{2} \{ [Na^+] + [H^+] + [OH^-] + [L^-] + [ClO_4^-] \}, \quad \ldots (3.11) \]

which, in view of the electroneutrality condition,
\[ [\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{L}^-] + [\text{ClO}_4^-], \quad \ldots(3.12) \]

becomes
\[ I = [\text{Na}^+] + [\text{H}^+], \quad \ldots(3.13) \]

where \([\text{Na}^+] = d = \text{concentration of NaClO}_4 \text{ added. Since, under the experimental conditions employed } [\text{H}^+] \text{ is negligibly small compared with} \]
\[ [\text{Na}^+] \approx 0.1, \text{ then} \]
\[ I = [\text{Na}^+]. \quad \ldots(3.14) \]

The activity coefficient \(f_1\) and all other activity coefficients used in the present work, were obtained from the Davies equation [reference [77] page 41] in the form
\[ -\log_{10} f_a = 0.5z^2 \left[ \frac{I^2}{1 + I^2} \right] - 0.3k, \quad \ldots(3.15) \]

with a possible error not exceeding \(\pm 2\%\).

In accordance with equation (3.10), the requisite values of the dissociation constants were found by plotting
\[ y_1 = (a - b) + (D - D_0) \frac{T_L}{(D_1 - D_0)} \text{ against } (D_1 - D) / f_1^2 (D - D_0). \]

For both acids very good straight lines were obtained, which are shown in figures (3.3) and (3.4). The slopes of these plots were evaluated by applying the method of least squares.

The precision of the experimental data was estimated by calculating the standard deviation \(\sigma_y\) of \(y_1 = (a - b) + (D - D_0) \frac{T_L}{(D_1 - D_0)}\). This is defined by
\[ \sigma_y = \frac{\sum (Ay)^2}{(n - 1)^{\frac{3}{2}}} \], \quad \ldots(3.16) \]

where \(Ay = y_{\text{calc.}} - y_{\text{obs.}}\) and \(n\) is the number of observations. The standard deviation of the slope \(K_1\) is given by
\[ \sigma_{K_1} = \sigma_y \left( \frac{n}{\sum x_i^2} \right)^{\frac{3}{4}}, \quad \ldots(3.17) \]

in which \(x = (D_1 - D_0) / f_1^2 (D - D_0)\).
The experimental data and the results of these calculations are given in tables (3.2) and (3.3). In view of the small standard deviation (less than ±2%), found in the present work for the two dissociation constants, we may conclude that the procedure discussed here is reliable. It should be noted however, that the values of $K_1$ found in the present work are about 10% higher than those reported by Postmus, Magnusson and Craig [59].
TABLE 3.2 DETERMINATION OF $K_1$ FOR 3-NITRO SALICYLALDEHYDE

$T_L = 4.653 \times 10^{-5}$ mole/l.; $I = 0.1$; $\lambda = 425$ m$\mu$; $l = 4$ cm; $D_0 = 0.019$; $D_1 = 1.552$.

<table>
<thead>
<tr>
<th>$a \times 10^4$ mole/l.</th>
<th>$b \times 10^4$ mole/l.</th>
<th>$d \times 10^2$ mole/l.</th>
<th>$D$</th>
<th>$y_1 \times 10^5$</th>
<th>$x'$</th>
<th>$\Delta y_1 \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.364</td>
<td>1.287</td>
<td>9.999</td>
<td>0.701</td>
<td>1.150</td>
<td>1.249</td>
<td>+0.040</td>
</tr>
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<td>0.532</td>
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<td>-0.058</td>
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</table>

$K_1 = 5.870 \times 10^{-6}$; $\sigma_{K_1} = \pm 0.040 \times 10^{-6}$. 
FIGURE 3.3 DISSOCIATION CONSTANT OF 3-NITRO SALICYLALDEHYDE.
TABLE 3.3 DETERMINATION OF $K_1$ FOR 5-NITRO SALICYLALDEHYDE

$T_L = 1.060 \times 10^{-4}$ mole/l.; $I = 0.1$; $\lambda = 360 \text{m} \mu$; $l = 2 \text{cm}$; $D_0 = 0.239$; $D_1 = 3.165$.

<table>
<thead>
<tr>
<th>$a \times 10^b$</th>
<th>$b \times 10^b$</th>
<th>$c \times 10^d$</th>
<th>$D$</th>
<th>$y_1 \times 10^5$</th>
<th>$x^1$</th>
<th>$\Delta y_1 \times 10^5$</th>
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<td>0.960</td>
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<td>0.384</td>
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<td>0.354</td>
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<td>9.928</td>
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<td>0.332</td>
<td>21.659</td>
<td>46.45</td>
<td>+0.061</td>
</tr>
</tbody>
</table>

$K_1 = 4.676 \times 10^{-6}$; $\sigma_{K_1} = \pm 0.083 \times 10^{-6}$. 
FIGURE 3.4. DISSOCIATION CONSTANT OF 5-NITRO SALICYLALDEHYDE.
SECTION IV

THE SPECTROPHOTOMETRIC DETERMINATION OF THE ASSOCIATION CONSTANTS OF THE ION PAIRS OF THE LANTHANUM ION WITH SOME SUBSTITUTED SALICYLIC ACIDS AND SALICYLALDEHYDES.
Since, the stability constant of the lanthanum salicylate complex has been already determined potentiometrically by Cefola et alia [58], the lanthanum - salicylic acid system appeared to be the most suitable starting point for the present work.

THE LANTHANUM - SALICYLIC ACID SYSTEM

EVIDENCE FOR ION PAIRING

In order to obtain evidence for ion pairing in the present system, the procedure described in the Experimental Section was used. Accordingly, two series of solutions, A and B, were prepared, in which the stoichiometric concentration of salicylic acid $T_L$ and the stoichiometric concentration of lanthanum perchlorate $T_M$ was $2.5 \times 10^{-4}$ mole/l., and $1 \times 10^{-2}$ mole/l., respectively, and the ionic strength, $I = 0.1$. The pH of the solutions of both series ranged from $\sim 1.5$ to $\sim 5$, corresponding to a degree of dissociation of about $5\%$ to about $99\%$ of the acid. The absorption curves of these solutions were then recorded over the wavelength region $250 - 350\mu m$, as a function of pH.

It was found that over this spectral region, in which neither $\text{La(ClO}_4\text{)}_3$, $\text{NaClO}_4$, nor $\text{HClO}_4$ absorb light, the effect of the lanthanum ions on the absorption curves of salicylic acid was small. The largest effect was observed at $h^0$ (the hydrogen-ion concentration of the solutions of series B) $\approx 1 \times 10^{-3}$ mole/l. This is shown in figure (4.1) which represents the absorption curves for the solutions of series A and B, at this hydrogen-ion concentration.

Inspection of figure (4.1) shows that the largest differences in the optical density of the two solutions occurs at $\lambda = 326\mu m$. This wavelength, therefore, was adopted for the study of ion association in the
FIGURE 4.1
VARIATION OF D° AND D WITH WAVELENGTH - SALICYLIC ACID -

$T_L = 2.51 \times 10^{-4}$ mole/l,
$T_M = 1 \times 10^{-2}$ mole/l,
l = 1 cm.
lanthanum salicylate solutions. Another reason for adopting this particular wavelength is that, here, the pH variation of optical density was found to be the greatest. It is perhaps worth mentioning, in this connexion, that this was also the wavelength chosen by Ernst and Menashi [31] for their spectrophotometric evaluation of the first dissociation constant of salicylic acid.

To obtain a qualitative measure of the extent of ion pairing in the present system, the difference (ΔD) between the optical densities of corresponding solutions of series A (D) and series B (D°), at λ = 326 m, were plotted against h°. The variation of ΔD with h° is presented in figure (4.2) and table (4.1). It will be seen that, at this wavelength and over the pH range employed, D is always smaller than D°, and that the difference, ΔD = D° - D, increases at first with increasing h°, reaches a maximum at h° ~ 1 x 10^{-3} mole/l., and then decreases.

Since, in the pH region corresponding to this maximum, the ΔD values are significantly larger than the random experimental error involved in optical density measurement, the conclusion must be reached that some complex formation takes place in the lanthanum salicylate solutions.

On the right hand-side of the maximum, the quantities D and D° approach each other as h° decreases until at h° ~ 1 x 10^{-5} mole/l., when more than 99% of the salicylic acid has dissociated, they become virtually equal, at a value of about 0.230. On the right hand-side of the maximum, D and D° converge as h° increases and approach the value 0.690. It will be seen later that these two limiting values coincide with the values obtained in the present work, at I = 0.1, for the quantities

\[ D_1 = \varepsilon_1 T_L \text{I}, \]  \hspace{1cm} \text{ ...(4.1)}

and \[ D_0 = \varepsilon_0 T_L \text{I}, \]  \hspace{1cm} \text{ ...(4.2)}
<table>
<thead>
<tr>
<th>$h^\circ \times 10^3$</th>
<th>0.010</th>
<th>0.123</th>
<th>0.228</th>
<th>0.642</th>
<th>1.300</th>
<th>2.596</th>
<th>3.593</th>
<th>6.062</th>
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<th>800</th>
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<td>2.80</td>
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<td>2.21</td>
<td>1.52</td>
<td>1.21</td>
<td>0.31</td>
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<tr>
<td>$D^\circ$</td>
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<td>0.426</td>
<td>0.507</td>
<td>0.542</td>
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<td>0.683</td>
<td>0.696</td>
<td>0.720</td>
</tr>
<tr>
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<td>0.332</td>
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<td>$\Delta D$</td>
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<td>0.005</td>
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<td>0.019</td>
<td>0.027</td>
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<td>0.021</td>
<td>0.013</td>
<td>0.004</td>
<td>0.002</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$D_L = 0.228; \quad \Delta D_L = 0.000.$
FIGURE 4.2 VARIATION OF ΔD WITH pH FOR LANTHANUM SALICYLATE.

\[ L = 2.509 \times 10^{-4} \text{ mole/ L.} \]
\[ T_L = 1.002 \times 10^{-2} \text{ mole/ L.} \]
\[ \lambda = 326 \text{ m L.} \]
\[ L = 4 \text{ cm.} \]
\[ I = 0.1 \text{.} \]
respectively, in which \( \varepsilon_0 \) is the extinction coefficient of the undissociated salicylic acid molecules, \( \varepsilon_1 \) the extinction coefficient of the \( \text{HL}^- \) ion, and \( l \) the length of the optical path.

This type of behaviour can be best explained by assuming that, in the lanthanum salicylate solutions, ion pairing takes place between the \( \text{La}^{3+} \) ion and the singly ionized form of salicylic acid \( \text{HL}^- \) and that the extinction coefficient of the ion pair formed is not appreciably different from that of the \( \text{HL}^- \) ion. As will be seen later, this fact can be used in obtaining an approximate value for the association constant of the ion pair. At pH values, at which most of the salicylic acid (in the absence of lanthanum) would be in the undissociated form, little ion pairing occurs and hence the optical densities of both the solutions of series A and B will be approximately equal to \( \varepsilon_0 \), and \( \Delta \varepsilon \) will be very small. As \( h^0 \) decreases, the degree of dissociation of the salicylic acid increases, and consequently, the extent of ion pairing also increases; as a result, the concentration of both the undissociated salicylic acid molecules \( \text{H}_2\text{L} \) and the \( \text{HL}^- \) ion in the solutions of series A will be less than in the corresponding solutions which do not contain lanthanum (series B). Since, the extinction coefficient of the complex \( \varepsilon_c \) is approximately equal to that of the \( \text{HL}^- \) ion \( \varepsilon_1 \), the optical density of the A series of solutions will be less than that of the series B solutions, by an amount roughly proportional to the decrease in the concentration in \( \text{H}_2\text{L} \) brought about by ion pairing. Finally, at pH values at which most of the salicylic acid is in the singly ionized form, the contribution of \( \text{H}_2\text{L} \) to the total optical density will be small and both \( D^0 \) and \( D \) will be approximately equal to \( D_1 \).

The conclusion can thus be drawn that under the experimental conditions employed, ion association occurs between the \( \text{La}^{3+} \) and \( \text{HL}^- \) ion,
leading to the ion pair $\text{LaHL}^{2+}$. It appears, therefore, that contrary to Cefola's suggestion, no chelation occurs in this complex.

The fact that $\varepsilon_c \approx \varepsilon_1$, can be explained by assuming that the selected wavelength, $\lambda = 326\mu$, corresponds to an isosbestic point for the equilibrium between the $\text{HL}^-$ ion and the ion pair.

**THEORETICAL**

In accordance with the spectrophotometric evidence discussed in the foregoing section, it was assumed that in the lanthanum salicylate solutions, ion association mainly occurs between the $\text{La}^{3+}$- and $\text{HL}^-$ ions. Calculations based on data reported [106] on ion association in salts of sodium and univalent anions suggest that at the total concentrations of $\text{Na}^+$- ions and salicylic acid employed in the present work, the extent of ion pairing between the $\text{Na}^+$ and $\text{HL}^-$ ions would be much too small to be spectrophotometrically detectable; the species $\text{NaHL}$ can thus be disregarded. Since, in the pH range 1.5 - 5 adopted in the present work, the terms $[\text{OH}^-]$, $[\text{L}^2^-]$ and $[\text{LaOH}^{2+}]$ are negligible, the only equilibria which need to be considered in the case of the lanthanum salicylate solutions are

\[
\begin{align*}
\text{H}_2\text{L} & \rightleftharpoons \text{H}^+ + \text{HL}^- \\
\text{La}^{3+} + \text{HL}^- & \rightleftharpoons \text{LaHL}^{2+}.
\end{align*}
\]

The respective equilibrium constants are given by

\[
\begin{align*}
K_1 &= \frac{h[H^-]}{[\text{H}_2\text{L}]}, \\
K &= \frac{c_2}{[\text{La}^{3+}][\text{HL}^-]}f_1f_3,
\end{align*}
\]

where $h = [\text{H}^+]$, $c = [\text{LaHL}^{2+}]$, and $f_1$, $f_2$, and $f_3$ are the activity coefficients.
of the singly, doubly, and triply charged species, respectively.

The concentration terms $c$, $[\text{La}^{3+}]$, $[\text{HL}^-]$, and $[\text{H}_2\text{L}]$ are related
to one another by the expressions

$$T_L = c + [\text{HL}^-] + [\text{H}_2\text{L}], \quad \ldots(4.7)$$

$$T_M = [\text{La}^{3+}] + c \approx [\text{La}^{3+}] + c, \quad \ldots(4.8)$$
since, in the present case, $T_M \gg T_L$, and hence, a fortiori, $T_M \gg c$.

By combining equation (4.7) with (4.5), it follows that

$$[\text{HL}^-] = (T_L - c)K_1/(K_1 + hf_1^2), \quad \ldots(4.9)$$

$$[\text{H}_2\text{L}] = (T_L - c)hf_1^2/(K_1 + hf_1^2). \quad \ldots(4.10)$$

The electroneutrality condition here takes the form

$$h = (a-b) + c + [\text{HL}^-], \quad \ldots(4.11)$$

where $a$ and $b$ are the stoichiometric concentrations of perchloric acid
and sodium hydroxide added, respectively.

For the solutions of salicylic acid which do not contain lanthanum,
series B, equations (4.7), (4.9), (4.10), and (4.11) simplify to

$$T_L = [\text{HL}^-]^0 + [\text{H}_2\text{L}]^0, \quad \ldots(4.12)$$

$$[\text{HL}^-]^0 = T_LK_1/x, \quad \ldots(4.13)$$

$$[\text{H}_2\text{L}]^0 = T_Lh^0hf_1^2/x, \quad \ldots(4.14)$$

$$h^0 = (a-b) + [\text{HL}^-]^0, \quad \ldots(4.15)$$

where $x = K_1 + h^0f_1^2. \quad \ldots(4.16)$

By means of suitable combinations and rearrangements of the above
equations, it can be shown that

$$c = [\text{H}_2\text{L}]^0 - [\text{H}_2\text{L}] + [\text{HL}^-]^0 - [\text{HL}^-], \quad \ldots(4.17)$$

$$\Delta h = c - [\text{HL}^-]^0 - [\text{HL}^-], \quad \ldots(4.18)$$
\[ \Delta h = [H_2L]^0 - [H_2L], \]  \hspace{1cm} \text{(4.19)}

\[ \Delta h = h - h^0. \]  \hspace{1cm} \text{(4.20)}

Substituting for \([HL^-]\) and \([HL^-]^0\) from equations (4.9) and (4.13) into equation (4.18) yields
\[ \Delta h^2 x f_1^2 + \Delta h(x^2 + K_{\text{HL}_1} f_1^2 - c x f_1^2) - c x h_0^2 f_1^2 = 0, \]  \hspace{1cm} \text{(4.21)}

which is a quadratic equation in \(\Delta h\). Since, in the pH range employed in the present case, the term \(\Delta h^2 x f_1^2\) is negligibly small, equation (4.21) becomes
\[ \Delta h = c x h_0^2 f_1^2/(x^2 + K_{\text{HL}_1} f_1^2 - c x f_1^2). \]  \hspace{1cm} \text{(4.22)}

Substituting for \([HL^-]\) from equation (4.18) into equation (4.18) and rearranging, it follows that
\[ (\Delta h x + T_{\text{HL}_1} K_{\text{HL}_1})/c = \alpha x, \]  \hspace{1cm} \text{(4.23)}

in which \(\alpha = 1 + F/K_{\text{HL}_1} \),
\[ \text{where } F = f_2/(f_1 x f_2). \]  \hspace{1cm} \text{(4.24)}

Thus a plot of \(y = (\Delta h x + T_{\text{HL}_1} K_{\text{HL}_1})/c \) against \(x\) should yield a straight line with a slope equal to \(\alpha\).

The optical density of the solutions of series B is given by
\[ D^0 = \varepsilon_o [H_2L]^0 + \varepsilon_1 [HL^-]. \]  \hspace{1cm} \text{(4.26)}

In view of equations (4.13) and (4.14), the last equation can be also written in the form
\[ D^0 x = D_{\text{HL}_1} K_{\text{HL}_1} + D_0 h^0 x f_1^2. \]  \hspace{1cm} \text{(4.27)}

For the solutions of lanthanum salicylate (series A), the Lambert-Beer law takes the form
\[ D = \varepsilon_o [H_2L]^0 + \varepsilon_1 [HL^-] + \varepsilon_0 c L, \]  \hspace{1cm} \text{(4.26)}

where \(\varepsilon_o\) is the extinction coefficient of \(\text{LaHL}^{2+}\).
Upon substituting for $[\text{HL}^-]$ and $[\text{H}_2\text{L}]$ from equations (4.9) and (4.10) into equation (4.28) and solving for $c$, it follows that

$$c = \frac{D_1K_1 + h f_1^2D_0 - D_2K_1 + h f_1^2}{D_1K_1 + h f_1^2D_0 - D_2K_1 + h f_1^2},$$ \hspace{1cm} (4.29)

where $D_0 = e_0T_{\text{L}}^{-1}$. \hspace{1cm} (4.30)

Combination of equation (4.29) with equation (4.27) gives

$$c = \frac{\Delta D + h f_1^2(D_0 - D)}{D_1K_1 + h f_1^2D_0 - D_2K_1 + h f_1^2},$$ \hspace{1cm} (4.31)

Finally, subtracting equation (4.28) from equation (4.26) and rearranging, we have

$$\Delta h(D_0 - D_1) - \Delta D_{\text{L}} + D_1c = D_0c,$$ \hspace{1cm} (4.32)

from which it can be seen that if $y'' = \Delta h(D_0 - D_1) - \Delta D_{\text{L}} + D_1c$ is plotted against $c$, a straight line should be obtained with a slope equal to $D_0$.

RESULTS AND DISCUSSION

DETERMINATION OF $D_0$ AND $D_1$

The evaluation of the association constant $K$ requires a knowledge of $e_0$, $e_0'$, and $e_1$ at the selected wavelength, $\lambda = 326\mu\text{m}$. For the last two coefficients, Ernst and Menashi [31] have found the values $e_0 = 717$ at $I = 0.8$ and $e_1 = 200$ at $I \approx 10^{-3}$. However, as all solutions employed in the present work were maintained at $I = 0.1$, it was decided to re-determine these quantities by means of equation (4.27). This predicts that a plot of $y = D_{\text{L}}^2$ against $D_{\text{L}}^2$ should give a straight line with a slope and intercept equal to $D_0$ and $D_1K_1$, respectively.

The hydrogen ion concentration of the solutions of salicylic acid...
made up for this purpose was calculated using equation (4.15) in the form

\[ h^0 = (a-b) + K^1 T_L / (K^1 + h^0 f^2_1), \quad \ldots (4.33) \]

which can be transformed into a quadratic equation in \( h^0 \) and solved by standard methods.

The activity coefficients were evaluated by means of the Davies equation [reference[77] page 41], with a probable error not exceeding ± 2%. For I = 0.1, this yields the value \( f_1 = 0.785 \). The results of these calculations are given in table (4.2), where \( d \) represents the concentration of NaClO₄ in the experimental solutions. The plot of \( \chi = D^0 x \) against \( h^0 f^2_1 \) for salicylic acid is shown in figure (4.3). In order to avoid confusion between the quantity \( x \) and the multiplication sign, in tables and diagrams where these symbols appear together, the multiplication sign will be ringed.

The precision of the experimental data was estimated by calculating the standard deviation \( \sigma_y \) of \( y = D^0 x \). This is defined by the equation

\[ \sigma_y = \left[ \frac{\sum (Ay)^2}{(n-1)} \right]^{\frac{1}{2}}, \quad \ldots (4.35) \]

where \( \Delta y = y_{\text{calc}} - y_{\text{expt}} \) and \( n = \text{number of observations} \). The standard deviations of the slope and intercept were found from the expression \[ 107 \]

\[ \sigma_{\text{Slope}} = \sigma_y \left[ \frac{n \sum x^2}{(n-1)(n-2)} \right], \quad \ldots (4.36) \]

\[ \sigma_{\text{Intercept}} = \sigma_y \left[ \frac{n \sum x}{(n-1)(n-2)} \right], \quad \ldots (4.37) \]

where \( x = h^0 f^2_1 \).

It will be seen from the table that the values \( \varepsilon_0 = 688 \) and \( \varepsilon_1 = 228 \), found in the present work at I = 0.1, differ significantly from the corresponding values obtained by Ernst and Menashi (loc. cit.). Since, these differences cannot be completely accounted for by the inaccuracy of the Davies equation, it appears that \( \varepsilon_0 \), and to a much greater extent \( \varepsilon_1 \) vary with changing ionic strength. It has been reported before that,
TABLE 4.2 DETERMINATION OF \( D_0 \) AND \( D_1 \) FOR SALICYLIC ACID

\[ T_L = 2.509 \times 10^{-4} \text{ mole/l.}; \quad I = 0.1; \quad \lambda = 326 \text{ m\mu}; \quad l = 4 \text{ cm}. \]

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<tr>
<th>( a \times 10^3 ) mole/l</th>
<th>( d \times 10^2 ) mole/l</th>
<th>( D_0 )</th>
<th>( n^2 P_1^2 \times 10^3 )</th>
<th>( x \times 10^3 )</th>
<th>( y = D_0 x \times 10^3 )</th>
<th>( \Delta y \times 10^3 )</th>
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<td>0.459</td>
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<td>0.395</td>
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<td>9.644</td>
<td>0.542</td>
<td>2.214</td>
<td>3.278</td>
<td>1.776</td>
<td>-0.004</td>
</tr>
<tr>
<td>4.490</td>
<td>9.553</td>
<td>0.566</td>
<td>2.809</td>
<td>3.873</td>
<td>2.192</td>
<td>-0.009</td>
</tr>
<tr>
<td>6.006</td>
<td>9.400</td>
<td>0.586</td>
<td>3.735</td>
<td>4.799</td>
<td>2.812</td>
<td>+0.009</td>
</tr>
</tbody>
</table>

\[ D_0 = 0.690; \quad \sigma_{D_0} = \pm 0.003. \quad \varepsilon_0 = 688; \quad \sigma_{\varepsilon_0} = \pm 3. \]

\[ D_1 = 0.229; \quad \sigma_{D_1} = \pm 0.005. \quad \varepsilon_1 = 228; \quad \sigma_{\varepsilon_1} = \pm 5. \]

Previous work, \( \varepsilon_0 = 717 \) at \( I = 0.8 \) \( \{ \text{ref.}[31] \}\), \( \varepsilon_1 = 200 \) at \( I = 10^{-3} \).
FIGURE 4.3
DETERMINATION OF D₀ AND D₁ FOR SALICYLIC ACID.
certain charged species, the molar extinction coefficient is dependant on the species environment. Thus, Newton and Arcand [108] showed that $\varepsilon_{\text{Ce}^{3+}}$ and $\varepsilon_{\text{CeSO}_4^+}$ vary with changes in the ionic strength of solutions in which they were measured. Gates and King [109] have reported analogous effects concerning the absorption of $\text{Cr(H}_2\text{O)}_4\text{Cl}_2^+$ ion, and so have Coll and co-workers [110], for the $\text{FeCl}^{2+}$ ion pair. The latter workers attribute this effect to the dehydrating action of the perchlorates, used for controlling the ionic strength of the experimental solutions. Monk and his associates [111] have shown that the extinction coefficients of some uranyl ion pairs depend not only upon the salt concentration, but also upon the nature of the salt used to maintain a constant ionic strength. Biggs [112] has emphasized also, that it cannot be assumed that activity coefficients remain constant in mixtures of constant ionic strength but of varying composition unless one of the components is always in large excess.

Since, the ionic strength of the experimental solutions employed in the present work was 0.1 throughout, the values $D_0 = 0.690$ and $D_1 = 0.229$ were adopted for the determination of the association constant of the lanthanum salicylate ion pair. It was also found in the evaluation of $K$, that use of the present values for $\varepsilon_0$ and $\varepsilon_1$ gave more consistent results than those of Ernst and Menashi (loc. cit.)

**DETERMINATION OF THE ASSOCIATION CONSTANT**

An inspection of equations (4.33), (4.22), (4.23), and (4.31) shows that if $D_c$ were known, the values of $\Delta h$ and $c$, corresponding to any given value of $h^0$, could be calculated by solving equations (4.22) and (4.31). It would then be possible to evaluate the association constant $K$ by plotting $y' = (\Delta hx + T_LK_1)/c$ against $x$ and measuring the slope $\alpha$ of the straight
line so obtained. Thus, for example, the procedure leads to a value of 1.20 x 10^2 for K, if D_c is taken to be equal to D_1, an assumption which is justified by the experimental results discussed earlier. However, as the exact value of D_c was not known, it was decided to obtain the best possible value of K by the use of an optimization procedure which involved the evaluation of \( \alpha \) as a function of D_c. For this purpose, first the values of h^0 and x corresponding to any given value of (a - b) were obtained from equations (4.33) and (4.16), respectively. The value of D_c was then varied at 0.001 intervals over the range 0.21 - 0.24 and for each value of D_c, a set of \( \Delta h / c \) values was computed by means of equations (4.22) and (4.31), using the method of successive approximations. The values of y' were then found and the slope of the plot of y' against x determined by applying the method of least squares. The goodness of fit at a given value of D_c was assessed by calculating the standard deviation \([107]\) \( \sigma_\alpha \) of \( \alpha \). The variation of \( \sigma_\alpha \) with D_c is given in figure (4.4) from which it can be seen that as D_c increases, \( \sigma_\alpha \) decreases, passes through a minimum and then increases.

The values of \( \alpha \) and D_c corresponding to this minimum, and which enable the experimental data to be best fitted into equation (4.23) are \( \alpha = 4.597 \) and \( D_c = 0.226 \). From this it can be seen that, in accord with the experimental evidence discussed previously, the value of D_c is very close to D_1. It will also be noted that the optimum value of K does not significantly differ from the one found by assuming D_c = D_1.

The results of these calculations, leading to K for the lanthanum salicylate ion pair, are summarized in table (4.3), in which the precision of the experimental data is expressed in terms of the residuals \( \Delta y' \) and \( \Delta y'' \) and of the standard deviations \( \sigma_\alpha \), \( \sigma_K \) and \( \sigma_D_c \). The plot of
FIGURE 4.4 VARIATION OF $\sigma_\alpha$ WITH $D_c$ FOR LANTHANUM SALICYLATE.
<table>
<thead>
<tr>
<th>$a \times 10^3$ mole/l</th>
<th>$b \times 10^2$</th>
<th>$c \times 10^5$</th>
<th>$D$</th>
<th>$\Delta D$</th>
<th>$\Delta y' \times 10^3$</th>
<th>$\Delta y'' \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.459</td>
<td>3.957</td>
<td>1.050</td>
<td>0.687</td>
<td>-0.017</td>
<td>3.529</td>
<td>-0.747</td>
</tr>
<tr>
<td>1.157</td>
<td>3.846</td>
<td>1.464</td>
<td>0.834</td>
<td>-0.023</td>
<td>2.550</td>
<td>1.204</td>
</tr>
<tr>
<td>2.995</td>
<td>3.724</td>
<td>1.506</td>
<td>1.236</td>
<td>-0.021</td>
<td>2.046</td>
<td>1.970</td>
</tr>
<tr>
<td>3.511</td>
<td>3.522</td>
<td>2.046</td>
<td>2.288</td>
<td>-0.011</td>
<td>1.790</td>
<td>2.218</td>
</tr>
<tr>
<td>4.490</td>
<td>3.388</td>
<td>1.446</td>
<td>1.119</td>
<td>-0.012</td>
<td>1.146</td>
<td>3.304</td>
</tr>
</tbody>
</table>

$T = 2.509 \times 10^{-4}$ mole/l; $T = 1.000 \times 10^{-2}$ mole/l; $I = 0.1; \lambda = 326 \mu m; J_1 = 4 \times cm; D_0 = 0.226$.
DETERMINATION OF THE ASSOCIATION CONSTANT FOR LANTHANUM SALICYLATE.
FIGURE 4.6
DETERMINATION OF $D_C^*$ FOR LANTHANUM SALICYLATE.
\[ y' = \left( \Delta h x + T \frac{K}{c} \right) \]

In computing the value of \( K \) from the best values of \( D_c \) and \( \alpha \), the values \( f_1 = 0.785, f_2 = 0.3797 \), and \( f_3 = 0.1132 \) (obtained from the Davies equation (loc. cit.)), were used. The standard deviation of \( K \) is seen to be less than 1% thus indicating that satisfactory precision has been attained.

In conclusion, it can be said that the optimization procedure employed in the present case is quite capable of giving satisfactory results. However, it appears that an important condition for a successful application of this procedure is a knowledge of the approximate value of \( D_c \).

The present value for \( K \) is appreciably lower than the value \( 4.37 \times 10^2 \) obtained by Cefola, Tompa, Celiano and Gentile [58] at \( 30^\circ\text{C} \) using the Bjerrum method [113]. In determining the \( K \) value, these authors made no allowance for the activity coefficient of the \( \text{La}^{3+} \)-ion and more-over formulated lanthanum salicylate as a six membered chelate. Since, this assumption is contradicted by the spectrophotometric evidence obtained in the present work, the reliability of these authors' value must be regarded as questionable.

As a further test of the reliability of these calculations, the value of \( D_c \) was computed by means of equation (4.32) which predicts that a plot of \( y'' = \Delta h (D - D_1) - \Delta nL_1 + D_1 c \) against \( c \) should give a straight line with a slope equal to \( D_c \). In this procedure the values of \( y'' \) were calculated using the values of \( \Delta h \) and \( C \) shown in table (4.3), and slope of the plot of \( y'' \) against \( c \) obtained by applying the method of least squares. The results of these calculations are also given in table (4.3), and the plot of \( y'' \) against \( c \) in figure (4.6). The value 0.228 found by this means and shown in table (4.3) as \( D_c \) is in very good agreement with the value 0.226 obtained from the plot of \( \sigma \) against \( D_c \), The standard deviation
of $D_c$ is less than $0.5\%$ thus indicating that the plot of $y''$ against $c$ yields a very good straight line.

**THE LANTHANUM 3-METHYL, LANTHANUM 5-CHLORO, AND LANTHANUM 5-BROMO-SALICYLIC ACID SYSTEMS.**

**EVIDENCE FOR ION ASSOCIATION**

Evidence for ion association in the above systems was obtained using the same procedure as in the case of lanthanum salicylate. Just as in the latter case, the values of $\Delta D = D^0 - D$ were found to depend on both the wavelength and the hydrogen ion concentration and, in general, were small.

Figures (4.7), (4.8), and (4.9) show the relevant absorption curves for these three systems at the hydrogen ion concentrations at which the largest $\Delta D$ values were observed.

The wavelengths at which the pH variation of both $D^0$ and $D$ were the largest were adopted for the evaluation of the association constants for these ion pairs. It is worthwhile to note that the wavelengths adopted for lanthanum 5-chloro and lanthanum 5-bromo salicylates were also those chosen by Ernst and Menashi [31] for their spectrophotometric evaluation of the first dissociation constants of these salicylic acids. The variation of $\Delta D$ with $h^0$ at the wavelengths selected for all three systems is given in tables (4.4), (4.5), and (4.6). It will be seen that, in all cases, $\Delta D$ increases at first with increasing $h^0$, reaches a maximum at $h^0 \approx K_1$, and then decreases, finally becoming zero at $h^0 \approx 1 \times 10^{-4}$ mole/l.

Since, in the pH region corresponding to this maximum, the $\Delta D$
FIGURE 4.7 ABSORPTION CURVES OF LANTHANUM 3-METHYL SALICYLATE IN AQUEOUS SOLUTION.

\[ T_L = 2.63 \times 10^4 \text{ mole/l.} \]
\[ T_M = 1 \times 10^2 \text{ mole/l.} \]
\[ h^* = 1.02 \times 10^3 \text{ mole/l.} \]
\[ I = 0.1 \]
\[ l = 4 \text{ cm.} \]

\( \lambda (\text{m} \mu) \)

OPTICAL DENSITY

\( \lambda (\text{m} \mu) \)
TABLE 4.4 VARIATION OF \( \Delta D \) WITH \( n^o \) - LANTHANUM 3-METHYL SALICYLATE

\[
T_L = 2.589 \times 10^{-4} \text{ mole/l.}; \quad T_M = 1 \times 10^{-2} \text{ mole/l.}; \quad \lambda = 332\text{nm}; \quad l = 4\text{cm}; \quad I = 0.1.
\]

<table>
<thead>
<tr>
<th>( n^o \times 10^3 )</th>
<th>0.029</th>
<th>0.063</th>
<th>0.107</th>
<th>0.580</th>
<th>1.047</th>
<th>4.948</th>
<th>9.906</th>
<th>25.37</th>
<th>50.33</th>
<th>100.1</th>
<th>400</th>
<th>799</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{mole/l.} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D^o )</td>
<td>0.227</td>
<td>0.235</td>
<td>0.250</td>
<td>0.388</td>
<td>0.473</td>
<td>0.724</td>
<td>0.784</td>
<td>0.838</td>
<td>0.842</td>
<td>0.850</td>
<td>0.857</td>
<td>0.860</td>
</tr>
<tr>
<td>( D )</td>
<td>0.227</td>
<td>0.234</td>
<td>0.242</td>
<td>0.371</td>
<td>0.439</td>
<td>0.682</td>
<td>0.762</td>
<td>0.824</td>
<td>0.834</td>
<td>0.844</td>
<td>0.855</td>
<td>0.860</td>
</tr>
<tr>
<td>( \Delta D )</td>
<td>0.000</td>
<td>0.001</td>
<td>0.008</td>
<td>0.017</td>
<td>0.034</td>
<td>0.042</td>
<td>0.022</td>
<td>0.014</td>
<td>0.008</td>
<td>0.006</td>
<td>0.002</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\[
D_L = 0.227; \quad \Delta D_L = 0.000.
\]
FIGURE 4.8 ABSORPTION CURVES OF LANTHANUM 5-CHLORO SALICYLATE IN AQUEOUS SOLUTION.

$T_L = 2.444 \times 10^{-4}$ mole/$L$,
$T_M = 1 \times 10^{-2}$ mole/$L$,
$H^0 = 5.4 \times 10^{-3}$ mole/$L$,
$I = 0.1$,
$L = 4$ cm.

$D_0$ $D$
<table>
<thead>
<tr>
<th>$h^0 \times 10^3$</th>
<th>0.012</th>
<th>0.050</th>
<th>0.099</th>
<th>0.504</th>
<th>1.22</th>
<th>2.44</th>
<th>4.41</th>
<th>6.36</th>
<th>8.34</th>
<th>10.04</th>
<th>25.30</th>
<th>50.0</th>
<th>100</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^0$</td>
<td>0.231</td>
<td>0.232</td>
<td>0.235</td>
<td>0.289</td>
<td>0.355</td>
<td>0.432</td>
<td>0.510</td>
<td>0.553</td>
<td>0.572</td>
<td>0.602</td>
<td>0.684</td>
<td>0.708</td>
<td>0.720</td>
<td>0.786</td>
</tr>
<tr>
<td>$D$</td>
<td>0.231</td>
<td>0.232</td>
<td>0.231</td>
<td>0.274</td>
<td>0.336</td>
<td>0.408</td>
<td>0.484</td>
<td>0.529</td>
<td>0.551</td>
<td>0.583</td>
<td>0.672</td>
<td>0.699</td>
<td>0.716</td>
<td>0.786</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.004</td>
<td>0.015</td>
<td>0.019</td>
<td>0.024</td>
<td>0.026</td>
<td>0.024</td>
<td>0.021</td>
<td>0.019</td>
<td>0.012</td>
<td>0.009</td>
<td>0.004</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$D_L = 0.231; \quad \Delta D_L = 0.000.$
FIGURE 4.9  ABSORPTION CURVES OF LANTHANUM 5 - BROMO SALICYLATE IN AQUEOUS SOLUTION.

\[ T_L = 2.584 \times 10^{-4} \text{ mole/l.} \]
\[ T_M = 1 \times 10^{-2} \text{ mole/l.} \]
\[ h^0 = 4.786 \times 10^{-3} \text{ mole/l.} \]
\[ I = 0.1. \]
\[ l = 4 \text{ cm.} \]

\[ D^0 \]
\[ D \]

OPTICAL DENSITY

\[ \lambda \ (m\mu) \]

240 50 60 70 80 90 100 120 130 150 180 210 240 270 300 330 360 400 450 500

0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5
TABLE 4.6 VARIATION OF ΔD WITH h° - LANTHANUM 5-BROMO SALICYLATE

\[ T_L = 2.621 \times 10^{-4} \text{ mole/l.}; \quad T_M = 9.984 \times 10^{-2} \text{ mole/l.}; \quad \lambda = 337\text{m\textmu}; \quad l = 4\text{cm}; \quad I = 0.1. \]

<table>
<thead>
<tr>
<th>h°x10^3</th>
<th>0.021</th>
<th>0.058</th>
<th>0.099</th>
<th>0.519</th>
<th>1.28</th>
<th>2.45</th>
<th>4.40</th>
<th>6.40</th>
<th>8.35</th>
<th>10.04</th>
<th>25.30</th>
<th>50.30</th>
<th>100</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>D°</td>
<td>0.279</td>
<td>0.280</td>
<td>0.287</td>
<td>0.354</td>
<td>0.458</td>
<td>0.554</td>
<td>0.645</td>
<td>0.712</td>
<td>0.749</td>
<td>0.778</td>
<td>0.868</td>
<td>0.920</td>
<td>0.940</td>
<td>0.954</td>
</tr>
<tr>
<td>D</td>
<td>0.279</td>
<td>0.280</td>
<td>0.283</td>
<td>0.340</td>
<td>0.437</td>
<td>0.527</td>
<td>0.616</td>
<td>0.685</td>
<td>0.725</td>
<td>0.756</td>
<td>0.854</td>
<td>0.912</td>
<td>0.936</td>
<td>0.954</td>
</tr>
<tr>
<td>ΔD</td>
<td>0.000</td>
<td>0.000</td>
<td>0.004</td>
<td>0.014</td>
<td>0.021</td>
<td>0.027</td>
<td>0.029</td>
<td>0.027</td>
<td>0.024</td>
<td>0.022</td>
<td>0.014</td>
<td>0.008</td>
<td>0.004</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\[ D_L = 0.279; \quad ΔD_L = 0.000. \]
values are significantly larger than the random experimental error involved in optical density measurement, it may be concluded that ion association occurs in the present systems. The fact that with increasing pH, $D$ tends towards $D_1$ indicates that in each case, $\varepsilon_0$ is virtually equal to $\varepsilon_1$; this means that just as the lanthanum salicylate complex, the lanthanum 3-methyl, lanthanum 5-chloro, and lanthanum 5-bromo salicylates are to be regarded as ion pairs of the type $\text{LaHL}^{2+}$.

**RESULTS AND DISCUSSION**

**DETERMINATION OF $D_0$ AND $D_1$**

The quantities $D_0$ and $D_1$, for the three substituted salicylic acids were determined in exactly the same way as for salicylic acid i.e. using equation (4.27). This predicts that a plot of $y = D_0 x$ against $h_1^2$ should yield a straight line with a slope and intercept equal to $D_0$ and $D_1 K_1$, respectively.

The results of these calculations are summarised in tables (4.7), (4.8), and (4.9), where the values of $D_0$ and $D_1$ found by Ernst and Menashi [31] at the same wavelength, are also given. It can be seen that the standard deviations $\sigma_{D_0}$ and $\sigma_{D_1}$ are less than 2%, thus indicating that satisfactory precision has been attained. It is noteworthy that, just as in the case of salicylic acid, the present values of $D_0$ and $D_1$ differ significantly from those reported by Ernst and Menashi (loc. cit.). For reasons already explained in the treatment of lanthanum salicylate, the present values for $D_0$ and $D_1$ have been employed, in preference to those of Ernst and Menashi, for the determination of the association constants for lanthanum 3-methyl-, 5-chloro- and 5-bromo salicylates.
TABLE 4.7 DETERMINATION OF D₀ AND D₁ FOR 3-METHYL SALICYLIC ACID

\[ T_L = 2.6248 \times 10^{-4} \text{ mole/l.}; \quad I = 0.1; \quad \lambda = 332 \mu \text{m}; \quad l = 4 \text{ cm}. \]

<table>
<thead>
<tr>
<th>a \times 10^3</th>
<th>d \times 10^2</th>
<th>D₀</th>
<th>h₀t² \times 10^3</th>
<th>\times 10^3</th>
<th>y = D₀x</th>
<th>Δy \times 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>mole/l.</td>
<td>mole/l.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.379</td>
<td>9.947</td>
<td>0.405</td>
<td>0.357</td>
<td>1.492</td>
<td>0.604</td>
<td>+0.027</td>
</tr>
<tr>
<td>0.778</td>
<td>9.947</td>
<td>0.479</td>
<td>0.586</td>
<td>1.721</td>
<td>0.824</td>
<td>+0.015</td>
</tr>
<tr>
<td>1.181</td>
<td>9.907</td>
<td>0.541</td>
<td>0.822</td>
<td>1.957</td>
<td>1.058</td>
<td>-0.007</td>
</tr>
<tr>
<td>2.375</td>
<td>9.804</td>
<td>0.646</td>
<td>1.532</td>
<td>2.667</td>
<td>1.723</td>
<td>-0.029</td>
</tr>
<tr>
<td>4.388</td>
<td>9.597</td>
<td>0.723</td>
<td>2.751</td>
<td>3.886</td>
<td>2.811</td>
<td>+0.015</td>
</tr>
<tr>
<td>6.377</td>
<td>9.389</td>
<td>0.767</td>
<td>3.966</td>
<td>5.100</td>
<td>3.913</td>
<td>-0.017</td>
</tr>
<tr>
<td>8.397</td>
<td>9.217</td>
<td>0.788</td>
<td>5.203</td>
<td>6.338</td>
<td>4.997</td>
<td>+0.016</td>
</tr>
<tr>
<td>10.355</td>
<td>9.010</td>
<td>0.808</td>
<td>6.405</td>
<td>7.540</td>
<td>6.092</td>
<td>+0.009</td>
</tr>
</tbody>
</table>

D₀ = 0.904; \quad \sigma_{D₀} = \pm 0.003. \quad \varepsilon₀ = 861; \quad \sigma_{\varepsilon₀} = \pm 3. \quad D₀ (direct measurement) = 0.940; \quad \varepsilon₀ = 895.

D₁ = 0.235; \quad \sigma_{D₁} = \pm 0.011. \quad \varepsilon₁ = 224; \quad \sigma_{\varepsilon₁} = \pm 10.
FIGURE 4.10 DETERMINATION OF $D_0$ AND $D_1$ FOR 3-METHYL SALICYLIC ACID.
TABLE 4.8 DETERMINATION OF \( D_0 \) AND \( D_1 \) FOR 5-CHLORO SALICYLIC ACID

\[ T_L = 2.444 \times 10^{-4} \text{ mole/l.}, \; I = 0.1; \; \lambda = 338\text{m} \mu; \; l = 4\text{cm}. \]

<table>
<thead>
<tr>
<th>( a \times 10^3 )</th>
<th>( d \times 10^2 )</th>
<th>( D_0 )</th>
<th>( h_1^0 \times 10^3 )</th>
<th>( x \times 10^3 )</th>
<th>( y = D_0x )</th>
<th>( \Delta y \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.039</td>
<td>9.912</td>
<td>0.355</td>
<td>0.753</td>
<td>2.983</td>
<td>1.059</td>
<td>+0.011</td>
</tr>
<tr>
<td>2.295</td>
<td>9.808</td>
<td>0.432</td>
<td>1.505</td>
<td>3.734</td>
<td>1.610</td>
<td>+0.004</td>
</tr>
<tr>
<td>4.300</td>
<td>9.599</td>
<td>0.510</td>
<td>2.719</td>
<td>4.948</td>
<td>2.524</td>
<td>-0.024</td>
</tr>
<tr>
<td>6.270</td>
<td>9.391</td>
<td>0.553</td>
<td>3.919</td>
<td>6.148</td>
<td>3.401</td>
<td>-0.023</td>
</tr>
<tr>
<td>8.263</td>
<td>9.217</td>
<td>0.572</td>
<td>5.142</td>
<td>7.367</td>
<td>4.298</td>
<td>+0.028</td>
</tr>
<tr>
<td>10.316</td>
<td>9.008</td>
<td>0.602</td>
<td>6.418</td>
<td>8.626</td>
<td>5.215</td>
<td>+0.017</td>
</tr>
</tbody>
</table>

\( D_0 = 0.728; \; \sigma_{D_0} = \pm 0.004. \; \varepsilon_0 = 745; \; \sigma_{\varepsilon_0} = \pm 4. \) \( D_0 \) (direct measurement) = 0.786; \( \varepsilon_0 = 804. \)

\( D_1 = 0.228; \; \sigma_{D_1} = \pm 0.005. \; \varepsilon_1 = 233; \; \sigma_{\varepsilon_1} = \pm 5. \)

Previous work, \( \varepsilon_0 = 807 \) at \( I = 0.3 \) \cite{ref. [31]}. \( \varepsilon_1 = 225 \) at \( I = 10^{-3} \)
FIGURE 4.11 DETERMINATION OF $D_0$ AND $D_1$ FOR 5-CHLORO-SALICYLIC ACID.
TABLE 4.9 DETERMINATION OF $D_0$ AND $D_1$ FOR 5-BROMO-SALICYLIC ACID

$T_L = 2.621 \times 10^{-4}$ mole/l.; $I = 0.1$; $\lambda = 337\text{m}\mu$; $l = 4\text{cm}$.  

<table>
<thead>
<tr>
<th>$a \times 10^3$</th>
<th>$d \times 10^2$</th>
<th>$D^0$</th>
<th>$h o f_1^2 \times 10^3$</th>
<th>$x \times 10^3$</th>
<th>$y = D^0x$</th>
<th>$\Delta y \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.089</td>
<td>9.894</td>
<td>0.458</td>
<td>0.790</td>
<td>2.990</td>
<td>1.369</td>
<td>-0.004</td>
</tr>
<tr>
<td>2.291</td>
<td>9.752</td>
<td>0.554</td>
<td>1.507</td>
<td>3.707</td>
<td>2.053</td>
<td>+0.006</td>
</tr>
<tr>
<td>4.281</td>
<td>9.599</td>
<td>0.645</td>
<td>2.710</td>
<td>4.910</td>
<td>3.168</td>
<td>+0.022</td>
</tr>
<tr>
<td>6.305</td>
<td>9.402</td>
<td>0.712</td>
<td>3.943</td>
<td>6.143</td>
<td>4.372</td>
<td>-0.012</td>
</tr>
<tr>
<td>8.270</td>
<td>9.206</td>
<td>0.749</td>
<td>5.145</td>
<td>7.345</td>
<td>5.500</td>
<td>+0.001</td>
</tr>
<tr>
<td>10.295</td>
<td>9.009</td>
<td>0.778</td>
<td>6.385</td>
<td>8.585</td>
<td>6.681</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

$D_0 = 0.950$; $\sigma_{D_0} = \pm 0.003$. $\varepsilon_0 = 906$; $\sigma_{\varepsilon_0} = +3$. $D_0$ (direct measurement) = 0.956; $\varepsilon_0 = 911$.

$D_1 = 0.280$; $\sigma_{D_1} = \pm 0.005$. $\varepsilon_1 = 267$; $\sigma_{\varepsilon_1} = +5$.

Previous work $\varepsilon_0 = 909$ at $I = 0.8$  
$\varepsilon_1 = 251$ at $I = 10^{-3}$  
[ref. [31]].
FIGURE 4.12
DETERMINATION OF $D_0$ AND $D_1$ FOR 5-BROMO-SALICYLIC ACID.
Figures (4.10), (4.11), and (4.12) represent the plots of $y = D^0 x$ against $h^0 f^2$ for the three salicylic acids which show that in each case, the experimental points lie on a very good straight line.

**DETERMINATION OF THE ASSOCIATION CONSTANTS**

Since, in all three cases, the limiting value of $AD$ at sufficiently high pH values is zero, thus indicating that $D_c$ is virtually equal to $D_1$, the association constants of these three ion pairs were determined by the optimization procedure already described. It was found that, in all three cases, the plot of the standard deviation $\sigma$ of $\sigma$ against $D_c$ was very similar to that observed for lanthanum salicylate and gave a well defined minimum. The values of $\sigma$ and $D_c$ corresponding to these minima, and which enable the experimental data to be best fitted into equation (4.23), are given in tables (4.10), (4.11), and (4.12). It can be seen that the values of $D_c$ agree reasonably well with the corresponding values of $D_1$.

The results of these calculations are summarised in tables (4.10), (4.11), and (4.12). The standard deviation of each of these $K$ values is less than 2%, thus indicating that also here satisfactory precision was attained. As no literature values for the three association constants appear to be available, no assessment of the absolute reliability of these results can be made. The plots of $y' = (\Delta h x + T_p L_p)/c$ against $x$ for the three ion pairs are shown in figures (4.13), (4.14), and (4.15), from which it can be seen that the experimental points lie on very good straight lines.

The value of $D_c$, for each of these ion pairs, was also computed by means of equation (4.32). This predicts that a plot of $y'' = \Delta h (D_c - D_1) - \Delta DT_{L_p} + D_1 c$ against $c$ should give a straight line with a slope equal to $D_c$. 
The results of these calculations are summarised in tables (4.10), (4.11), and (4.12). It will be noted that the values of $D_0$ found by use of equation (4.32) are in very good agreement with those obtained from the plots of $\alpha_x$ against $D_0$. The plots of $y''$ against $c$ are given in figures (4.16), (4.17), (4.18). Again, it will be seen that very good straight lines were obtained.

THE LANTHANUM 3- AND 5-NITRO SALICYLIC ACID SYSTEMS

EVIDENCE FOR ION ASSOCIATION

Experimental evidence for ion association in these systems was obtained using the same procedure as in previous cases. It will be remembered that a successful application of the procedure requires:

1. The choice of a suitable concentration of the ligand $T_L$.

2. The choice of a suitable wavelength, that is one, at which the pH variations of $D_0$, $D$, and $\Delta D$ are the most pronounced and the values of $\Delta D$ themselves are as large as possible. These conditions were found to be best satisfied at $\lambda = 410\mu$ for lanthanum 3-nitro salicylate and at $\lambda = 390\mu$ for lanthanum 5-nitro salicylate. Figures (4.19) and (4.20) represent the absorption curves for the solutions of series A and B at the hydrogen ion concentration at which the $\Delta D$ values for the two systems were found to be the largest. The variation of $D_0$, $D$, and $\Delta D$ with $h^0$, at the selected wavelengths, is given in tables (4.13) and (4.14). An inspection of these tables show that the lanthanum nitro salicylate systems differ from the
<table>
<thead>
<tr>
<th>a x 10³</th>
<th>d x 10²</th>
<th>D</th>
<th>ΔD</th>
<th>Δh x 10⁵</th>
<th>c x 10⁵</th>
<th>y' x 10²</th>
<th>Δy' x 10²</th>
<th>y'' x 10⁵</th>
<th>Δy'' x 10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.379</td>
<td>3.958</td>
<td>0.377</td>
<td>0.028</td>
<td>1.042</td>
<td>4.631</td>
<td>0.677</td>
<td>+0.005</td>
<td>1.191</td>
<td>-0.059</td>
</tr>
<tr>
<td>0.778</td>
<td>3.924</td>
<td>0.443</td>
<td>0.036</td>
<td>1.308</td>
<td>4.023</td>
<td>0.796</td>
<td>-0.010</td>
<td>0.998</td>
<td>-0.015</td>
</tr>
<tr>
<td>1.181</td>
<td>3.889</td>
<td>0.498</td>
<td>0.043</td>
<td>1.549</td>
<td>3.822</td>
<td>0.859</td>
<td>+0.037</td>
<td>0.901</td>
<td>+0.033</td>
</tr>
<tr>
<td>2.375</td>
<td>3.786</td>
<td>0.601</td>
<td>0.045</td>
<td>1.679</td>
<td>2.978</td>
<td>1.151</td>
<td>+0.068</td>
<td>0.680</td>
<td>+0.048</td>
</tr>
<tr>
<td>4.308</td>
<td>3.580</td>
<td>0.689</td>
<td>0.034</td>
<td>1.330</td>
<td>1.896</td>
<td>1.844</td>
<td>-0.068</td>
<td>0.446</td>
<td>+0.018</td>
</tr>
<tr>
<td>6.377</td>
<td>3.373</td>
<td>0.738</td>
<td>0.029</td>
<td>1.135</td>
<td>1.467</td>
<td>2.425</td>
<td>-0.093</td>
<td>0.345</td>
<td>+0.014</td>
</tr>
<tr>
<td>8.397</td>
<td>3.201</td>
<td>0.762</td>
<td>0.026</td>
<td>1.038</td>
<td>1.269</td>
<td>2.866</td>
<td>+0.031</td>
<td>0.306</td>
<td>+0.004</td>
</tr>
<tr>
<td>10.355</td>
<td>2.995</td>
<td>0.785</td>
<td>0.023</td>
<td>0.912</td>
<td>1.076</td>
<td>3.407</td>
<td>+0.010</td>
<td>0.258</td>
<td>+0.005</td>
</tr>
</tbody>
</table>

α = 4.571; σ_α = ± 0.045. \( D_c \) = 0.244; σ_\( D_c \) = ± 0.004. \( K \) = 119.7; σ_\( K \) = ± 1.3.
FIGURE 4.13 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM 3-METHYL SULFATE.
FIGURE 4.14 DETERMINATION OF $D_c^*$ FOR LANTHANUM 3-METHYL SALICYLATE.
TABLE 4.11 ASSOCIATION CONSTANT OF LANTHANUM-5-CHLORO SALICYLATE

\[ T_L = 2.444 \times 10^{-4} \text{ mole/l.} \quad T_M = 9.984 \times 10^{-3} \text{ mole/l.} \quad I = 0.1 \quad \lambda = 338 \text{ nm} \quad l = 4 \text{ cm} \quad D_c = 0.200 \]

<table>
<thead>
<tr>
<th>a x 10^3 mole/l.</th>
<th>d x 10^2 mole/l.</th>
<th>D</th>
<th>ΔD</th>
<th>Δh x 10^5</th>
<th>c x 10^5</th>
<th>y' x 10^2</th>
<th>Δy' x 10^2</th>
<th>y'' x 10^6</th>
<th>Δy'' x 10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.039</td>
<td>3.930</td>
<td>0.336</td>
<td>0.019</td>
<td>0.742</td>
<td>3.032</td>
<td>1.871</td>
<td>-0.057</td>
<td>6.186</td>
<td>-0.090</td>
</tr>
<tr>
<td>2.295</td>
<td>3.791</td>
<td>0.408</td>
<td>0.024</td>
<td>1.031</td>
<td>2.610</td>
<td>2.236</td>
<td>+0.034</td>
<td>5.258</td>
<td>-0.010</td>
</tr>
<tr>
<td>4.301</td>
<td>3.617</td>
<td>0.484</td>
<td>0.026</td>
<td>1.130</td>
<td>2.079</td>
<td>2.890</td>
<td>+0.118</td>
<td>4.064</td>
<td>+0.117</td>
</tr>
<tr>
<td>6.270</td>
<td>3.408</td>
<td>0.529</td>
<td>0.024</td>
<td>1.061</td>
<td>1.676</td>
<td>3.641</td>
<td>+0.098</td>
<td>3.294</td>
<td>+0.077</td>
</tr>
<tr>
<td>8.263</td>
<td>3.200</td>
<td>0.551</td>
<td>0.027</td>
<td>0.963</td>
<td>1.388</td>
<td>4.437</td>
<td>+0.042</td>
<td>2.873</td>
<td>-0.081</td>
</tr>
<tr>
<td>10.316</td>
<td>2.991</td>
<td>0.583</td>
<td>0.019</td>
<td>0.843</td>
<td>1.141</td>
<td>5.414</td>
<td>-0.168</td>
<td>2.262</td>
<td>-0.032</td>
</tr>
</tbody>
</table>

\[ \alpha = 6.081; \quad \sigma_\alpha = \pm 0.07 \frac{1}{2} \quad D_c^K = 0.201; \quad \sigma_{D_c}^K = \pm 0.002 \quad K = 8.4.1; \quad \sigma_K = \pm 1.4. \]
FIGURE 4.15
DETERMINATION OF THE ASSOCIATION CONSTANT FOR LANTHANUM 5-CHLORO-SALICYLATE.
FIGURE 4.16  DETERMINATION OF $D_c^*$ FOR LANTHANUM 5-CHLORO-SALICYLATE.
TABLE 4.12 ASSOCIATION CONSTANT OF LANTHANUM 5-BROMO SALICYLATE

\[ T_L = 2.621 \times 10^{-4} \text{ mole/l.}; \ T_M = 9.984 \times 10^{-3} \text{ mole/l.}; \ I = 0.1; \ \lambda = 337 \mu; \ \lambda = 4 \text{ cm}; \ D_c = 0.270. \]

<table>
<thead>
<tr>
<th>( a \times 10^3 )</th>
<th>( d \times 10^2 )</th>
<th>( D )</th>
<th>( \Delta D )</th>
<th>( \Delta h \times 10^5 )</th>
<th>( c \times 10^5 )</th>
<th>( y' \times 10^2 )</th>
<th>( \Delta y' \times 10^2 )</th>
<th>( y'' \times 10^6 )</th>
<th>( \Delta y'' \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.089</td>
<td>3.898</td>
<td>0.437</td>
<td>0.021</td>
<td>0.758</td>
<td>2.967</td>
<td>2.020</td>
<td>-0.049</td>
<td>7.977</td>
<td>+0.033</td>
</tr>
<tr>
<td>2.292</td>
<td>3.800</td>
<td>0.527</td>
<td>0.027</td>
<td>1.003</td>
<td>2.521</td>
<td>2.435</td>
<td>-0.009</td>
<td>6.774</td>
<td>+0.032</td>
</tr>
<tr>
<td>4.281</td>
<td>3.604</td>
<td>0.616</td>
<td>0.029</td>
<td>1.109</td>
<td>2.033</td>
<td>3.105</td>
<td>+0.132</td>
<td>5.590</td>
<td>-0.101</td>
</tr>
<tr>
<td>6.305</td>
<td>3.407</td>
<td>0.685</td>
<td>0.027</td>
<td>1.029</td>
<td>1.616</td>
<td>3.959</td>
<td>+0.091</td>
<td>4.341</td>
<td>+0.023</td>
</tr>
<tr>
<td>8.270</td>
<td>3.210</td>
<td>0.725</td>
<td>0.024</td>
<td>0.906</td>
<td>1.300</td>
<td>4.948</td>
<td>-0.106</td>
<td>3.517</td>
<td>-0.008</td>
</tr>
<tr>
<td>10.295</td>
<td>3.014</td>
<td>0.756</td>
<td>0.022</td>
<td>0.844</td>
<td>1.140</td>
<td>5.695</td>
<td>-0.036</td>
<td>3.079</td>
<td>-0.014</td>
</tr>
</tbody>
</table>

\[ \alpha = 6.592; \ \sigma_\alpha = \pm 0.062; \ D_c^\alpha = 0.270; \ \sigma_{D_c}^\alpha = \pm 0.001; \ K = 76.4; \ \sigma_K = \pm 0.8. \]
FIGURE 4.17
DETERMINATION OF THE ASSOCIATION CONSTANT FOR LANTHANUM 5-BROMO-SALICYLATE.
FIGURE 4.18
DETERMINATION OF D\(c^2\) FOR LANTHANUM 5-BROMO-SALICYLATE.

\[ y = -10x + 5 \]

\[ c \times 10^5 \]

\[ 1 \]

\[ 2 \]

\[ 3 \]

\[ 4 \]

\[ 0 \to 8 \]

\[ 0 \to 6 \]

\[ 0 \to 4 \]

\[ 0 \to 2 \]
previous cases, in two main respects. Firstly, in contrast to lanthanum salicylate, the value of AD at sufficiently high pH, tends toward a finite constant value and secondly, the value of AD, at both very low and intermediate pH values, is zero.

Since, the value of $D_c$ cannot be directly deduced from the limiting value of AD ($AD_L$) as in previous cases, it would appear, at first sight, that the application of the optimization procedure, which requires a knowledge of a fairly accurate value of $D_c$, is not possible. However, as shown below, a rough assessment of $D_c$ is possible by making use of the limiting value of D ($D_L$) and, in particular, of the properties of the AD cross-over point, that is the point at which AD changes sign.

**ESTIMATION OF $D_c$**

Some idea of the value of $D_c$ may be gained from the limiting value $D_L$ which the optical density of an A solution reaches at a pH (pH~5), at which the dissociation of the first stage on ionization of the nitro salicylic acid is virtually complete but that of the second stage negligible. The optical density $D_L$ of a solution of series A, at such a pH value, is given by

$$D_L = [H_2L]L^+ + [HL^-]L^- + c_L e_c,$$

where the subscript L denotes the limiting value of the quantities under these conditions. Since, $[H_2L]_L \approx 0$ and $[HL^-]_L \approx (T_L - c_L)$, equation (4.38) becomes,

$$D_L = D_1 + c_L(D_c - D_1)/T_L.$$  ...(4.39)

On rearranging equation (4.35), it follows that

$$\frac{(D_L - D_1)}{(D_c - D_1)} = \frac{c_L}{T_L}.$$  ...(4.40)

from which it can be seen that if the extent of ion pairing is large, $D_L \approx D_c$. 
An accurate value of \( D_c \) could be deduced from the properties of the cross-over point if the value of \( \Delta h/c \) corresponding to this point were known accurately. This can be seen from equation (4.32) which, for \( \Delta D = 0 \), takes the form

\[
\Delta h/c = \frac{(D_1 - D_c)}{(D_1 - D_o)}, \quad \ldots \tag{4.41}
\]

or

\[
D_c = D_1 - \frac{\Delta h}{c} (D_1 - D_o). \quad \ldots \tag{4.42}
\]

On substituting for \( \Delta h/c \) from equation (4.22), into the last equation, we find

\[
D_c = D_1 - xh^o f_1^2 (D_1 - D_o)/(x^2 + T_1 K f_1^2 - c x f_1^2). \quad \ldots \tag{4.43}
\]

Since, in the present case, at the hydrogen ion concentration of the cross-over point, the term \( c x f_1^2 \) is negligibly small, equation (4.43) simplifies to

\[
D_c = D_1 - xh^o f_1^2 (D_1 - D_o)/(x^2 + T_1 K f_1^2). \quad \ldots \tag{4.44}
\]

Thus, \( D_c \) can be calculated provided \( h^o \) is known. Unfortunately, only a rough estimate of \( h^o \) at the cross-over point is possible. Referring to tables (4.13) and (4.14), we see that these values are \( h^o = 4.29 \times 10^{-2} \) mole/l. for lanthanum 3-nitro salicylate and \( h^o = 3.34 \times 10^{-2} \) mole/l. for lanthanum 5-nitro salicylate. Substituting these values into equation (4.44) we find the values \( D_c = 0.356 \) for lanthanum 3-nitro salicylate and \( D_c = 1.290 \) for lanthanum 5-nitro salicylate. Thus, to both systems, the following condition applies

\[
D_1 > D_c > D_o. \quad \ldots \tag{4.45}
\]

This condition can be used to account for the peculiarities of the variation of \( \Delta D \) with \( h^o \), in the following way:

In very acid solutions, that is at high values of \( h^o \), the degree of dissociation of the nitro salicylic acid (whether 3- or 5- ) is small.
and very little ion pairing takes place; under these conditions the optical
densities of the solutions of series A and B will be virtually the same
so that $\Delta D \approx 0$. As the pH increases, the degree of dissociation of the
nitro salicylic acid increases and consequently the extent of ion pairing
also increases. Since $D_1 > D_0 > D_0^\circ$ and since, in addition, the concentration
of $H_2L$ and $HL^-$ in the solutions of series A are always smaller than those
of the corresponding solutions of series B; D is at first greater than $D^\circ$
and accordingly $\Delta D < 0$. As the pH increases still further, $\Delta D$ decreases,
passes through a minimum, and again becomes zero. At this point, the amount
of complex formed in the lanthanum nitro salicylate solutions is large
enough to bring down its optical density to that of the corresponding
nitro salicylic acid solution. Beyond that point, the extent of complex
formation in the lanthanum nitro salicylate solutions increases very
rapidly with increasing pH and consequently its optical density falls below
that of the corresponding solution which contains nitro salicylic acid alone.
At about pH 5, the first stage of ionization of the nitro salicylic acid
is virtually complete and the extent of ion pairing reaches a maximum.
Beyond pH 5, further increase in pH therefore can have no effect on either
$D^\circ$ or $D_1$, and $\Delta D$ becomes constant.

**DETERMINATION OF $D_0$ AND $D_1$**

These quantities for the nitro salicylic acids at the selected
wavelengths were found in exactly the same way as before i.e. by means
of equation (4.27). The results of these calculations are summarised in
tables (4.15) and (4.16), and the plots of $y = D^\circ x$ against $h^o_{x1} 2$, so obtained,
shown in figures (4.21) and (4.22). It will be seen that, in each case,
as the standard deviations $\sigma_{D_0}$ and $\sigma_{D_1}$ are less than 3%, the experimental
FIGURE 4.19

ABSORPTION CURVES OF LANTHANUM 3-NITRO SALICYLATE IN AQUEOUS SOLUTION

$T_L = 2.772 \times 10^{-4}$ mole/l.

$T_M = 1 \times 10^{-2}$ mole/l.

$I = 0.1$

$L = 4$ cm.

$\lambda (\text{m}\mu)$

OPTICAL DENSITY
### TABLE 4.13 VARIATION OF ΔD WITH $h^\circ$ - LANTHANUM 3-NITRO SALICYLATE

$T_L = 2.772 \times 10^{-4} \text{ mole/l.}; T_M = 1 \times 10^{-2} \text{ mole/l.}; \lambda = 410 \text{ nm}; \ell = 4 \text{ cm}; I = 0.1.$

<table>
<thead>
<tr>
<th>$h^\circ \times 10^3$ mole/l.</th>
<th>0.132</th>
<th>0.488</th>
<th>0.961</th>
<th>0.594</th>
<th>1.191</th>
<th>5.558</th>
<th>10.54</th>
<th>50.32</th>
<th>100.2</th>
<th>249.6</th>
<th>499.2</th>
<th>799.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^0$</td>
<td>0.862</td>
<td>0.862</td>
<td>0.862</td>
<td>0.856</td>
<td>0.838</td>
<td>0.722</td>
<td>0.643</td>
<td>0.336</td>
<td>0.231</td>
<td>0.147</td>
<td>0.113</td>
<td>0.099</td>
</tr>
<tr>
<td>$D$</td>
<td>0.822</td>
<td>0.822</td>
<td>0.822</td>
<td>0.818</td>
<td>0.802</td>
<td>0.699</td>
<td>0.630</td>
<td>0.339</td>
<td>0.241</td>
<td>0.152</td>
<td>0.114</td>
<td>0.099</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>0.040</td>
<td>0.040</td>
<td>0.040</td>
<td>0.038</td>
<td>0.036</td>
<td>0.023</td>
<td>0.013</td>
<td>-0.003</td>
<td>-0.010</td>
<td>-0.005</td>
<td>-0.001</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$D_L = 0.822; \quad \Delta D_L = 0.040.$
Absorption Curves of Lanthanum 5-Nitro Salicylate in Aqueous Solution.

$T_L = 2.497 \times 10^{-4}$ mole/l.
$T_M = 1 \times 10^{-2}$ mole/l.
$h^o = 5.82 \times 10^{-3}$ mole/l.
$I = 0.1$
$L = 4$ cm.

Optical Density

$\lambda (\text{m} \mu)$

0 10 20 30 40 50 60 70 80 90 100 200 250
TABLE 4.14. VARIATION OF $\Delta D$ WITH $h^0$ - LANTHANUM 5-NITRO SALICYLATE

$T_L = 9.994 \times 10^{-4}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $\lambda = 390\mu$; $L = 2\text{cm}; I = 0.1$.

<table>
<thead>
<tr>
<th>$h^0 \times 10^3$</th>
<th>0.004</th>
<th>0.048</th>
<th>0.093</th>
<th>0.460</th>
<th>1.232</th>
<th>6.008</th>
<th>10.88</th>
<th>50.43</th>
<th>100.3</th>
<th>200.5</th>
<th>350.4</th>
<th>500.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^0$</td>
<td>1.374</td>
<td>1.372</td>
<td>1.360</td>
<td>1.330</td>
<td>1.128</td>
<td>0.927</td>
<td>0.752</td>
<td>0.372</td>
<td>0.287</td>
<td>0.237</td>
<td>0.213</td>
<td>0.203</td>
</tr>
<tr>
<td>$D$</td>
<td>1.330</td>
<td>1.330</td>
<td>1.318</td>
<td>1.290</td>
<td>1.092</td>
<td>0.895</td>
<td>0.739</td>
<td>0.382</td>
<td>0.303</td>
<td>0.241</td>
<td>0.216</td>
<td>0.204</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>0.044</td>
<td>0.042</td>
<td>0.042</td>
<td>0.040</td>
<td>0.036</td>
<td>0.032</td>
<td>0.013</td>
<td>-0.010</td>
<td>-0.016</td>
<td>-0.004</td>
<td>-0.003</td>
<td>-0.001</td>
</tr>
</tbody>
</table>

$D_L = 1.330$; $\Delta D_L = 0.044$. 
**TABLE 4.15 DETERMINATION OF \( D_0 \) AND \( D_1 \) FOR 3-NITRO SALICYLIC ACID**

\[ T_L = 2.567 \times 10^{-4} \text{mole/l.} \quad \lambda = 410 \mu \text{m} \quad l = 4 \text{cm.} \]

<table>
<thead>
<tr>
<th>( a \times 10^3 ) mole/l.</th>
<th>( d \times 10^2 ) mole/l.</th>
<th>( D^0 )</th>
<th>( h^0 f^2 \times 10^3 )</th>
<th>( x \times 10^2 )</th>
<th>( y = D^0 x \times 10^2 )</th>
<th>( \Delta y \times 10^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.350</td>
<td>9.016</td>
<td>0.590</td>
<td>0.900</td>
<td>1.430</td>
<td>1.108</td>
<td>-0.001</td>
</tr>
<tr>
<td>8.293</td>
<td>9.184</td>
<td>0.622</td>
<td>1.266</td>
<td>1.467</td>
<td>1.111</td>
<td>0.000</td>
</tr>
<tr>
<td>6.300</td>
<td>9.380</td>
<td>0.556</td>
<td>2.787</td>
<td>1.619</td>
<td>1.128</td>
<td>+0.001</td>
</tr>
<tr>
<td>4.300</td>
<td>9.587</td>
<td>0.597</td>
<td>4.004</td>
<td>1.740</td>
<td>1.142</td>
<td>+0.001</td>
</tr>
<tr>
<td>1.820</td>
<td>9.789</td>
<td>0.758</td>
<td>5.229</td>
<td>1.863</td>
<td>1.159</td>
<td>-0.002</td>
</tr>
<tr>
<td>1.220</td>
<td>9.890</td>
<td>0.775</td>
<td>6.485</td>
<td>1.989</td>
<td>1.173</td>
<td>+0.001</td>
</tr>
</tbody>
</table>

\( D_0 = 0.118 \pm 0.003 \), \( \varepsilon_0 = 114 \), \( \varepsilon_0 = 3 \). \( D_0 \) (direct measurement) \( = 0.099 \), \( \varepsilon_0 = 96 \).

\( D_1 = 0.818 \pm 0.007 \), \( \varepsilon_1 = 797 \), \( \varepsilon_1 = 7 \).
FIGURE 4.21
DETERMINATION OF D₀ AND D₁ FOR 3-NITRO SALICYLIC ACID.
TABLE 4.16 DETERMINATION OF $D_0$ AND $D_1$ FOR 5-NITRO SALICYLIC ACID

$T_L = 9.9833 \times 10^{-7}$ mole/l.; $I = 0.1$; $\lambda = 390$ nm; $l = 1$ cm.

<table>
<thead>
<tr>
<th>$a \times 10^2$ (mole/l.)</th>
<th>$d \times 10^2$ (mole/l.)</th>
<th>$D^0$</th>
<th>$h_1^0 f_1^2 \times 10^3$</th>
<th>$x \times 10^2$</th>
<th>$y = D^0 x$</th>
<th>$\Delta y \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.323</td>
<td>8.999</td>
<td>0.628</td>
<td>0.759</td>
<td>0.833</td>
<td>5.228</td>
<td>+0.010</td>
</tr>
<tr>
<td>1.326</td>
<td>9.201</td>
<td>0.598</td>
<td>1.340</td>
<td>0.891</td>
<td>5.330</td>
<td>-0.027</td>
</tr>
<tr>
<td>3.320</td>
<td>9.402</td>
<td>0.537</td>
<td>2.508</td>
<td>1.008</td>
<td>5.415</td>
<td>+0.019</td>
</tr>
<tr>
<td>5.337</td>
<td>9.604</td>
<td>0.492</td>
<td>3.702</td>
<td>1.127</td>
<td>5.546</td>
<td>+0.022</td>
</tr>
<tr>
<td>7.330</td>
<td>9.805</td>
<td>0.461</td>
<td>4.891</td>
<td>1.246</td>
<td>5.741</td>
<td>-0.039</td>
</tr>
<tr>
<td>9.323</td>
<td>9.906</td>
<td>0.426</td>
<td>6.086</td>
<td>1.366</td>
<td>5.820</td>
<td>+0.015</td>
</tr>
</tbody>
</table>

$D_0 = 0.112$; $\sigma_{D_0} = \pm 0.006$. $\varepsilon_0 = 112$; $\sigma_{\varepsilon_0} = \pm 6$. $D_0$ (direct measurement) = 0.102; $\varepsilon_0 = 102$.

$D_1 = 0.681$; $\sigma_{D_1} = \pm 0.000$. $\varepsilon_1 = 680$; $\sigma_{\varepsilon_1} = \pm 0$. 
FIGURE 4.22 DETERMINATION OF D₀ AND D₁ FOR 5-NITRO SALICYLIC ACID.

h₀ × 10⁻³

5 6 7 8

D₀ × 10⁻³

0 5 10
points lie on a good straight line.

**DETERMINATION OF THE ASSOCIATION CONSTANTS**

**OF LANTHANUM 3-, AND 5- NITRO SALICYLATES**

In applying the optimization procedure to the determination of the association constants in the present case, the calculated values $D_c = 0.356$ and $D_c = 0.645$ (l = 1 cm.) for lanthanum 3-, and 5- nitro salicylates, respectively, were used. (see page 95). It was found that, in each case, the plot of $\alpha$ against $D_c$ gave a well defined minimum. The values of $\alpha$ and $D_c$ corresponding to these minima are given in tables (4.17) and (4.18). These show that, under favourable conditions, the procedure is capable of determining association constants as small as 40, with a standard deviation less than 3%. An inspection of the plots of $y' = (\Delta x + T L_1)/c$ against $x$ for the two ion pairs, shown in figures (4.23) and (4.24), indicate that the experimental points lie on good straight lines.

The values of $D_c$, for each ion pair, was also computed by means of equation (4.32). The results of these calculations are given in tables (4.17) and (4.18) which show that the values of $D_c$ found by this means are in perfect agreement with those obtained from the plots of $\alpha$ against $D_c$. The plots of $y'' = \Delta h(D_o - D_1) - \Delta x T L + D_1 c$ against $c$, are given in figures (4.25), and (4.26). These show that in each case, the experimental points lie on very good straight lines.

In conclusion, it may be said the optimization procedure appears to lead to a satisfactory value for the association constant, providing that the value of $D_c$ is fairly accurately known beforehand.
<table>
<thead>
<tr>
<th>a x 10^3</th>
<th>d x 10^2</th>
<th>D</th>
<th>ΔD</th>
<th>Δh x 10^6</th>
<th>c x 10^5</th>
<th>y' x 10</th>
<th>Δy' x 10</th>
<th>y'' x 10^6</th>
<th>Δy'' x 10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.350</td>
<td>2.994</td>
<td>0.577</td>
<td>0.032</td>
<td>1.273</td>
<td>2.041</td>
<td>1.694</td>
<td>+0.009</td>
<td>7.514</td>
<td>+0.017</td>
</tr>
<tr>
<td>8.293</td>
<td>3.196</td>
<td>0.507</td>
<td>0.030</td>
<td>1.660</td>
<td>1.940</td>
<td>1.786</td>
<td>-0.039</td>
<td>7.159</td>
<td>0.000</td>
</tr>
<tr>
<td>6.303</td>
<td>3.398</td>
<td>0.536</td>
<td>0.023</td>
<td>3.071</td>
<td>1.797</td>
<td>1.942</td>
<td>-0.020</td>
<td>6.643</td>
<td>-0.012</td>
</tr>
<tr>
<td>4.301</td>
<td>3.599</td>
<td>0.574</td>
<td>0.020</td>
<td>4.033</td>
<td>1.764</td>
<td>1.990</td>
<td>+0.083</td>
<td>6.523</td>
<td>+0.014</td>
</tr>
<tr>
<td>1.820</td>
<td>3.801</td>
<td>0.728</td>
<td>0.015</td>
<td>4.284</td>
<td>1.535</td>
<td>2.293</td>
<td>-0.074</td>
<td>5.653</td>
<td>+0.009</td>
</tr>
<tr>
<td>1.224</td>
<td>3.902</td>
<td>0.743</td>
<td>0.013</td>
<td>4.917</td>
<td>1.515</td>
<td>2.335</td>
<td>+0.033</td>
<td>5.588</td>
<td>+0.002</td>
</tr>
</tbody>
</table>

α = 11.91; \( \sigma_\alpha = \pm 0.13 \); \( D_c^\alpha = 0.369 \); \( \sigma_{D_c^\alpha} = \pm 0.001 \). \( K = 39.2 \); \( \sigma_K = \pm 1.4 \).
FIGURE 4.23 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM 3-NITRO SALICYLATE.
FIGURE 4.24
DETERMINATION OF $D^*$ FOR LANTHANUM 3-NITRO SALICYLATE.

$0 \times 10^6$

$C \times 10^6$

10

20

15

25

0
### TABLE 4.18 ASSOCIATION CONSTANT OF LANTHANUM 5-NITRO SALICYLATE

\[ T_L = 9.9833 \times 10^{-4} \text{ mole/l.}; \quad T_M = 1 \times 10^{-2} \text{ mole/l.}; \quad I = 0.1; \quad \lambda = 390 \text{ m} \mu; \quad l = 1 \text{ cm}; \quad D_c = 0.293. \]

<table>
<thead>
<tr>
<th>( a \times 10^3 )</th>
<th>( d \times 10^2 )</th>
<th>( D )</th>
<th>( \Delta D )</th>
<th>( \Delta h \times 10^5 )</th>
<th>( c \times 10^5 )</th>
<th>( y' \times 10 )</th>
<th>( \Delta y' \times 10 )</th>
<th>( y'' \times 10^5 )</th>
<th>( \Delta y'' \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.323</td>
<td>2.988</td>
<td>0.603</td>
<td>0.025</td>
<td>0.639</td>
<td>7.449</td>
<td>1.022</td>
<td>-0.119</td>
<td>2.191</td>
<td>-0.009</td>
</tr>
<tr>
<td>1.326</td>
<td>3.190</td>
<td>0.575</td>
<td>0.023</td>
<td>1.054</td>
<td>7.384</td>
<td>1.036</td>
<td>-0.071</td>
<td>2.140</td>
<td>+0.023</td>
</tr>
<tr>
<td>3.320</td>
<td>3.392</td>
<td>0.519</td>
<td>0.018</td>
<td>1.727</td>
<td>7.227</td>
<td>1.070</td>
<td>+0.027</td>
<td>2.130</td>
<td>-0.013</td>
</tr>
<tr>
<td>5.337</td>
<td>3.593</td>
<td>0.478</td>
<td>0.014</td>
<td>2.197</td>
<td>6.911</td>
<td>1.129</td>
<td>+0.093</td>
<td>2.037</td>
<td>-0.020</td>
</tr>
<tr>
<td>7.330</td>
<td>3.795</td>
<td>0.450</td>
<td>0.011</td>
<td>2.392</td>
<td>6.259</td>
<td>1.255</td>
<td>+0.096</td>
<td>1.812</td>
<td>+0.021</td>
</tr>
<tr>
<td>9.323</td>
<td>3.895</td>
<td>0.419</td>
<td>0.007</td>
<td>2.222</td>
<td>5.100</td>
<td>1.540</td>
<td>-0.062</td>
<td>1.498</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

\( \alpha = 10.840; \quad \sigma_\alpha = \pm 0.338. \quad D_c^\lambda = 0.293; \quad \sigma_{D_c^\lambda} = \pm 0.001. \quad K = 43.4; \quad \sigma_K = \pm 1.6. \)
FIGURE 4.25
DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM 5-NITRO SALICYLATE.
FIGURE 4.26 DETERMINATION OF $D^*_c$ FOR LANTHANUM 5-NITRO SALICYLATE.
THE LANTHANUM SALICYLALDEHYDE SYSTEMS.

The experimental evidence which we have obtained leads to the conclusion that all the lanthanum salicylate ion pairs studied in the present work, are formed through ion association between the \( \text{La}^{3+} \) and the \( \text{HL}^{-} \) ion and do not involve the phenolate group. Since, the values of the second dissociation constants of the salicylic acids employed in the present work, vary from \( 10^{-11} - 10^{-14} \) [31], this type of behaviour is to be expected. It is possible, however, that the stability of these ion pairs is somewhat enhanced by ion-dipole interaction with the phenolate group. The question now arises as to the conditions under which the \( \text{La}^{3+} \) ion will interact with the phenolate group. That such interaction is possible has already been shown by Postmus et alia [59], who studied ion association between the \( \text{La}^{3+} \)-ion and some substituted salicylaldehydes. Nevertheless, to test the applicability of the optimization procedure to these systems, it was decided to redetermine the association constants of the ion pairs of the \( \text{La}^{3+} \)-ion with the anions of some salicylaldehydes.

EVIDENCE FOR ION ASSOCIATION

Evidence for ion association in the present systems, was found by use of the procedure described in the case of the lanthanum salicylates. Accordingly, two series of solutions, A and B, were prepared whose hydrogen ion concentration ranged from \( h^0 \approx 1 \times 10^{-3} - 1 \times 10^{-6} \) mole/l., for the \( \text{La}^{3+} \)-ion/salicylaldehyde system, and from \( h^0 \approx 1 \times 10^{-3} - 1 \times 10^{-5} \) mole/l., for the \( \text{La}^{3+} \)-ion /3-, and 5-nitro salicylaldehyde systems. Just as in the case of the lanthanum salicylates, the concentration of \( \text{La}^{3+} \)-ions in all solutions of series A was made much greater than that of the ligand so as to minimize the formation of ion pairs containing more than one ligand per metal ion.
and thus, to satisfy the fundamental assumption underlying the optimization procedure. The absorption curves of these series of solution were then recorded as a function of pH. Some of the absorption curves obtained are shown in figures (4.27)-(4.29), (4.30)-(4.33), and (4.34)-(4.37) for the \( \text{La}^{3+}/\text{salicylaldehyde} \) and the \( \text{La}^{3+}/\text{3-} \), and 5-nitro salicylaldehyde systems, respectively.

It will be noticed that, in each case, the absorption curves of the solutions of series A (the \( \text{La}^{3+}/\text{salicylaldehyde} \) systems) are very different from those of the corresponding solutions of series B (salicylaldehyde only). The differences observed are discussed in greater detail below.

**THE pH DEPENDENCE OF THE ABSORPTION CURVES OF THE LANTHANUM/SALICYLALDEHYDE SYSTEM**

The effect of varying the pH in the range 1-3 on the absorption curves of the solutions of series A, has been found to be negligible. In this pH range, the absorption spectra of the solutions of series A exhibit a single absorption band in the wavelength region 270-450\( \mu \text{m} \), with a maximum at \( \lambda = 325\mu\text{m} \). Above pH3, increasing pH has a very profound effect on the absorption curves of solutions of series A in that the absorption band at \( \lambda = 325\mu\text{m} \) gradually decreases while a new band seems to appear at \( \lambda = 380\mu\text{m} \). At about pH=7, the absorption band at \( \lambda = 325\mu\text{m} \) has disappeared and the development of the new band at \( \lambda = 380\mu\text{m} \) is virtually complete. Above pH=8, further increase in pH has no effect on the absorption curves of the lanthanum/salicylaldehyde solutions. This type of behaviour can be best explained by assuming that, at this stage, the extent of complex formation
has reached a maximum. In fact, due to the large excess of lanthanum ions, under these conditions virtually all the ligand has been converted into complex; the absorption band of the A solutions can thus be regarded as being characteristic of the lanthanum/salicylaldehyde ion pair.

Since, the dissociation constant of salicylaldehyde is relatively small \( K_1 = 10^{-3.37} \), the effect of increasing the pH on the absorption curves of solutions of series B is negligible up to about pH=6. In this pH range, the absorption curves of these solutions also exhibit a single absorption band at \( \lambda = 325\text{mÅ} \) (see figure (4.27)). From about pH=6 onwards, considerable changes in the absorption curves of the B solutions take place: the absorption band at \( \lambda = 325\text{mÅ} \) gradually disappears while a new band appears at \( \lambda = 380\text{mÅ} \). Above pH=10, the absorption curves consist of a single band at \( \lambda = 380\text{mÅ} \), which does not change with further increase in pH. For the sake of comparison, the absorption curves of an A solution at pH=6, and of a B solution at pH=13, are shown in figure (4.29). Although the single absorption bands exhibited by the two types of solution have maxima at the same wavelength \( (\lambda = 380\text{mÅ}) \), the band for the A solutions is considerably higher than that of the B solutions. Since the pH variation of the optical density of the A series of solutions was the largest at \( \lambda = 380\text{mÅ} \), this wavelength was adopted for the study of ion association in the \( \text{La}^{3+}/\text{salicylaldehyde} \) system. The variation of \( D^0, D \) and \( \Delta D \) at this wavelength is given in table (4.19).

The fact that the absorption maximum, for both the salicylaldehyde anion and the lanthanum-salicylaldehyde system, occurs at the same wavelength seems to indicate that complex formation occurs here, through ion association. The large difference in the heights of the two absorption bands, also suggests that the \( \text{La}^{3+}/\text{salicylaldehyde} \) ion pair should be considerably
more stable than the ion pair of the lanthanum salicylate system. It is
rather surprising that Postmus et alia [59], who also studied the lanthanum/
salicylaldehyde system, made no mention of the appearance of the characteristic
absorption band of the La$^{3+}$/salicylaldehyde ion pair.

THE pH DEPENDENCE OF THE ABSORPTION CURVES OF THE
LANTHANUM/3-, AND 5-NITRO SALICYLALDEHYDE SYSTEMS

The pH dependence of the absorption curves for both series of
solutions in the present case, was found to be essentially the same as
that observed for the lanthanum/salicylaldehyde system. In both cases,
the limiting absorption bands of the ion pairs observed at sufficiently
high pH values, (pH ~ 6), were considerably higher than those of the
corresponding absorption bands of the anions. However, in contrast to the
La$^{3+}$/salicylaldehyde system, the maxima of the limiting absorption curves
of the ion pairs did not coincide with those of the corresponding anions
but were found to be shifted by about 20μm towards shorter wavelength
(see figures (4.33) and (4.37)). The wavelengths at which these maxima
occur were adopted for the determination of the association constants of
these ion pairs. The variation of $D^0$, $D$ and $ΔD$, for the two systems at these
wavelengths are given in tables (4.20) and (4.21).

DETERMINATION OF $D_0$ AND $D_1$

For both 3- and 5-nitro salicylaldehyde, the quantities $D_0$ and $D_1$
were found in the usual way, that is, by means of equation (4.27). The
results of these experiments are summarised in tables (4.22) and (4.23).
FIGURES 4.27 - 4.29

ABSORPTION CURVES FOR THE LANTHANUM
SALICYLALDEHYDE SYSTEM

LEGEND

$T_L = 1.031 \times 10^{-4}$ mole/l.

$T_M = 1 \times 10^{-2}$ mole/l.

$I = 0.1$

$l = 4$ cm.

-- Series A

--------- Series B

FIGURE 4.27. $h^0 = 6.714 \times 10^{-4}$ mole/l.

FIGURE 4.28. $h^0 = 4.187 \times 10^{-5}$ mole/l.

Series A pH $\sim 8$.

Series B pH $\sim 13$. 
TABLE 4.19 VARIATION OF ΔD WITH h° - THE LANTHANUM/SALICYLALDEHYDE SYSTEM

\[ T_L = 1.031 \times 10^{-4} \text{ mole/l.}; T_M = 1 \times 10^{-2} \text{ mole/l.}; \lambda = 380 \text{ m}\mu; \, l = 2 \text{ cm}; \, I = 0.1. \]

<table>
<thead>
<tr>
<th>h° mole/l. ( \times 10^{-8} )</th>
<th>1d10</th>
<th>9.376</th>
<th>3.782</th>
<th>1.006</th>
<th>3.091</th>
<th>5.231</th>
<th>1.006</th>
<th>5.114</th>
<th>1.046</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \times 10^{-7} )</td>
<td>1d10</td>
<td>9.376</td>
<td>3.782</td>
<td>1.006</td>
<td>3.091</td>
<td>5.231</td>
<td>1.006</td>
<td>5.114</td>
<td>1.046</td>
</tr>
<tr>
<td>( \times 10^{-6} )</td>
<td>1d10</td>
<td>9.376</td>
<td>3.782</td>
<td>1.006</td>
<td>3.091</td>
<td>5.231</td>
<td>1.006</td>
<td>5.114</td>
<td>1.046</td>
</tr>
<tr>
<td>( \times 10^{-5} )</td>
<td>1d10</td>
<td>9.376</td>
<td>3.782</td>
<td>1.006</td>
<td>3.091</td>
<td>5.231</td>
<td>1.006</td>
<td>5.114</td>
<td>1.046</td>
</tr>
<tr>
<td>( \times 10^{-4} )</td>
<td>1d10</td>
<td>9.376</td>
<td>3.782</td>
<td>1.006</td>
<td>3.091</td>
<td>5.231</td>
<td>1.006</td>
<td>5.114</td>
<td>1.046</td>
</tr>
<tr>
<td>( \times 10^{-3} )</td>
<td>1d10</td>
<td>9.376</td>
<td>3.782</td>
<td>1.006</td>
<td>3.091</td>
<td>5.231</td>
<td>1.006</td>
<td>5.114</td>
<td>1.046</td>
</tr>
<tr>
<td>( \times 10^{-2} )</td>
<td>1d10</td>
<td>9.376</td>
<td>3.782</td>
<td>1.006</td>
<td>3.091</td>
<td>5.231</td>
<td>1.006</td>
<td>5.114</td>
<td>1.046</td>
</tr>
</tbody>
</table>

| \( D^0 \) | - | - | - | - | 0.010 | 0.008 | 0.008 | 0.008 | 0.008 | 0.008 | 0.008 | 0.008 |
| \( D \)    | 1.258 | 1.258 | 1.248 | 1.021 | 0.733 | 0.582 | 0.327 | 0.266 | 0.244 | 0.102 | 0.017 | 0.009 |
| \( \Delta D \) | - | - | - | - | -0.723 | -0.574 | -0.319 | -0.258 | -0.236 | -0.094 | -0.009 | -0.001 |

\[ D_L = 1.258; \, D_1 = 0.676; \, \Delta D_L = -0.582. \]
FIGURES 4.30 - 4.33

ABSORPTION CURVES FOR THE LANTHANUM/3-NITRO SALICYLALDEHYDE SYSTEM

LEGEND

$T_L = 4.653 \times 10^{-5}$ mole/l.

$T_M = 1 \times 10^{-2}$ mole/l.

$I = 0.1$

$l = 2$ cm.

--- Series A

--- Series B

FIGURE 4.30. $h^0 = 5.015 \times 10^{-4}$ mole/l.

FIGURE 4.31. $h^0 = 2.407 \times 10^{-4}$ mole/l.

FIGURE 4.32. $h^0 = 1.444 \times 10^{-4}$ mole/l.

Series A, $h^0 = 8.61 \times 10^{-6}$ mole/l.

Series B, pH $\sim$ 13.
TABLE 4.20 VARIATION OF $\Delta D$ WITH $h^o$ - THE LANTHANUM/3-NITRO SALICYLALDEHYDE SYSTEM

$T_L = 4.653 \times 10^{-5}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $\lambda = 405$ $\mu$m, $l = 2$ cm, $I = 0.1$.

<table>
<thead>
<tr>
<th>$h^o \times 10^5$ mole/l.</th>
<th>0.107</th>
<th>0.542</th>
<th>0.861</th>
<th>2.915</th>
<th>14.44</th>
<th>17.20</th>
<th>28.75</th>
<th>67.03</th>
<th>138.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^o$</td>
<td>-</td>
<td>-</td>
<td>0.605</td>
<td>0.468</td>
<td>0.079</td>
<td>0.072</td>
<td>0.056</td>
<td>0.048</td>
<td>0.040</td>
</tr>
<tr>
<td>$D$</td>
<td>0.786</td>
<td>0.786</td>
<td>0.783</td>
<td>0.780</td>
<td>0.552</td>
<td>0.314</td>
<td>0.209</td>
<td>0.123</td>
<td>0.077</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>-</td>
<td>-</td>
<td>-0.178</td>
<td>-0.312</td>
<td>-0.473</td>
<td>-0.242</td>
<td>-0.153</td>
<td>-0.085</td>
<td>-0.033</td>
</tr>
</tbody>
</table>

$D_L = 0.786$; $D_M = 0.619$; $\Delta D_L = -0.167$. 
ABSORPTION CURVES OF THE LANTHANUM/5- NITRO SALICYLALDEHYDE SYSTEM

LEGEND

$T_L = 1.074 \times 10^{-4}$ mole/l.

$T_M = 1 \times 10^{-2}$ mole/l.

$I = 0.1$

$l = 1$ cm.

Series A

Series B

FIGURE 4.34 $h^0 = 4.005 \times 10^{-4}$ mole/l.

FIGURE 4.35 $h^0 = 2.214 \times 10^{-4}$ mole/l.

FIGURE 4.36 $h^0 = 1.623 \times 10^{-4}$ mole/l.

Series A $h^0 = 1.424 \times 10^{-5}$ mole/l.

FIGURE 4.37

Series B pH $\approx 13$
**TABLE 4.21 VARIATION OF $\Delta D$ WITH $h^0$ - THE LANTHANUM/5-NITRO SALICYLALDEHYDE SYSTEM**

$T_L = 1.074 \times 10^{-4}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $\lambda = 360m\mu$; $l = 1cm$; $I = 0.1$.

<table>
<thead>
<tr>
<th>$h^0 \times 10^5$ mole/l</th>
<th>0.012</th>
<th>0.156</th>
<th>1.424</th>
<th>5.101</th>
<th>10.45</th>
<th>16.23</th>
<th>22.14</th>
<th>28.08</th>
<th>40.05</th>
<th>117.3</th>
<th>570.0</th>
<th>1070</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^0$</td>
<td>1.568</td>
<td>1.462</td>
<td>0.704</td>
<td>0.313</td>
<td>0.199</td>
<td>0.167</td>
<td>0.155</td>
<td>0.143</td>
<td>0.136</td>
<td>0.134</td>
<td>0.131</td>
<td>0.124</td>
<td>0.123</td>
</tr>
<tr>
<td>$D$</td>
<td>1.823</td>
<td>1.823</td>
<td>1.821</td>
<td>1.812</td>
<td>1.802</td>
<td>1.086</td>
<td>0.724</td>
<td>0.483</td>
<td>0.332</td>
<td>0.183</td>
<td>0.141</td>
<td>0.127</td>
<td>0.124</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>-0.256</td>
<td>-0.361</td>
<td>-1.117</td>
<td>-1.499</td>
<td>-1.603</td>
<td>-0.919</td>
<td>-0.569</td>
<td>-0.340</td>
<td>-0.196</td>
<td>-0.049</td>
<td>-0.010</td>
<td>-0.003</td>
<td>-0.001</td>
</tr>
</tbody>
</table>

$D_L = 1.823$; $D_I = 1.602$; $\Delta D_L = -0.221$. 
Table 4.22 Determination of $D_0$ and $D_1$ for 3-Nitro Salicyaldehyde

<table>
<thead>
<tr>
<th>$a \times 10^5$ (mole/l.)</th>
<th>$b \times 10^5$ (mole/l.)</th>
<th>$d \times 10^2$</th>
<th>$D_0 \times 10^4$</th>
<th>$D_1 \times 10^4$</th>
<th>$x_1 \times 10^5$</th>
<th>$y_1 \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0 75</td>
<td>7.7 48</td>
<td>9.9 99</td>
<td>0.157</td>
<td>0.716</td>
<td>1.217</td>
<td>-0.016</td>
</tr>
<tr>
<td>9.0 75</td>
<td>7.7 49</td>
<td>9.9 99</td>
<td>0.132</td>
<td>0.836</td>
<td>1.279</td>
<td>-0.030</td>
</tr>
<tr>
<td>9.0 75</td>
<td>6.5 5 7</td>
<td>9.9 99</td>
<td>0.112</td>
<td>1.562</td>
<td>1.393</td>
<td>+0.027</td>
</tr>
<tr>
<td>9.0 75</td>
<td>4.8 3 5</td>
<td>9.9 99</td>
<td>0.102</td>
<td>2.619</td>
<td>1.815</td>
<td>-0.093</td>
</tr>
<tr>
<td>9.0 75</td>
<td>2.6 4 9</td>
<td>9.9 99</td>
<td>0.095</td>
<td>3.967</td>
<td>2.731</td>
<td>-0.102</td>
</tr>
</tbody>
</table>

$D_0 = 0.081$; $D_1 = 1.016$; $\sigma_{D_0} = \pm 0.001$; $\sigma_{D_1} = \pm 0.041$; $\varepsilon_0 = 4.36$; $\varepsilon_1 = 5.395$; $\varepsilon_0 = 4.30$; $\varepsilon_1 = +217$. $D_0$ (direct measurement) = 0.080; $D_1$ (direct measurement) = 1.239; $\varepsilon_0 = 6.652$. 

$T = 4.653 \times 10^{-5}$ mole/l.; $I = 0.1$; $\lambda = 4.055 \mu m$; $\ell = 4.5 cm$. 

$\varepsilon_0 = 4.36$; $\varepsilon_1 = 5.395$.
DETERMINATION OF $D_0$ AND $D$, FOR 3-NITRO SALICYLALDEHYDE

Figure 4.38

$g / D_0 	imes 10^5$

$10^4 h^2 t^2$
### Table 4.23 Determination of $D_o$ and $D_1$ for 5-Nitro Salicylaldehyde

$T_L = 7.508 \times 10^{-5}$ mole/l.; $I = 0.1$; $\lambda = 360 \mu\lambda$; $\ell = 2$ cm.

<table>
<thead>
<tr>
<th>$a \times 10^3$</th>
<th>$b \times 10^3$</th>
<th>$d \times 10^2$</th>
<th>$D^0$</th>
<th>$h_{r1}^2 \times 10^4$</th>
<th>$x \times 10^5$</th>
<th>$y = D^0 \times \Delta y$</th>
<th>$\Delta y \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.362</td>
<td>1.203</td>
<td>9.967</td>
<td>0.261</td>
<td>0.998</td>
<td>1.045</td>
<td>2.424</td>
<td>-0.006</td>
</tr>
<tr>
<td>1.362</td>
<td>1.122</td>
<td>9.967</td>
<td>0.232</td>
<td>1.494</td>
<td>1.541</td>
<td>3.282</td>
<td>-0.037</td>
</tr>
<tr>
<td>1.362</td>
<td>1.040</td>
<td>9.967</td>
<td>0.217</td>
<td>1.993</td>
<td>2.041</td>
<td>4.100</td>
<td>-0.020</td>
</tr>
<tr>
<td>1.362</td>
<td>0.959</td>
<td>9.967</td>
<td>0.207</td>
<td>2.494</td>
<td>2.541</td>
<td>4.980</td>
<td>+0.020</td>
</tr>
<tr>
<td>1.362</td>
<td>0.884</td>
<td>9.967</td>
<td>0.201</td>
<td>2.953</td>
<td>3.000</td>
<td>5.760</td>
<td>+0.020</td>
</tr>
<tr>
<td>1.362</td>
<td>0.732</td>
<td>9.967</td>
<td>0.196</td>
<td>3.580</td>
<td>3.627</td>
<td>6.782</td>
<td>-0.018</td>
</tr>
</tbody>
</table>

$D_o = 0.169$; $\sigma_{D_o} = \pm 0.001$; $\epsilon_o = 1.125$; $\sigma_{\epsilon_o} = \pm 7$. $D_o$ (direct measurement) = 0.165; $\epsilon_o = 1.102$.

$D_1 = 2.228$; $\sigma_{D_1} = \pm 0.044$. $\epsilon_1 = 14,838$; $\sigma_{\epsilon_1} = \pm 293$. $D_1$ (direct measurement) = 2.238; $\epsilon_1 = 14,904$. 

DETERMINATION OF $D_0$ AND $D_I$ FOR 5-NITRO SALICYLALDEHYDE
Judging by the standard deviations $\sigma_D$ and $\sigma_{D_1}$ and also by the plots of $y = D^0x$ against $h_{D_1}^2$ shown in figures (4.38) and (4.39), the precision attained here is seen to be good.

Since, as already mentioned, the dissociation constant of salicylaldehyde is relatively small, the determination of $D_o$ and $D_1$ for this ligand by this means would require the use of suitable buffers. For this reason, it was decided to determine these quantities directly by measuring the optical density of salicylaldehyde in sufficiently acid solution and in sufficiently alkaline solution, respectively. The values of $D_o$ and $D_1$, so obtained, are given in table (4.24).

**DETERMINATION OF THE ASSOCIATION CONSTANTS OF THE La^{3+}/SALICYLALDEHYDE SYSTEM ION PAIRS BY MEANS OF THE OPTIMIZATION PROCEDURE**

On the basis of the cases studied so far, it appears that a successful application of the optimization procedure requires a knowledge of a fairly accurate value of $D_c$. Since, no direct information regarding the magnitude of $D_c$ was available in the present cases, it was decided to employ for this purpose, the highest $D$ values ($D_L$) at the selected wavelengths. Accordingly, the value of $D_c$ was varied around the value of $D_L$ and the standard deviation of $\alpha$ ($\sigma_\alpha$), corresponding to any given value of $D_c$, calculated. In all three cases, however, the plots of $\sigma_\alpha$ against these trial values of $D_c$ failed to show a minimum from which the best values of $\alpha$ and $D_c$ could be obtained.

In view of this failure, a new procedure for determining association constants was developed. The theoretical basis of this procedure is discussed in the following section.
APPROXIMATION PROCEDURES FOR THE DETERMINATION

OF ASSOCIATION CONSTANTS

In the following discussion the symbol HL will be used to represent
the salicylaldehydes. Under the experimental conditions employed, ion
pairing between the La$^{3+}$-ion and the anion of the salicylaldehydes can
thus be represented by the equation

$$La^{3+} + L^- \rightleftharpoons LaL^2+. \quad \ldots (4.45)$$

Since, in the process of associating with the La$^{3+}$-ion, the salicylic acids
act as mono-protic acids, all the equations derived for these systems are
applicable in the present case after suitable modification. Thus, the
thermodynamic association constant for the La$^{3+}$/salicylaldehyde ion pair
is defined by

$$K = \frac{c_2}{T_H^2} \left[ \frac{1}{L^-} \right] f^2, \quad \ldots (4.46)$$

and the concentrations of L$^-$ and HL being given by

$$[L^-] = \left( T_L - c \right) \frac{K_1}{(K_1 + hf_1^2)}, \quad \ldots (4.47)$$

$$[HL] = \left( T_L - c \right) \frac{hf_1^2}{(K_1 + hf_1^2)}. \quad \ldots (4.48)$$

On substituting for [L$^-$] from equation (4.47) into equation (4.46) and
rearranging we get

$$c = \frac{KT_H T_L K_L}{(K_L + K) + hf_1^2}. \quad \ldots (4.49)$$

As the pH increases indefinitely, that is, as the hydrogen ion
concentration tends toward zero, the above equations simplify to

$$c_L = \frac{KT_H T_L}{(K_T + F)}, \quad \ldots (4.50)$$

$$[L^-]_L = T_L - c_L, \quad \ldots (4.51)$$

$$[HL]_L \approx 0, \quad \ldots (4.52)$$
the subscript \( L \), referring to the limiting values of these quantities, reached at sufficiently high \( \text{pH} \) values.

Since, under these conditions the concentration of \( \text{HL} \) is seen to be vanishingly small, the limiting value of the optical density of solutions of series \( A \) is given by

\[
D_L = [L^-]_L e_L + c_L e_L. \quad \ldots (4.53)
\]

On substituting for \([L^-]_L\) and \(c_L\) from equations (4.51) and (4.50), respectively, equation (4.53) becomes

\[
D_c = D_L + \frac{F}{K_M} (D_L - D_L). \quad \ldots (4.54)
\]

The last equation forms an essential part of the new procedure developed for the spectrophotometric determination of association constants of ion pairs. Some idea about the usefulness of this equation can be obtained by considering it under various conditions.

1. When \( D_L = D_L \) and consequently the limiting value of \( AD (AD_L) \) zero, the equation simplifies to \( D_c = D_L \). This type of behaviour was observed in the case of lanthanum salicylate and lanthanum 5-bromo, lanthanum 5-chloro and lanthanum 5-bromo salicylate.

2. The condition \( D_L = D_L \) also obtains for values of \( K \) sufficiently large to make the second term negligibly small compared with \( D_L \). It will be seen later that this condition is indeed satisfied in the case of the lanthanum/salicylaldehyde system.

3. Inspection of the equation also shows that, in some cases, it should be possible to reduce the value of the second term by increasing the concentration of lanthanum as much as possible. However, the usefulness of this procedure is limited by the requirement of maintaining the ionic strength of the solutions at \( I = 0.1 \).
The validity of this equation can also be tested by calculating from it the values of $D_c$, for the two lanthanum nitro salicylate ion pairs. For this purpose, the above equation can be written in the form

$$D_c = D_L - \frac{F_{ADL}}{KT_M}, \quad \cdots (4.55)$$

where $AD^L$ is the limiting value of $AD$, at sufficiently high pH. On substituting for $D_L$, $AD_L$, and $K$, the values given in tables (4.13) and (4.17), (4.14) and (4.18), the values $D_c = 0.386$ and $D_c = 0.448$ are found for the lanthanum 3- and 5-nitro salicylates, respectively, in fairly good agreement with the values calculated by the optimization procedure.

There are a number of ways in which equation (4.54) can be employed in developing an iteration procedure for the spectrophotometric determination of association constants of ion pairs. The simplest way of utilizing this equation is to incorporate it into the optimization procedure after suitable modifications. Accordingly, an iteration procedure was developed involving the following steps:

First a reasonable value for $F/KT_M$ is assumed and a rough value of $D_c$ is obtained by means of equation (4.54). The latter value is then used to compute $\Delta h$ and $c$ values for the experimental solutions, using equations (4.21) and (4.31), respectively. An improved value if $F/KT_M$ is then obtained by means of equation (4.23), that is, by plotting $y=(\Delta hx+T_LK_1)/c$ against $x$, calculating the slope by applying the method of least squares. The improved value of $F/KT_M$ is introduced into equation (4.54) and a new cycle of approximations started. The process of successive approximations is continued until the values of $F/KT_M$ found from two successive cycles agree to within ± 0.01%.

This procedure, (which we shall call iteration procedure No.1), was programmed in terms of the algol code and all calculations were carried
out using either an Elliot 503 or an I.B.M. 1905F computer. A scheme for the evaluation of the standard deviation of the association constant was also incorporated into the program. The flow diagram showing details of the program is given in the appendix.

Before proceeding to the discussion of the application of this procedure, a few remarks about the general principles underlying approximation methods seem to be in order.

Iteration methods have been widely used in the determination of the dissociation constants of weak acids, association constants of ion pairs, and stability constants of complexes \([105, 108, 21]\). The essential condition for the successful application of any iteration process is the judicious choice of the starting value for the process of successive approximations.

There are a number of conditions which must be satisfied in order for the process of successive approximation to converge. A succinct account of the general principles underlying approximation procedures and their limitations can be found in "Handbook of Numerical Methods for Solutions of Equations", by V.L. Zaguskin, [114].

**EVALUATION OF THE ASSOCIATION CONSTANTS OF THE**

\[ La^{3+}-/\text{SALICYLALDEHYDE AND THE } La^{3+}-/\text{3-} \]

**AND 5-NITRO SALICYLALDEHYDE ION PAIRS**

**USING ITERATION PROCEDURE No.1**

Although the intense absorption bands found, in the present work, for these three ion pairs suggested that their association constants are considerably higher than those reported by Postmus et alia [59], it was decided to employ the latter values in starting the iteration procedure.
However, it should be mentioned that in calculating the association constants of these ion pairs, these authors ignored the activity coefficient of the ion pair and of the $\text{La}^{3+}$-ion. Tables (4.24), (4.25), and (4.26) give these authors values after correcting for these activity coefficients.

In all three cases, the iteration process was found to converge rapidly towards a definite value of $K$. The results of these calculations are summarised in tables (4.24), (4.25), and (4.26). The results are also illustrated in figures (4.40), (4.41), and (4.42) which show the plots of $y' = (?x + T\cdot K)$ against $x$, for the three ion pairs. It will be seen from the tables that in all three cases, the standard deviation of the association constants is less than $3\%$, thus indicating that satisfactory precision has been achieved. It will be noticed that there is very good agreement between the present value of the association constant of the $\text{La}^{3+}$/5-nitro salicylaldehyde ion pair and that reported by Postmus et alia and only fair agreement in the case of the $\text{La}^{3+}$/3-nitro salicylaldehyde ion pair. There is, however, no simple explanation for the inordinately large difference between the present value of the association constant of the lanthanum/salicylaldehyde ion pair. It is possible that in determining the association constant for this ion pair, the authors worked at a pH range ($\text{pH} < 4$), which in view of the small dissociation constant ($10^{-8.7}$) for the salicylaldehyde, is much too low for any reliable pH variations of the optical density to be observed.

However, to verify the results obtained by iteration procedure No. 1, and also to simplify this procedure, it was decided to explore other possible iteration processes. The results of these considerations are given in the following sections.
TABLE 4.24 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/
SALICYLALDEHYDE ION PAIR - ITERATION PROCEDURE No. 1

\[ T_L = 1.031 \times 10^{-4} \text{mole/l.}; \quad T_M = 1 \times 10^{-2} \text{mole/l.}; \quad I = 0.1; \quad \lambda = 380 \mu \text{m}; \quad \delta = 2 \text{cm}; \]

\[ F/\kappa T_M \text{ (starting value) } = 2 \times 10^{-4}; \quad D_L = 1.258; \quad D_C = 1.258; \quad D_O = 0.008; \quad D_L = 0.676 \]

<table>
<thead>
<tr>
<th>a x 10^4</th>
<th>b x 10^3</th>
<th>d x 10^2</th>
<th>D</th>
<th>ΔD</th>
<th>Δh x 10^5</th>
<th>c x 10^5</th>
<th>y^1 x 10^5</th>
<th>Δy^1 x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.996</td>
<td>6.903</td>
<td>4.007</td>
<td>0.733</td>
<td>-0.723</td>
<td>5.970</td>
<td>5.978</td>
<td>0.578</td>
<td>-0.001</td>
</tr>
<tr>
<td>6.996</td>
<td>6.789</td>
<td>4.007</td>
<td>0.641</td>
<td>-0.633</td>
<td>5.217</td>
<td>5.220</td>
<td>1.278</td>
<td>+0.001</td>
</tr>
<tr>
<td>6.996</td>
<td>6.618</td>
<td>4.007</td>
<td>0.582</td>
<td>-0.574</td>
<td>4.732</td>
<td>4.733</td>
<td>2.331</td>
<td>0.000</td>
</tr>
<tr>
<td>6.996</td>
<td>6.390</td>
<td>4.007</td>
<td>0.557</td>
<td>-0.549</td>
<td>4.526</td>
<td>4.527</td>
<td>3.736</td>
<td>0.000</td>
</tr>
<tr>
<td>6.996</td>
<td>6.218</td>
<td>4.007</td>
<td>0.491</td>
<td>-0.483</td>
<td>3.982</td>
<td>3.983</td>
<td>4.796</td>
<td>-0.001</td>
</tr>
<tr>
<td>6.996</td>
<td>5.990</td>
<td>4.007</td>
<td>0.327</td>
<td>-0.319</td>
<td>2.630</td>
<td>2.631</td>
<td>6.201</td>
<td>-0.001</td>
</tr>
</tbody>
</table>

\[ F/\kappa T_M \text{ (final value) } = 1.2 \times 10^{-4}; \quad \sigma_{F/\kappa T_M} = \pm 0.001 \times 10^{-4}. \]

\[ K \text{ (present value) } = 3.525 \times 10^6; \quad \sigma_K = \pm 0.003 \times 10^6. \quad K \text{ (previous value) } = 1.07 \times 10^6 \]
FIGURE 4.40 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/SALICYLALDEHYDE ION PAIR —

ITERATION PROCEDURE No1
## Table 4.25
Determination of the Association Constant of the Lanthanum/3-nitro Salicylaldehyde Ion Pair - Iteration Procedure No. 1

<table>
<thead>
<tr>
<th>a x 10^4</th>
<th>b x 10^4</th>
<th>d x 10^2</th>
<th>D</th>
<th>ΔD</th>
<th>Δh x 10^5</th>
<th>c x 10^5</th>
<th>y' x 10^5</th>
<th>Δy' x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.075</td>
<td>7.948</td>
<td>4.005</td>
<td>1.022</td>
<td>-0.865</td>
<td>2.494</td>
<td>2.725</td>
<td>0.310</td>
<td>+0.067</td>
</tr>
<tr>
<td>9.075</td>
<td>7.749</td>
<td>4.005</td>
<td>0.627</td>
<td>-0.484</td>
<td>1.395</td>
<td>1.513</td>
<td>1.006</td>
<td>+0.007</td>
</tr>
<tr>
<td>9.075</td>
<td>7.484</td>
<td>4.005</td>
<td>0.560</td>
<td>-0.428</td>
<td>1.239</td>
<td>1.325</td>
<td>1.192</td>
<td>+0.002</td>
</tr>
<tr>
<td>9.075</td>
<td>6.557</td>
<td>4.005</td>
<td>0.418</td>
<td>-0.306</td>
<td>0.894</td>
<td>0.932</td>
<td>1.847</td>
<td>+0.013</td>
</tr>
<tr>
<td>9.075</td>
<td>4.835</td>
<td>4.005</td>
<td>0.318</td>
<td>-0.216</td>
<td>0.637</td>
<td>0.653</td>
<td>3.032</td>
<td>+0.001</td>
</tr>
<tr>
<td>9.075</td>
<td>2.649</td>
<td>4.005</td>
<td>0.246</td>
<td>-0.151</td>
<td>0.447</td>
<td>0.455</td>
<td>4.564</td>
<td>+0.010</td>
</tr>
</tbody>
</table>

F/KT_M (final value) = 0.132; \( \sigma_{F/KT_M} = \pm 0.001 \).

\( K \) (present work) = 3.243 x 10^3; \( K \) (previous work) = 4.58 x 10^3 \[59\].
FIGURE 4.41  DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/3-NITRO SALICYLALDEHYDE ION PAIR—

ITERATION PROCEDURE No 1
**TABLE 4.26 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/5-NITRO SALICYLALDEHYDE ION PAIR - ITERATION PROCEDURE No.1**

\[ T_L = 7.508 \times 10^{-5}\text{ mole/l.}; T_M = 1 \times 10^{-2}\text{ mole/l.}; I = 0.1; \lambda = 360\text{ m\mu}; l = 2\text{ cm}; \]

\[ F/KT_M \text{ (starting value) } = 0.4; D_L = 2.556; D_c = 2.608. \]

<table>
<thead>
<tr>
<th>(a \times 10^3)</th>
<th>(b \times 10^3)</th>
<th>(d \times 10^2)</th>
<th>(D)</th>
<th>(\Delta D)</th>
<th>(\Delta h \times 10^5)</th>
<th>(c \times 10^5)</th>
<th>(y^1 \times 10^4)</th>
<th>(\Delta y^1 \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.362</td>
<td>1.203</td>
<td>4.011</td>
<td>1.118</td>
<td>-0.857</td>
<td>2.639</td>
<td>2.793</td>
<td>1.114</td>
<td>+0.097</td>
</tr>
<tr>
<td>1.362</td>
<td>1.122</td>
<td>4.011</td>
<td>0.680</td>
<td>-0.448</td>
<td>1.384</td>
<td>1.438</td>
<td>1.731</td>
<td>+0.055</td>
</tr>
<tr>
<td>1.362</td>
<td>1.040</td>
<td>4.011</td>
<td>0.550</td>
<td>-0.333</td>
<td>1.031</td>
<td>1.060</td>
<td>2.319</td>
<td>+0.045</td>
</tr>
<tr>
<td>1.362</td>
<td>0.959</td>
<td>4.011</td>
<td>0.462</td>
<td>-0.255</td>
<td>0.790</td>
<td>0.807</td>
<td>2.926</td>
<td>+0.018</td>
</tr>
<tr>
<td>1.362</td>
<td>0.884</td>
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<td>0.391</td>
<td>-0.190</td>
<td>0.589</td>
<td>0.599</td>
<td>3.539</td>
<td>-0.062</td>
</tr>
<tr>
<td>1.362</td>
<td>0.782</td>
<td>4.011</td>
<td>0.365</td>
<td>-0.169</td>
<td>0.524</td>
<td>0.532</td>
<td>4.242</td>
<td>-0.039</td>
</tr>
</tbody>
</table>

\(F/KT_M\) (final value) = 0.159; \(\sigma_{F/KT_M} = \pm 0.002\).

\(K\) (present work) = 2.689 \times 10^3; \(\sigma_K = \pm 0.025 \times 10^3\). \(K\) (previous work) = 2.29 \times 10^3 \[59\].
FIGURE 4.42 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/5-NITRO SALICYLALDEHYDE ION PAIR — ITERATION PROCEDURE No1
ITERATION PROCEDURE No.2.

Both the optimization procedure and the iteration method No.1, make use of the optical density measurements carried out, not only on solutions of series A but also on those of series B. To simplify the iteration process a new procedure was developed which, apart from the quantities $D_0$ and $D_1$, relies solely on the optical density measurements carried out on solutions A. For this purpose, an expression relating the concentrations of the complex directly to the optical densities of the solutions A was derived as follows:

The optical density of solutions of salicylaldehyde of series A is given by

$$D/T_1 = D_0[HL] + D_1[L^-] + D_0c.$$  ...(4.56)

Upon substituting for $[L^-]$ from equation (4.47) and remembering that

$$T_1 = [HL] + [L^-] + c,$$  ...(4.57)

equation (4.56) becomes,

$$(D-D_0)T_1 = c\frac{P}{K_{TM}}(D_1-D_0) + (D_0-D_0).$$  ...(4.58)

Combining this equation with equation (4.54) and rearranging we finally obtain

$$c = (D-D_0)T_1/[((D_1-D_0)(1+P/K_{TM})].$$  ...(4.59)

For the purpose of computing the association constant of a given ion pair, a reasonable value of $P/K_{TM}$ is first assumed, and the corresponding concentrations of the ion pairs of the experimental solutions calculated by means of the last equation. The approximate values of $c$, so obtained, are then used to evaluate the values of $\Delta h$ from equation (4.21). Next, a
better value of $P/KT_M$ is found by means of equation (4.23), that is, by plotting $y' = (Ahx + T_{1L})/c$ against $x$ and measuring the slope of the plot, so obtained, with the aid of the method of least squares. A second cycle of operations is then started using the so improved value of $P/KT_M$. The process of iteration is continued until the values of $P/KT_M$ found from two successive cycles agree to within $\pm 0.01\%$.

This procedure was programmed in terms of the algol code and all calculations were carried out using an I.B.M. 1905F computer. A scheme for the evaluation of the standard deviation of the association constant was also incorporated into the program. The flow diagram showing details of the program is given in the appendix.

In all three cases, the process of iteration was successfully completed leading to definite values of the association constants. The results of these calculations are summarised in tables (4.27), (4.28), and (4.29). Plots of $y' = (Ahx + T_{1L})/c$ against $x$, based upon these results, gave very good straight lines, which are not shown here as they are virtually identical with those obtained by the use of iteration procedure No.1. It will be seen from the tables that the values for the association constants found by means of iteration procedure 2 are in excellent agreement with those obtained by iteration procedure No.1. It appears, therefore, that the present values for the lanthanum/salicylaldehyde ion pairs are correct and consequently, that of Postmus et alia for the lanthanum/salicylaldehyde ion pair itself is in error.

However, in order to test the reliability of the present values for the association constants of lanthanum/salicylaldehyde ion pairs still further, a third iteration process was evolved. Like the second iteration process, this also makes use of the properties of solutions A alone,
TABLE 4.27 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/
SALICYLALDEHYDE ION PAIR - ITERATION PROCEDURE No. 2

\[ T_L = 1.031 \times 10^{-4} \text{ mole/l.}; T_M = 1 \times 10^{-2} \text{ mole/l.}; I = 0.1; \lambda = 380 \mu; L = 2 \text{ cm}; \]

\[ F/KT_M \text{ (starting value)} = 2 \times 10^{-4}; D_o = 0.008; D_1 = 0.676; D_L = 1.258; D_c = 1.258 \]

<table>
<thead>
<tr>
<th>a x 10^4</th>
<th>b x 10^4</th>
<th>d x 10^2</th>
<th>D</th>
<th>( \Delta h \times 10^5 )</th>
<th>c x 10^5</th>
<th>y' x 10^5</th>
<th>( \Delta y' \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.996</td>
<td>6.903</td>
<td>4.007</td>
<td>0.733</td>
<td>5.971</td>
<td>5.979</td>
<td>0.578</td>
<td>0.000</td>
</tr>
<tr>
<td>6.996</td>
<td>6.789</td>
<td>4.007</td>
<td>0.641</td>
<td>5.217</td>
<td>5.220</td>
<td>1.278</td>
<td>+0.001</td>
</tr>
<tr>
<td>6.996</td>
<td>6.618</td>
<td>4.007</td>
<td>0.582</td>
<td>4.732</td>
<td>4.733</td>
<td>2.331</td>
<td>0.000</td>
</tr>
<tr>
<td>6.996</td>
<td>6.390</td>
<td>4.007</td>
<td>0.557</td>
<td>4.526</td>
<td>4.527</td>
<td>3.736</td>
<td>-0.001</td>
</tr>
<tr>
<td>6.996</td>
<td>6.218</td>
<td>4.007</td>
<td>0.491</td>
<td>3.982</td>
<td>3.983</td>
<td>4.796</td>
<td>-0.001</td>
</tr>
<tr>
<td>6.996</td>
<td>5.990</td>
<td>4.007</td>
<td>0.327</td>
<td>2.630</td>
<td>2.631</td>
<td>6.201</td>
<td>-0.001</td>
</tr>
</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 1.2 \times 10^{-4}; \quad \sigma_{F/KT_M} = + 0.001 \times 10^{-4}. \]

\[ K = 3.524 \times 10^6; \quad \sigma_K = + 0.003 \times 10^6. \]
TABLE 4.28 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/3-NITRO SALICYLALDEHYDE ION PAIR - ITERATION PROCEDURE No. 2

\[ T_L = 4.653 \times 10^{-5} \text{ mole/l.}; \ T_M = 1 \times 10^{-2} \text{ mole/l.}; I = 0.1; \lambda = 405 \mu; l = 4 \text{ cm}; \]

\[ F/KT_M \text{ (starting value)} = 0.4; D_o = 0.081; D_1 = 1.016; D_L = 1.570; D_c = 1.643. \]

<table>
<thead>
<tr>
<th>(a \times 10^k)</th>
<th>(b \times 10^k)</th>
<th>(d \times 10^2)</th>
<th>(D)</th>
<th>(\Delta h \times 10^5)</th>
<th>(c \times 10^5)</th>
<th>(y' \times 10^k)</th>
<th>(\Delta y' \times 10^k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.075</td>
<td>7.948</td>
<td>4.005</td>
<td>1.022</td>
<td>2.377</td>
<td>2.598</td>
<td>0.814</td>
<td>+0.063</td>
</tr>
<tr>
<td>9.075</td>
<td>7.749</td>
<td>4.005</td>
<td>0.627</td>
<td>1.390</td>
<td>1.507</td>
<td>1.006</td>
<td>+0.006</td>
</tr>
<tr>
<td>9.075</td>
<td>7.484</td>
<td>4.005</td>
<td>0.560</td>
<td>1.236</td>
<td>1.322</td>
<td>1.193</td>
<td>+0.001</td>
</tr>
<tr>
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<td>6.557</td>
<td>4.005</td>
<td>0.418</td>
<td>0.892</td>
<td>0.930</td>
<td>1.848</td>
<td>-0.014</td>
</tr>
<tr>
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<td>4.835</td>
<td>4.005</td>
<td>0.318</td>
<td>0.638</td>
<td>0.654</td>
<td>3.032</td>
<td>-0.002</td>
</tr>
<tr>
<td>9.075</td>
<td>2.649</td>
<td>4.005</td>
<td>0.246</td>
<td>0.448</td>
<td>0.455</td>
<td>4.563</td>
<td>-0.008</td>
</tr>
</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 0.132; \sigma_F/KT_M = \pm 0.001. \]

\[ K = 3.244 \times 10^3; \sigma_K = \pm 0.016 \times 10^3. \]
### Table 4.29

**Determination of the Association Constant of the Lanthanum/5-Nitro Salicylaldehyde Ion Pair - Iteration Procedure No. 2**

\[ T_L = 7.508 \times 10^{-5} \text{ mole/l.}; T_M = 1 \times 10^{-2} \text{ mole/l.}; I = 0.1; \lambda = 360 \text{ m\(\mu\)}; l = 2 \text{ cm}; \]

\[ F/KT_M \text{ (starting value)} = 0.4; D_0 = 0.169; D_L = 2.228; D_R = 2.556; D_C = 2.608 \]

<table>
<thead>
<tr>
<th>(a \times 10^3)</th>
<th>(b \times 10^3)</th>
<th>(d \times 10^2)</th>
<th>(D)</th>
<th>(\Delta h \times 10^5)</th>
<th>(c \times 10^5)</th>
<th>(y' \times 10^4)</th>
<th>(\Delta y' \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.362</td>
<td>1.203</td>
<td>4.011</td>
<td>1.118</td>
<td>2.456</td>
<td>2.601</td>
<td>1.123</td>
<td>+0.088</td>
</tr>
<tr>
<td>1.362</td>
<td>1.122</td>
<td>4.011</td>
<td>0.680</td>
<td>1.348</td>
<td>1.400</td>
<td>1.737</td>
<td>+0.049</td>
</tr>
<tr>
<td>1.362</td>
<td>1.040</td>
<td>4.011</td>
<td>0.550</td>
<td>1.015</td>
<td>1.044</td>
<td>2.325</td>
<td>+0.040</td>
</tr>
<tr>
<td>1.362</td>
<td>0.959</td>
<td>4.011</td>
<td>0.462</td>
<td>0.785</td>
<td>0.802</td>
<td>2.929</td>
<td>+0.015</td>
</tr>
<tr>
<td>1.362</td>
<td>0.884</td>
<td>4.011</td>
<td>0.391</td>
<td>0.597</td>
<td>0.608</td>
<td>3.531</td>
<td>-0.055</td>
</tr>
<tr>
<td>1.362</td>
<td>0.782</td>
<td>4.011</td>
<td>0.365</td>
<td>0.529</td>
<td>0.537</td>
<td>4.236</td>
<td>-0.034</td>
</tr>
</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 0.159; \sigma_{F/KT_M} = \pm 0.001. \]

\[ K = 2.693 \times 10^3; \sigma_K = \pm 0.022 \times 10^3. \]
(apart from $D_0$ and $D_1$), but differs from the former in that it replaces the quantity $\Delta h$ by $h$.

**ITERATION PROCEDURE No. 3**

In the present case, the electroneutrality condition takes the form

$$h = (\alpha - b) + c + [L^-], \quad \ldots (4.60)$$

which in view of equation (4.47) becomes

$$h = (\alpha - b) + c + \left(\frac{mL-c}{(K_{12} + hf_{12}^2)}\right). \quad \ldots (4.61)$$

It can be seen that equation (4.61), which is of the second order with respect to $h$, enables the evaluation of $h$ provided $c$ is known.

In developing the new iteration procedure use was made of the last equation together with equation (4.59) and equation (4.49), which for this purpose was put into the form

$$\left(\frac{mL-c}{c}\right) = \left(\frac{F/\xi}{K_{12}}\right) (1 + hf_{12}^2/K_{12}). \quad \ldots (4.62)$$

Hence, if $y = (mL-c)/c$ is plotted against $1 + hf_{12}^2/K_{12}$, a straight line should be obtained with a slope equal to $F/\xi K_{12}$.

Just as in the previous case, the iteration procedure is started by assuming a reasonable value of $F/\xi K_{12}$ and calculating the concentrations of the ion pairs in the experimental solutions by means of equation (4.59). These approximate $c$ values are then used to evaluate the corresponding values of the hydrogen ion concentration of the $A$ solutions from equation (4.61). Next, an improved value of $F/\xi K_{12}$ is found by means of equation (4.62), that is, by plotting $y = (mL-c)/c$ against $1 + hf_{12}^2/K_{12}$ and measuring the slope of the plot, so obtained, with the aid of the method of least squares. The so improved value of $F/\xi K_{12}$ is then used to start a second
cycle of approximations. The process of iteration is continued until the values of $F/\text{KT}_M$ found from two successive cycles agree to within $\pm 0.01\%$.

This procedure was programmed in terms of the algol code and all calculations were carried out using an I.B.M. 1905F computer. A scheme for the evaluation of the standard deviation of the association constant was also incorporated into the program. The flow diagram showing details of the program is given in the appendix.

The results of these calculations are summarised in tables (4.30) (4.31), and (4.32), and illustrated in figures (4.43), (4.44), and (4.45). It will be seen from the tables that, with the exception of the $\text{La}^{3+}$/salicylaldehyde ion pair, all the results are in excellent agreement with those found by iteration procedures 1 and 2. However, the association constant found for $\text{La}^{3+}$/salicylaldehyde ion pair by iteration procedure No. 3 is about 10% higher than that obtained by iteration procedures 1 and 2. All attempts to trace this discrepancy to errors in programming or in the paper tape which records the experimental data have failed.

**THE LANTHANUM/4-HYDROXY BENZALDEHYDE SYSTEM**

Of all the ion pairs studied so far, the $\text{La}^{3+}$/salicylaldehyde ion pair is the most stable. The high stability of this ion pair may be ascribed partly to the strong ionic interaction between the $\text{La}^{3+}$-ion and the salicylaldehyde anion, and partly to the $\text{La}^{3+}$-ion chelating through ion-dipole interaction with the oxygen atom of the aldehyde group. For the purpose of testing the latter possibility, ion pairing in the $\text{La}^{3+}$-ion/4-hydroxy benzaldehyde system, in which such ion-dipole interaction is not possible, was studied.
TABLE 4.30 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/ 
SALICYLALDEHYDE ION PAIR - ITERATION PROCEDURE No. 3

\[ T_L = 1.031 \times 10^{-4} \text{ mole/l.}; T_M = 1 \times 10^2 \text{ mole/l.}; I = 0.1; \lambda = 380 \mu; \lambda = 2 \text{ cm.} \]

\[ F/KT_M \text{ (starting value)} = 2 \times 10^{-6}; D_o = 0.008; D_1 = 0.676; D_L = 1.258; D_c = 1.258 \]

<table>
<thead>
<tr>
<th>a x 10^4</th>
<th>b x 10^4</th>
<th>d x 10^2</th>
<th>D</th>
<th>h x 10^4</th>
<th>c x 10^5</th>
<th>( x = 1 + \frac{hf^2}{K} )</th>
<th>( y = \frac{T_L - c}{c} )</th>
<th>( \Delta y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.996</td>
<td>6.903</td>
<td>4.007</td>
<td>0.733</td>
<td>0.691</td>
<td>5.979</td>
<td>1.007</td>
<td>0.724</td>
<td>-0.036</td>
</tr>
<tr>
<td>6.996</td>
<td>6.789</td>
<td>4.007</td>
<td>0.641</td>
<td>0.729</td>
<td>5.220</td>
<td>1.063</td>
<td>0.975</td>
<td>-0.016</td>
</tr>
<tr>
<td>6.996</td>
<td>6.618</td>
<td>4.007</td>
<td>0.582</td>
<td>0.851</td>
<td>4.733</td>
<td>1.241</td>
<td>1.178</td>
<td>-0.015</td>
</tr>
<tr>
<td>6.996</td>
<td>6.390</td>
<td>4.007</td>
<td>0.557</td>
<td>1.059</td>
<td>4.527</td>
<td>1.544</td>
<td>1.277</td>
<td>+0.038</td>
</tr>
<tr>
<td>6.996</td>
<td>6.218</td>
<td>4.007</td>
<td>0.491</td>
<td>1.176</td>
<td>3.983</td>
<td>1.715</td>
<td>1.588</td>
<td>+0.025</td>
</tr>
<tr>
<td>6.996</td>
<td>5.990</td>
<td>4.007</td>
<td>0.327</td>
<td>1.269</td>
<td>2.631</td>
<td>1.850</td>
<td>2.919</td>
<td>+0.094</td>
</tr>
</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 1.072 \times 10^{-6}; \sigma_{F/KT_M} = \pm 0.014 \times 10^{-6}. \]

\[ K = 3.987 \times 10^6; \sigma_K = \pm 0.053 \times 10^6. \]
FIGURE 4.43  DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/SALICYLALDEHYDE ION PAIR —

ITERATION PROCEDURE No 3
TABLE 4.31 DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM/3-NITRO SALICYLALDEHYDE ION PAIR - ITERATION PROCEDURE No. 3

\[ T_L = 4.653 \times 10^{-5} \text{ mole/l.}; T_M = 1 \times 10^{-2} \text{ mole/l.}; I = 0.1; \lambda = 405 \text{ m} \mu; L = 4 \text{ cm}; \\
F/KT_M \text{ (starting value)} = 0.4; D_0 = 0.081; D_1 = 1.016; D_L = 1.570; D_c = 1.643. \]

<table>
<thead>
<tr>
<th>a \times 10^k</th>
<th>b \times 10^k</th>
<th>d \times 10^2</th>
<th>D</th>
<th>h \times 10^4</th>
<th>c \times 10^5</th>
<th>\frac{hf_1^2}{K_1}</th>
<th>\frac{(T_L-c)}{c}</th>
<th>\Delta y</th>
<th>x \times 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.075</td>
<td>7.948</td>
<td>4.005</td>
<td>1.022</td>
<td>1.400</td>
<td>2.600</td>
<td>1.570</td>
<td>0.790</td>
<td>+0.114</td>
<td></td>
</tr>
<tr>
<td>9.075</td>
<td>7.749</td>
<td>4.005</td>
<td>0.627</td>
<td>1.496</td>
<td>1.508</td>
<td>1.670</td>
<td>2.085</td>
<td>+0.102</td>
<td></td>
</tr>
<tr>
<td>9.075</td>
<td>7.484</td>
<td>4.005</td>
<td>0.560</td>
<td>1.741</td>
<td>1.323</td>
<td>1.927</td>
<td>2.516</td>
<td>+0.008</td>
<td></td>
</tr>
<tr>
<td>9.075</td>
<td>6.557</td>
<td>4.005</td>
<td>0.418</td>
<td>2.624</td>
<td>0.931</td>
<td>2.855</td>
<td>3.999</td>
<td>-0.261</td>
<td></td>
</tr>
<tr>
<td>9.075</td>
<td>4.835</td>
<td>4.005</td>
<td>0.318</td>
<td>4.314</td>
<td>0.654</td>
<td>4.629</td>
<td>6.110</td>
<td>-0.049</td>
<td></td>
</tr>
<tr>
<td>9.075</td>
<td>2.649</td>
<td>4.005</td>
<td>0.246</td>
<td>6.482</td>
<td>0.455</td>
<td>6.904</td>
<td>9.215</td>
<td>-0.174</td>
<td></td>
</tr>
</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 0.131; \sigma_{F/KT_M} = \pm 0.006. \]

\[ K = 3.263 \times 10^3; \sigma_K = \pm 0.157 \times 10^3. \]
Figure 4.44
Determination of the Association Constant of the Lanthanum 3-Nitro Salicylaldehyde Pair
Iteration Procedure No.3

\[(1+hf_1/K_1) \times 10\]

\(c/c\text{'}\)


<table>
<thead>
<tr>
<th>a x 10^3</th>
<th>b x 10^3</th>
<th>d x 10^2</th>
<th>D</th>
<th>h x 10^4</th>
<th>c x 10^5</th>
<th>( x=1+\frac{hf^2}{K_1} )</th>
<th>( y=\frac{(T_L-c)}{c} )</th>
<th>( \Delta y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.362</td>
<td>1.203</td>
<td>4.011</td>
<td>1.118</td>
<td>1.866</td>
<td>2.603</td>
<td>2.557</td>
<td>1.912</td>
<td>+0.230</td>
</tr>
<tr>
<td>1.362</td>
<td>1.122</td>
<td>4.011</td>
<td>0.680</td>
<td>2.560</td>
<td>1.401</td>
<td>3.471</td>
<td>4.409</td>
<td>+0.106</td>
</tr>
<tr>
<td>1.362</td>
<td>1.040</td>
<td>4.011</td>
<td>0.550</td>
<td>3.336</td>
<td>1.045</td>
<td>4.493</td>
<td>6.256</td>
<td>+0.820</td>
</tr>
<tr>
<td>1.362</td>
<td>0.959</td>
<td>4.011</td>
<td>0.462</td>
<td>4.126</td>
<td>0.803</td>
<td>5.532</td>
<td>8.437</td>
<td>+0.241</td>
</tr>
<tr>
<td>1.362</td>
<td>0.884</td>
<td>4.011</td>
<td>0.391</td>
<td>4.853</td>
<td>0.608</td>
<td>6.489</td>
<td>11.46</td>
<td>-0.121</td>
</tr>
<tr>
<td>1.362</td>
<td>0.782</td>
<td>4.011</td>
<td>0.365</td>
<td>5.863</td>
<td>0.537</td>
<td>7.820</td>
<td>13.11</td>
<td>-0.079</td>
</tr>
</tbody>
</table>

F/KT_M (final value) = 0.157; \( \sigma_{F/KT_M} = +0.010 \).
K = \( 2.713 \times 10^2 \); \( \sigma_K = +0.171 \times 10^2 \).
FIGURE 4.45  DETERMINATION OF THE ASSOCIATION CONSTANT OF THE LANTHANUM 5-NITRO SALICYLALDEHYDE ION PAIR — ITERATION PROCEDURE No: 3

\[ \frac{(T_c-c)}{c} = \left(1 + \frac{h_f^2}{K_1}\right) \times 10 \]
EVIDENCE FOR ION PAIRING IN THE La$^{3+}$-ION/4-HYDROXY BENZALDEHYDE SYSTEM

To obtain evidence for ion pairing in this system, the experimental procedure used in all previous cases was applied. Accordingly, absorption curves for both A and B types of solutions were measured as a function of pH. A pair of absorption curves, obtained at pH\approx 8, is shown in figure (4.46). It was found that over the pH range 3-7, the absorption curves of solutions A coincide with the absorption curves of corresponding solutions of series B. From pH=7 onwards, however, slight differences in the two types of curves were seen, thus indicating that some ion pairing occurs. However, attempts to obtain the limiting absorption curve of the A solutions by increasing the pH failed, as at pH=8.25 lanthanum oxide started to precipitate from the solution.

Since, not even an approximate value for $D_L$ was known and since, the $\Delta D$ values observed, even under the most favourable conditions, were small, the determination of a reliable value for the association constant was not possible. This type of behaviour indicates that the La$^{3+}$/4-hydroxy benzaldehyde ion pair is considerably less stable than that formed by the La$^{3+}$-ion with the anion of salicylaldehyde. Since, both acids have approximately the same dissociation constant, it appears that in the La$^{3+}$/salicylaldehyde ion pair, some ion-dipole interaction of the La$^{3+}$-ion with the oxygen atom of the aldehyde group occurs.

THE LANTHANUM/BENZOIC ACID SYSTEMS

It was mentioned earlier that ion-dipole interaction between the La$^{3+}$-ion and the phenolic group may have a stabilizing effect on the lanthanum salicylate ion pairs. Although, judging by the magnitude of the
FIGURE 4.46
ABSORPTION CURVES FOR THE LANTHANUM/4-HYDROXY BENZALDEHYDE SYSTEM.

T_L = 2.606 \times 10^{-5} \text{ mole} / \text{l.}

T_M = 1 \times 10^{-2} \text{ mole} / \text{l.}

h = 1 \times 10^{-8} \text{ mole} / \text{l.}

I = 0.1

l = 4 \text{ cm.}

Series A

Series B

OPTICAL DENSITY

\lambda (\text{m\mu})
association constants of these ion pairs this effect cannot be very large, nevertheless, it was decided to investigate it by studying ion association of the La$^{3+}$-ion with the anions of some benzoic acids. For this purpose, benzoic acid and 4-hydroxy, 3-bromo, and 4-nitro benzoic acids were selected.

**EVIDENCE FOR ION ASSOCIATION IN THE LANTHANUM BENZOATE SYSTEMS**

To obtain spectrophotometric evidence for ion pairing in these systems, the experimental procedure used in all previous cases was applied. Accordingly, for each system, two series of solutions, A and B, were prepared. As the dissociation constants of all these acids are about $10^{-4}$, the hydrogen ion concentration of these series of solutions was varied from $1 \times 10^{-3} - 1 \times 10^{-5}$ mole/l. The absorption curves of these solutions were then recorded as a function of pH. A set of typical absorption curves observed for each system, is shown in figures (4.47), (4.48), (4.49), and (4.50), respectively. The wavelengths at which the pH variation of $D^0$, $D$ and $\Delta D$ are the most pronounced and the values of $\Delta D$ themselves are as large as possible were chosen for the study of ion association in these systems. The wavelengths, so selected, are given in tables (4.33), (4.34), (4.35), and (4.36). These tables also show the variation of $D^0$, $D$ and $\Delta D$ at the optimum wavelength for these systems. It will be seen that in the case of lanthanum 4-nitro benzoate, in the pH range 2.5 - 4.5, $\Delta D$ increases rapidly with increasing pH. Beyond that pH range, the rate of increase of optical density with pH slows down and by about pH 5-6, $\Delta D$ attains a constant finite value. Very similar behaviour to this was also observed with lanthanum 4-hydroxy benzoate except that as the second stage of ionization of the 4-hydroxy benzoic acid starts to occur beyond pH $\sim 6.5$, ...
the direct measurement of $D_L$ was not possible. However, as the value of $\Delta D$ was found to be constant over the pH range 5-6, this value of $\Delta D$ was assumed to be numerically equal to $\Delta D_L$, and the quantity $D_L$ was estimated from the relationship

$$D_L = D_1 - \Delta D_L. \quad \ldots (4.63)$$

The variation of $\Delta D$ with $h^0$ observed for lanthanum benzoate and lanthanum 3-bromo benzoate differs from that found for the other two lanthanum benzoates, in that, the value of $\Delta D$ changes sign at an intermediate pH value. This type of behaviour is similar to that observed previously with the lanthanum nitro salicylates. The values of the hydrogen ion concentration at which the values of $\Delta D$ change sign, were used to estimate the values of $D_0$ for lanthanum benzoate and lanthanum 3-bromo benzoate by means of equation (4.44). The values of $D_0$, found in this way, were $D_0 = 0.603$ for lanthanum benzoate and $D_0 = 0.753$ for lanthanum 3-bromo benzoate.

Since, the values of $\Delta D$ observed with all the lanthanum benzoates, studied in the present work, are significantly larger than the error associated with optical density measurements, it may be concluded that ion association occurs also here.

**DETERMINATION OF $D_0$ AND $D_1$**

The quantities $D_0$ and $D_1$ at the selected wavelengths for the present systems, were found in the usual way, that is, by means of equation (4.27). The results of these calculations are summarised in tables (4.37), (4.38), (4.39) and (4.40) and illustrated in figures (4.51), (4.52), (4.53), and (4.54). Since, the standard deviation of both $D_0$ and $D_1$, in each case, is less than 2%, the precision attained in this work must be regarded as satisfactory.
FIGURE 4.47 ABSORPTION CURVES OF LANTHANUM BENZOATE.

\[ T_L = 6.36 \times 10^{-5} \text{ mole/l.} \]
\[ T_M = 1 \times 10^{-2} \text{ mole/l.} \]
\[ h^o = 4.82 \times 10^{-5} \text{ mole/l.} \]
\[ I = 0.1 \]
\[ l = 4 \text{ cm.} \]

--- Series A
--- Series B
### Table 4.33 Variation of $\Delta D$ with $h^\circ$ - Lanthanum Benzoate

$T_L = 6.361 \times 10^{-5}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $\lambda = 240 \mu$; $\mu = 2$ cm; $I = 0.1$.

<table>
<thead>
<tr>
<th>$h^\circ \times 10^5$ mole/l</th>
<th>$D^\circ$</th>
<th>$D$</th>
<th>$\Delta D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.106</td>
<td>0.378</td>
<td>0.492</td>
<td>-0.114</td>
</tr>
<tr>
<td>0.513</td>
<td>0.379</td>
<td>0.494</td>
<td>-0.115</td>
</tr>
<tr>
<td>1.423</td>
<td>0.386</td>
<td>0.498</td>
<td>-0.112</td>
</tr>
<tr>
<td>2.773</td>
<td>0.432</td>
<td>0.508</td>
<td>-0.076</td>
</tr>
<tr>
<td>5.188</td>
<td>0.500</td>
<td>0.541</td>
<td>-0.041</td>
</tr>
<tr>
<td>10.52</td>
<td>0.586</td>
<td>0.598</td>
<td>-0.012</td>
</tr>
<tr>
<td>50.78</td>
<td>0.762</td>
<td>0.746</td>
<td>0.016</td>
</tr>
<tr>
<td>91.39</td>
<td>0.802</td>
<td>0.784</td>
<td>0.016</td>
</tr>
<tr>
<td>501.0</td>
<td>0.833</td>
<td>0.827</td>
<td>0.006</td>
</tr>
</tbody>
</table>

$D_L = 0.492; \quad \Delta D_L = -0.114.$
FIGURE 4.48 ABSORPTION CURVES OF LANTHANUM 4 - HYDROXY BENZOATE.

\[ T_L = 4.2176 \times 10^{-5} \text{ mole/l.} \]
\[ T_M = 1 \times 10^{-2} \text{ mole/l.} \]
\[ I = 0.1 \]
\[ L = 4 \text{ cm.} \]

Series A
Series B

Optical Density

\( \lambda \) (m

---
<table>
<thead>
<tr>
<th>h°x10^5 mole/l</th>
<th>~0.001</th>
<th>~0.005</th>
<th>0.008</th>
<th>0.017</th>
<th>0.127</th>
<th>1.187</th>
<th>7.203</th>
<th>10.70</th>
<th>504.5</th>
<th>90.94</th>
<th>261.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>D⁰</td>
<td>0.389</td>
<td>0.318</td>
<td>0.281</td>
<td>0.296</td>
<td>0.330</td>
<td>0.400</td>
<td>0.711</td>
<td>0.774</td>
<td>0.968</td>
<td>0.982</td>
<td>0.984</td>
</tr>
<tr>
<td>D</td>
<td>0.527</td>
<td>0.352</td>
<td>0.309</td>
<td>0.313</td>
<td>0.320</td>
<td>0.361</td>
<td>0.672</td>
<td>0.740</td>
<td>0.944</td>
<td>0.970</td>
<td>0.982</td>
</tr>
<tr>
<td>ΔD</td>
<td>-0.038</td>
<td>-0.034</td>
<td>-0.028</td>
<td>-0.017</td>
<td>0.010</td>
<td>0.039</td>
<td>0.039</td>
<td>0.034</td>
<td>0.024</td>
<td>0.012</td>
<td>0.002</td>
</tr>
</tbody>
</table>

ΔD_L = 0.039; D_L = 0.242.
FIGURE 4.49 ABSSORPTION CURVES OF LANTHANUM -3- BROMO BENZOATE.

$T_L = 9.82 \times 10^5$ mole/l.

$T_M = 1 \times 10^{-2}$ mole/l.

$h^0 = 9.6 \times 10^{-6}$ mole/l.

$I = 0.1$

$l = 4$ cm.

--- Series A

--- Series B
TABLE 4.35 VARIATION OF ΔD WITH $h^0$ - LANTHANUM 3-BROMO BENZOATE

$T_L = 9.817 \times 10^{-5}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $\lambda = 242 \mu m$; $l = 2 \text{ cm}; I = 0.1$.

<table>
<thead>
<tr>
<th>$h^0 \times 10^5$ mole/l</th>
<th>0.139</th>
<th>0.337</th>
<th>0.673</th>
<th>5.009</th>
<th>7.562</th>
<th>10.20</th>
<th>50.57</th>
<th>92.85</th>
<th>499.7</th>
<th>1012</th>
<th>2679</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^0$</td>
<td>0.410</td>
<td>0.412</td>
<td>0.414</td>
<td>0.514</td>
<td>0.551</td>
<td>0.600</td>
<td>0.800</td>
<td>0.866</td>
<td>0.966</td>
<td>0.972</td>
<td>0.976</td>
</tr>
<tr>
<td>$D$</td>
<td>0.502</td>
<td>0.501</td>
<td>0.522</td>
<td>0.574</td>
<td>0.596</td>
<td>0.626</td>
<td>0.796</td>
<td>0.858</td>
<td>0.956</td>
<td>0.968</td>
<td>0.976</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>-0.092</td>
<td>-0.089</td>
<td>-0.078</td>
<td>-0.060</td>
<td>-0.045</td>
<td>-0.026</td>
<td>0.004</td>
<td>0.008</td>
<td>0.010</td>
<td>0.004</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$D_L = 0.502$; $\Delta D_L = -0.092$. 
FIGURE 4.50 ABSORPTION CURVES FOR LANTHANUM 4-NITRO BENZOATE.

\[ T_L = 1 \times 10^{-6} \text{ mole/l.} \]
\[ T_M = 1 \times 10^{-2} \text{ mole/l.} \]
\[ h^0 = 1.65 \times 10^{-5} \text{ mole/l.} \]
\[ I = 0.1 \]
\[ l = 4 \text{ cm.} \]

---

Graph showing absorption curves for Lanthanum 4-nitro benzoate.

- **Series A**
- **Series B**

\[ \lambda (\text{m/\mu}) \]

OPTICAL DENSITY

---

200  10  20  30  40  50  60  70  80  90  100  200  300  400

0  1  2  3  4
### TABLE 4.36 VARIATION OF ΔD WITH $h^\circ$ - LANTHANUM 4-NITRO BENZOATE

$T_L = 9.999 \times 10^{-5}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $\lambda = 310\text{m}\mu$; $l = 2\text{cm}$; $I = 0.1$.

<table>
<thead>
<tr>
<th>$h^\circ \times 10^5$ mole/l.</th>
<th>0.097</th>
<th>0.607</th>
<th>1.016</th>
<th>1.715</th>
<th>10.14</th>
<th>49.98</th>
<th>94.57</th>
<th>590.8</th>
<th>1096</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^\circ$</td>
<td>0.700</td>
<td>0.699</td>
<td>0.692</td>
<td>0.682</td>
<td>0.674</td>
<td>0.584</td>
<td>0.516</td>
<td>0.428</td>
<td>0.418</td>
</tr>
<tr>
<td>$D$</td>
<td>0.652</td>
<td>0.652</td>
<td>0.652</td>
<td>0.646</td>
<td>0.642</td>
<td>0.566</td>
<td>0.508</td>
<td>0.424</td>
<td>0.416</td>
</tr>
<tr>
<td>$\Delta D$</td>
<td>0.048</td>
<td>0.047</td>
<td>0.040</td>
<td>0.036</td>
<td>0.028</td>
<td>0.018</td>
<td>0.008</td>
<td>0.004</td>
<td>0.002</td>
</tr>
</tbody>
</table>

$D_L = 0.652$; $\Delta D_L = 0.048$. 
### Table 4.37 Determination of $D_0$ and $D_1$ for Benzoic Acid

$T_L = 6.361 \times 10^{-5}\text{ mole/l.}$; $I = 0.1$; $\lambda = 240\mu$; $l = 2\text{ cm}$.

<table>
<thead>
<tr>
<th>$ax10^4$</th>
<th>$bx10^5$</th>
<th>$dx10$</th>
<th>$D^0$</th>
<th>$h_1^{\alpha}x10^5$</th>
<th>$x10^4$</th>
<th>$y = D_0x$</th>
<th>$\Delta y x10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.075</td>
<td>9.491</td>
<td>1.002</td>
<td>0.3962</td>
<td>0.648</td>
<td>0.694</td>
<td>2.751</td>
<td>-0.050</td>
</tr>
<tr>
<td>9.075</td>
<td>9.298</td>
<td>1.002</td>
<td>0.4318</td>
<td>1.466</td>
<td>0.776</td>
<td>3.351</td>
<td>+0.049</td>
</tr>
<tr>
<td>9.075</td>
<td>9.106</td>
<td>1.002</td>
<td>0.4768</td>
<td>2.337</td>
<td>0.863</td>
<td>4.116</td>
<td>+0.029</td>
</tr>
<tr>
<td>9.075</td>
<td>8.913</td>
<td>1.002</td>
<td>0.5145</td>
<td>3.255</td>
<td>0.955</td>
<td>4.913</td>
<td>+0.017</td>
</tr>
<tr>
<td>9.075</td>
<td>8.721</td>
<td>1.002</td>
<td>0.5512</td>
<td>4.213</td>
<td>1.051</td>
<td>5.792</td>
<td>-0.043</td>
</tr>
<tr>
<td>9.075</td>
<td>8.465</td>
<td>1.002</td>
<td>0.5808</td>
<td>5.539</td>
<td>1.183</td>
<td>6.873</td>
<td>+0.010</td>
</tr>
</tbody>
</table>

$D_0 = 0.855$; $\delta_{D_0} = \pm 0.011$. $\varepsilon_0 = 6.721$; $\delta_{\varepsilon_0} = \pm 86$. $D_0$ (direct measurement) = 0.860; $\varepsilon_0 = 6.760$.

$D_1 = 0.341$; $\delta_{D_1} = \pm 0.006$. $\varepsilon_1 = 2.681$; $\delta_{\varepsilon_1} = \pm 47$. $D_1$ (direct measurement) = 0.376; $\varepsilon_1 = 2.956$. 
FIGURE 4.51 DETERMINATION OF $D_0$ AND $D_1$ FOR BENZOIC ACID.
<table>
<thead>
<tr>
<th>$a \times 10^4$</th>
<th>$b \times 10^4$</th>
<th>$d \times 10^2$</th>
<th>$D_0$</th>
<th>$n_0 f_1^2 \times 10^4$</th>
<th>$x \times 10^4$</th>
<th>$y = D_0 x$</th>
<th>$\Delta y \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>8.644</td>
<td>9.929</td>
<td>0.3445</td>
<td>0.982</td>
<td>0.651</td>
<td>0.224</td>
<td>-0.004</td>
</tr>
<tr>
<td>9.090</td>
<td>7.805</td>
<td>9.929</td>
<td>0.4105</td>
<td>0.854</td>
<td>1.123</td>
<td>0.461</td>
<td>0.000</td>
</tr>
<tr>
<td>9.090</td>
<td>6.902</td>
<td>9.929</td>
<td>0.4410</td>
<td>1.390</td>
<td>1.660</td>
<td>0.732</td>
<td>+0.002</td>
</tr>
<tr>
<td>9.090</td>
<td>5.870</td>
<td>9.929</td>
<td>0.5750</td>
<td>2.015</td>
<td>2.284</td>
<td>1.042</td>
<td>+0.011</td>
</tr>
<tr>
<td>9.090</td>
<td>4.967</td>
<td>9.929</td>
<td>0.4688</td>
<td>2.565</td>
<td>2.835</td>
<td>1.329</td>
<td>+0.004</td>
</tr>
<tr>
<td>9.090</td>
<td>4.064</td>
<td>9.929</td>
<td>0.4795</td>
<td>3.118</td>
<td>3.387</td>
<td>1.624</td>
<td>-0.009</td>
</tr>
</tbody>
</table>

$D_0 = 0.510; \quad \sigma_{D_0} = \pm 0.003. \quad \varepsilon_0 = 605; \quad \sigma_{\varepsilon_0} = \pm 4. \quad D_0$ (direct measurement) = 0.522; $\varepsilon_0 = 619.$

$D_1 = 0.091; \quad \sigma_{D_1} = \pm 0.002. \quad \varepsilon_1 = 108; \quad \sigma_{\varepsilon_1} = \pm 3.$
FIGURE 4.52 DETERMINATION OF $D_o$ AND $D_i$ FOR 4-HYDROXY BENZOIC ACID.
TABLE 4.39 DETERMINATION OF $D_0$ AND $D_1$ FOR 3-BROMO BENZOIC ACID

$T_L = 9.817 \times 10^{-5}$ mole/l.; $I = 0.1; \lambda = 242 $m1; $l = 2$cm.

<table>
<thead>
<tr>
<th>$a \times 10^4$</th>
<th>$b \times 10^4$</th>
<th>$d \times 10^4$</th>
<th>$D^0$</th>
<th>$h/f_1 \times 10^5$</th>
<th>$x \times 10^4$</th>
<th>$y = D^0 x \times 10^4$</th>
<th>$\Delta y \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>9.968</td>
<td>1.001</td>
<td>0.4385</td>
<td>0.463</td>
<td>1.599</td>
<td>0.701</td>
<td>-0.007</td>
</tr>
<tr>
<td>9.090</td>
<td>9.713</td>
<td>1.001</td>
<td>0.4698</td>
<td>1.936</td>
<td>1.747</td>
<td>0.821</td>
<td>+0.016</td>
</tr>
<tr>
<td>9.090</td>
<td>9.393</td>
<td>1.001</td>
<td>0.5125</td>
<td>3.159</td>
<td>1.869</td>
<td>0.958</td>
<td>-0.003</td>
</tr>
<tr>
<td>9.090</td>
<td>9.074</td>
<td>1.001</td>
<td>0.5508</td>
<td>4.733</td>
<td>2.027</td>
<td>1.116</td>
<td>-0.008</td>
</tr>
<tr>
<td>9.090</td>
<td>8.754</td>
<td>1.001</td>
<td>0.5820</td>
<td>6.361</td>
<td>2.189</td>
<td>1.274</td>
<td>-0.008</td>
</tr>
<tr>
<td>9.090</td>
<td>8.435</td>
<td>1.001</td>
<td>0.6028</td>
<td>8.026</td>
<td>2.356</td>
<td>1.420</td>
<td>+0.008</td>
</tr>
</tbody>
</table>

$D_0 = 0.970; \quad \sigma_{D_0} = \pm 0.018. \quad \varepsilon_0 = 4,940; \quad \sigma_{\varepsilon_0} = \pm 92. \quad D_0$ (direct measurement) = 0.962; $\varepsilon_0 = 4,900. $

$D_1 = 0.418; \quad \sigma_{D_1} = \pm 0.005. \quad \varepsilon_1 = 2,129; \quad \sigma_{\varepsilon_1} = \pm 26. \quad D_1$ (direct measurement) = 0.410; $\varepsilon_1 = 2,088.$
<table>
<thead>
<tr>
<th>$a \times 10^6$</th>
<th>$b \times 10^6$</th>
<th>$d \times 10^2$</th>
<th>$h \times 10^4$</th>
<th>$y \times 10^6$</th>
<th>$\Delta y \times 10^6$</th>
<th>$y = D_0^2 \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>9.265</td>
<td>9.977</td>
<td>0.6570</td>
<td>0.441</td>
<td>0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>9.090</td>
<td>3.243</td>
<td>9.977</td>
<td>0.6252</td>
<td>1.004</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>9.090</td>
<td>7.039</td>
<td>9.977</td>
<td>0.5980</td>
<td>1.633</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>9.090</td>
<td>5.879</td>
<td>9.977</td>
<td>0.5758</td>
<td>3.352</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>9.090</td>
<td>4.729</td>
<td>9.935</td>
<td>0.5590</td>
<td>3.023</td>
<td>3.708</td>
<td>3.708</td>
</tr>
<tr>
<td>9.090</td>
<td>3.578</td>
<td>9.935</td>
<td>0.5470</td>
<td>3.701</td>
<td>3.999</td>
<td>-0.009</td>
</tr>
</tbody>
</table>

$T_L = 9.999 \times 10^{-5}$ mole/l; $I = 0.11; \lambda = 310 \text{mI} / \mu; \bar{D} = 2 \pi \text{cm}$.

**Table 4.40: Determination of $D_0$ and $D_1$ for 4-Nitro Benzoic Acid**

$T_L = 0.410; \bar{D}_0 = 0.002; \bar{D}_1 = 0.002; \bar{D}_0 = 3.425; \bar{D}_1 = 3.410$.

$D_0 = 0.396; \bar{D}_0 = 1.980; \bar{D}_1 = 0.396; \bar{D}_1 = 1.980$.
FIGURE 4.54 DETERMINATION OF $D_0$ AND $D_1$ FOR 4-NITRO BENZOIC ACID.
DETERMINATION OF THE ASSOCIATION CONSTANTS OF THE LANTHANUM BENZOATE ION PAIRS BY MEANS OF THE OPTIMIZATION PROCEDURE

As seen in the case of the La\(^{3+}\)/salicylaldehyde system, the optimization procedure is not generally valid, and the results obtained by this procedure should be treated with caution. Nevertheless, an attempt to evaluate the association constants of the present ion pairs by this procedure was made.

In applying the optimization procedure to the determination of the association constants of lanthanum benzoate and lanthanum 3-bromo benzoate, the values of \( D_c \), calculated on the basis of the cross-over point, were used. Since, no direct information regarding the magnitude of \( D_c \) was available in the case of lanthanum 4-hydroxy and lanthanum 4-nitro benzoate, the values of \( D_L \) at the selected wavelengths were employed for the purpose of the optimization procedure. Accordingly, the value of \( D_c \) was varied around these trial values of \( D_c \) and the standard deviation of \( \alpha, \sigma_{\alpha} \), corresponding to any given value of \( D_c \), calculated. It was found that, with the exception of lanthanum benzoate, in each case the plot of \( \sigma_{\alpha} \) against these trial values of \( D_c \) gave a well defined minimum. A summary of these calculations is given in tables (4.41), (4.42), and (4.43), which also show the values of \( \alpha \) and \( D_c \) corresponding to these minima. In each case, the standard deviation of the association constant is less than 2%, thus indicating that satisfactory precision was here attained. It will also be seen that the value of \( D_c \) found for lanthanum 3-bromo benzoate is in reasonable agreement with that obtained from consideration of the cross-over point. The plots of \( y' = (\Delta h x + T LK_L)/c \) against \( x \) for these three ion pairs are shown in figures (4.55), (4.56), and (4.57), from
which it can be seen that the experimental points lie on very good straight lines.

The values of $D_c$ for these ion pairs were also computed by means of equation (4.32). The results of these calculations are given in tables (4.41), (4.42), (4.43), which show that the values of $D_c$ found by this means ($D_c^*$) are in very good agreement with those obtained from the plots of $\alpha$ against $D_c$. The plots of $y'' = \Delta h(D_c - D_L) - ADT_L + D_1c$ against $c$ (not given here) show that the experimental points lie on very good straight lines.

In the case of the lanthanum benzoate ion pair, however, the plot of $\alpha$ against $D_c$ failed to show a minimum from which the best values of $\alpha$ and $D_c$ could be obtained. Use of the value of $D_c$, obtained from consideration of the cross-over point, in the optimization procedure leads to a value of $5.22 \times 10^2$ for the association constant for this ion pair, which, as will be seen later, is in only poor agreement with that found by means of the iteration procedures 2 and 3. In view of the failure of the optimization procedure in the present case, an attempt to evaluate these association constants by the three iteration methods was made.

EVALUATION OF THE ASSOCIATION CONSTANTS
OF THE LANTHANUM BENZOATE ION PAIRS
USING THE ITERATION PROCEDURES

ITERATION PROCEDURE No.1.

In applying the first iteration method to the evaluation of the association constants of the lanthanum benzoate ion pairs, only partial success was achieved. The iteration process failed to converge
TABLE 4.51 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM

4-HYDROXY BENZOATE - OPTIMIZATION PROCEDURE

\[ T_L = 4.218 \times 10^{-5} \text{mole/l.}; \quad T_M = 1 \times 10^{-2} \text{mole/l.}; \quad I = 0.1; \quad \lambda = 275 \text{m} \mu; \quad L = 2 \text{cm}; \quad D_c = 0.270. \]

<table>
<thead>
<tr>
<th>( a \times 10^2 )</th>
<th>( b \times 10^2 )</th>
<th>( d \times 10^2 )</th>
<th>( D )</th>
<th>( \Delta D \times 10^6 )</th>
<th>( e \times 10^6 )</th>
<th>( y' \times 10^4 )</th>
<th>( \Delta y' \times 10^2 )</th>
<th>( y'' \times 10^6 )</th>
<th>( \Delta y'' \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>8.645</td>
<td>3.980</td>
<td>0.3210</td>
<td>0.0235</td>
<td>9.612</td>
<td>17.812</td>
<td>0.989</td>
<td>+0.268</td>
<td>4.655</td>
</tr>
<tr>
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<td>7.805</td>
<td>3.980</td>
<td>0.3880</td>
<td>0.0225</td>
<td>5.435</td>
<td>7.465</td>
<td>2.339</td>
<td>+0.172</td>
<td>2.007</td>
</tr>
<tr>
<td>9.090</td>
<td>6.902</td>
<td>3.980</td>
<td>0.4185</td>
<td>0.0225</td>
<td>4.760</td>
<td>5.804</td>
<td>3.317</td>
<td>-0.115</td>
<td>1.573</td>
</tr>
<tr>
<td>9.090</td>
<td>5.870</td>
<td>3.980</td>
<td>0.4360</td>
<td>0.0200</td>
<td>4.057</td>
<td>4.653</td>
<td>4.432</td>
<td>-0.026</td>
<td>1.279</td>
</tr>
<tr>
<td>9.090</td>
<td>4.967</td>
<td>3.980</td>
<td>0.4497</td>
<td>0.0191</td>
<td>3.695</td>
<td>4.115</td>
<td>5.305</td>
<td>+0.163</td>
<td>1.117</td>
</tr>
<tr>
<td>9.090</td>
<td>4.064</td>
<td>3.980</td>
<td>0.4635</td>
<td>0.0160</td>
<td>2.976</td>
<td>3.252</td>
<td>6.592</td>
<td>-0.058</td>
<td>0.868</td>
</tr>
</tbody>
</table>

\( \alpha = 1.929; \quad \sigma_\alpha = \pm 0.032. \quad D_c^K = 0.264; \quad \sigma_{D_c^K} = \pm 0.002. \)

\( K = 4.598 \times 10^2; \quad \sigma_K = \pm 0.076 \times 10^2. \)
FIGURE 4.55 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM - 4 - HYDROXY BENZOATE — OPTIMIZATION PROCEDURE.


**TABLE 4.42 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM**

3-BROMO BENZOATE - OPTIMIZATION PROCEDURE

\[ T_L = 9.817 \times 10^{-5} \text{ mole/l.}; \ T_M = 1 \times 10^{-2} \text{ mole/l.}; \ I = 0.1; \ \lambda = 242 \mu \text{; } \ \ell = 2 \text{ cm}; \ \ D_c = 0.726. \]

<table>
<thead>
<tr>
<th>ax10^5</th>
<th>bx10^5</th>
<th>dx10^2</th>
<th>D</th>
<th>ΔD</th>
<th>Δhx10^6</th>
<th>cx10^5</th>
<th>y'x10^5</th>
<th>Δy'x10^5</th>
<th>y''x10^5</th>
<th>Δy''x10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>9.968</td>
<td>3.978</td>
<td>0.5215</td>
<td>-0.0830</td>
<td>0.643</td>
<td>2.802</td>
<td>5.478</td>
<td>+0.155</td>
<td>2.022</td>
<td>+0.012</td>
</tr>
<tr>
<td>9.090</td>
<td>9.773</td>
<td>3.978</td>
<td>0.5220</td>
<td>-0.0722</td>
<td>2.401</td>
<td>2.649</td>
<td>5.913</td>
<td>+0.239</td>
<td>1.949</td>
<td>-0.026</td>
</tr>
<tr>
<td>9.090</td>
<td>9.413</td>
<td>3.978</td>
<td>0.5635</td>
<td>-0.0510</td>
<td>3.055</td>
<td>2.182</td>
<td>7.249</td>
<td>-0.666</td>
<td>1.582</td>
<td>+0.002</td>
</tr>
<tr>
<td>9.090</td>
<td>9.074</td>
<td>3.978</td>
<td>0.5955</td>
<td>-0.0447</td>
<td>4.501</td>
<td>2.260</td>
<td>7.149</td>
<td>-0.011</td>
<td>1.632</td>
<td>+0.009</td>
</tr>
<tr>
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<td>8.754</td>
<td>3.978</td>
<td>0.6185</td>
<td>-0.0365</td>
<td>5.494</td>
<td>2.175</td>
<td>7.562</td>
<td>+0.149</td>
<td>1.571</td>
<td>+0.008</td>
</tr>
<tr>
<td>9.090</td>
<td>8.435</td>
<td>3.978</td>
<td>0.6330</td>
<td>-0.0302</td>
<td>6.142</td>
<td>2.041</td>
<td>8.180</td>
<td>+0.117</td>
<td>1.489</td>
<td>-0.007</td>
</tr>
</tbody>
</table>

\[ \alpha = 3.522; \ \sigma_\alpha = \pm 0.069. \ \ D_c^\alpha = 0.726; \ \sigma_{D_c}^\alpha = \pm 0.002. \]

\[ \lambda = 1.694 \times 10^2; \ \sigma_\lambda = \pm 0.033 \times 10^2. \]
TABLE 4.43 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM

4-NITRO BENZOATE - OPTIMIZATION PROCEDURE

\( T_L = 9.999 \times 10^{-5} \text{ mole/l.}; \ T_M = 1 \times 10^{-2} \text{ mole/l.}; \ I = 0.1; \ \lambda = 310 \mu; \ \ell = 2 \text{ cm}; \ D_c = 0.325. \)

| \( ax \times 10^4 \) | \( bx \times 10^4 \) | \( dx \times 10^2 \) | \( D \) | \( \Delta D \) | \( \Delta h \times 10^6 \) | \( c \times 10^6 \) | \( y' \times 10^3 \) | \( \Delta y' \times 10^3 \) | \( y'' \times 10^6 \) | \( \Delta y'' \times 10^6 \) |
|----------------|----------------|----------------|-----|-------|----------------|--------|------|---------|--------|--------|---------|
| 9.090          | 9.265          | 3.982          | 0.6215 | 0.0355 | 1.028          | 10.588 | 3.449 | -0.544   | 3.424   | +0.017  |
| 9.090          | 8.243          | 3.982          | 0.5947 | 0.0305 | 1.987          | 9.988  | 3.706 | -0.389   | 3.248   | -0.002  |
| 9.090          | 7.093          | 3.982          | 0.5703 | 0.0277 | 2.911          | 9.935  | 3.788 | -0.005   | 3.269   | -0.040  |
| 9.090          | 5.879          | 3.982          | 0.5513 | 0.0245 | 3.566          | 9.548  | 4.000 | +0.283   | 3.111   | -0.008  |
| 9.090          | 4.729          | 3.940          | 0.5380 | 0.0210 | 3.820          | 8.768  | 4.406 | +0.362   | 2.856   | -0.006  |
| 9.090          | 3.578          | 3.940          | 0.5303 | 0.0167 | 3.583          | 7.349  | 5.268 | -0.013   | 2.380   | +0.008  |

\( \alpha = 7.188; \quad \sigma_\alpha = \pm 0.256. \quad D_c \times 10^2 = 0.325; \quad \sigma_{D_c} = \pm 0.001. \)

\( K = 69.05; \quad \sigma_K = \pm 2.46. \)
FIGURE 4.57 DETERMINATION OF THE ASSOCIATION CONSTANT FOR LANTHANUM -4- NITRO BENZOATE — OPTIMIZATION PROCEDURE.
in the case of the lanthanum benzoate and lanthanum 4-nitro benzoate ion pairs, in spite of the fact that the initial value of \( F/KT_M \) was varied over a wide range.

On the other hand, the iteration process was found to converge rapidly in the case of the lanthanum 4-hydroxy benzoate ion pair and gave the value 281 for the association constant with a standard deviation of \( \pm 3\% \). The results of these calculations, in which no difficulties regarding the starting value of \( F/KT_M \) were encountered, are summarised in Table (4.44) and illustrated in figure (4.58).

The case of the lanthanum 3-bromo benzoate ion pair is interesting in that it stresses the importance of a judicious choice for the starting value of \( F/KT_M \). Here, convergence was reached only after the initial value of \( F/KT_M \) was pinpointed to the third decimal place. The results for this ion pair are presented in Table (4.45) and illustrated in figure (4.59). It will be noticed that the values for \( K \), found by this means, are much less than those obtained by use of the optimization procedure.

Thus, it appears that even when results are obtained by the optimization procedure, they cannot be regarded as reliable, unless the calculated value of \( D_0 \) agrees reasonably well with that found experimentally, or by other means.

The failure of the first iteration method in the case of the lanthanum benzoate and the lanthanum 4-nitro benzoate ion pairs, suggests that the choice of a suitable value for starting the iteration process is not the only condition that must be satisfied in order for a given approximation method to be successful. The second condition is concerned with the properties of the matrix \( A \) which consists of the partial derivatives of the functions underlying a given approximation procedure and will be discussed in greater detail in the Conclusions.
ITERATION PROCEDURES 2 AND 3

Since, the application of these iteration procedures leads to virtually the same results for the association constants, it will be convenient to consider them together. Just as the first iteration procedure, these methods failed in the case of the lanthanum 4-nitro benzoate ion pair but were successful in the remaining cases. The results of the calculations obtained by the two procedures are summarised in tables (4.46) - (4.51) from which it can be seen that the values obtained by the two methods agree very well with one another. The poor agreement between the value of the association constant for lanthanum benzoate obtained on the basis of the cross-over point and the latter values, is clearly due to the difficulties of correctly assessing the hydrogen-ion concentration at that point.

Plots of $y' = (Ah + T_L K_1)/c$ against $x$, based on these results for iteration procedure No.2, gave very good straight lines. Only the plot for lanthanum benzoate is given here (figure (4.60)), as those obtained for lanthanum 4-hydroxy and lanthanum 3-bromo benzoate are virtually identical with the plots found by use of iteration procedure No.1. Plots of $y = (T_L - c)/c$ against $1 + hf_1^2/K_1$, based on the results for iteration procedure No.3, also gave good straight lines, and are shown in figures (4.61) - (4.63).

APPLICATION OF THE ITERATION PROCEDURES

TO THE LANTHANUM SALICYLATE ION PAIRS

To test the reliability of the iteration procedures still further, they were applied to the recalculation of the association constants of the lanthanum salicylate ion pairs. The results of the calculations are
TABLE 4.44 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM

4-HYDROXY BENZOATE - ITERATION PROCEDURE No. 1

\[ T_L = 4.218 \times 10^{-5} \text{ mole/l.}; \ T_M = 1 \times 10^{-2} \text{ mole/l.}; \ I = 0.1; \ \lambda = 275 \mu \text{;} \ \ell = 2 \text{ cm}; \]

\[ F/\kappa T_M \text{ (starting value)} = 1.0; \ D_L = 0.121; \ D_c = 0.170. \]

<table>
<thead>
<tr>
<th>ax10^4</th>
<th>bx10^5</th>
<th>dx10^2</th>
<th>D</th>
<th>A D</th>
<th>Ax10^6</th>
<th>cx10^6</th>
<th>y'x10^4</th>
<th>Ay'x10^4</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.622</td>
<td>2.052</td>
<td>-0.411</td>
</tr>
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<td>9.090</td>
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<td>3.980</td>
<td>0.3880</td>
<td>0.0225</td>
<td>3.006</td>
<td>4.148</td>
<td>3.551</td>
<td>-0.721</td>
</tr>
<tr>
<td>9.090</td>
<td>6.902</td>
<td>3.980</td>
<td>0.4185</td>
<td>0.0225</td>
<td>2.921</td>
<td>3.567</td>
<td>4.542</td>
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</tr>
<tr>
<td>9.090</td>
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<td>0.4360</td>
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<td>2.969</td>
<td>5.814</td>
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<td>3.980</td>
<td>0.4597</td>
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<td>2.421</td>
<td>2.697</td>
<td>6.755</td>
<td>+0.387</td>
</tr>
<tr>
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<td>4.064</td>
<td>3.980</td>
<td>0.4635</td>
<td>0.0160</td>
<td>1.989</td>
<td>2.173</td>
<td>8.325</td>
<td>+0.009</td>
</tr>
</tbody>
</table>

\[ F/\kappa T_M \text{ (final value)} = 1.520; \ \bar{\sigma}_{F/\kappa T_M} = \pm 0.053. \]

\[ K = 2.812 \times 10^2; \ \bar{\sigma}_K = \pm 0.098 \times 10^2. \]
FIGURE 4.58 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM -4- HYDROXY BENZOATE ITERATION PROCEDURE 1
<table>
<thead>
<tr>
<th>( t \times 10^4 )</th>
<th>( D \times 10^2 )</th>
<th>( \Delta D \times 10^5 )</th>
<th>( y \times 10^4 )</th>
<th>( \Delta y \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.968</td>
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<td>0.580</td>
</tr>
<tr>
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</tr>
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</tr>
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<td>0.6185</td>
<td>-0.0165</td>
<td>8.141</td>
</tr>
<tr>
<td>8.435</td>
<td>3.978</td>
<td>0.6330</td>
<td>-0.01   0.0127</td>
<td>8.172</td>
</tr>
<tr>
<td>8.104</td>
<td>3.978</td>
<td>0.6485</td>
<td>-0.0097</td>
<td>8.824</td>
</tr>
<tr>
<td>7.774</td>
<td>3.978</td>
<td>0.6630</td>
<td>-0.0062</td>
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</tr>
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<td>7.444</td>
<td>3.978</td>
<td>0.6775</td>
<td>-0.0027</td>
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</tr>
</tbody>
</table>

\( t = 9.817 \times 10^{-5} \text{ mole/L} \); \( T_M = 1 \times 10^{-2} \text{ mole/L} \); \( I = 0.1 \); \( \lambda = \frac{242 \mu l}{c m} \); \( D_L = 0.5016 \); \( D_c = 0.755 \).
FIGURE 4.59 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM -3- BROMO BENZOATE — ITERATION PROCEDURE 1.
TABLE 4.46 DETERMINATION OF THE ASSOCIATION CONSTANT OF

LANTHANUM BENZOATE - ITERATION PROCEDURE No. 2

\[ T_L = 6.361 \times 10^{-5} \text{ mole/l.}; \ T_M = 1 \times 10^{-2} \text{ mole/l.}; \ I = 0.1; \ \lambda = 240 \text{ m}\mu; \ L = 2\text{ cm}; \]

\[ F/\kappa T_M \text{ (starting value)} = 0.4; \ D_0 = 0.855; \ D_1 = 0.341; \ D_L = 0.492; \ D_c = 0.572. \]

<table>
<thead>
<tr>
<th>(a \times 10^b)</th>
<th>(b \times 10^b)</th>
<th>(d \times 10^b)</th>
<th>(D)</th>
<th>(\Delta \kappa \times 10^7)</th>
<th>(e \times 10^5)</th>
<th>(y \times 10^4)</th>
<th>(\Delta y \times 10^4)</th>
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</thead>
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<td>0.328</td>
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<td>1.025</td>
<td>+0.037</td>
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<td>9.298</td>
<td>4.006</td>
<td>0.5075</td>
<td>0.657</td>
<td>3.983</td>
<td>1.133</td>
<td>+0.054</td>
</tr>
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<td>9.106</td>
<td>4.006</td>
<td>0.5287</td>
<td>0.898</td>
<td>3.740</td>
<td>1.278</td>
<td>+0.042</td>
</tr>
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<td>9.075</td>
<td>8.913</td>
<td>4.006</td>
<td>0.5578</td>
<td>1.039</td>
<td>3.407</td>
<td>1.467</td>
<td>-0.007</td>
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<td>8.721</td>
<td>4.006</td>
<td>0.5757</td>
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<td>3.202</td>
<td>1.632</td>
<td>-0.026</td>
</tr>
<tr>
<td>9.075</td>
<td>8.465</td>
<td>4.006</td>
<td>0.5980</td>
<td>1.267</td>
<td>2.946</td>
<td>1.868</td>
<td>-0.059</td>
</tr>
</tbody>
</table>

\[ F/\kappa T_M \text{ (final value)} = 0.529; \ \sigma_{F/\kappa T_M} = \pm 0.007. \]

\[ K = 8.079 \times 10^2; \ \sigma_K = \pm 0.104 \times 10^2. \]
DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM BENZOATE — ITERATION PROCEDURE 2.
TABLE 4.47 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM 4-HYDROXY BENZOATE - ITERATION PROCEDURE No. 2

\[ T_L = 4.218 \times 10^{-5} \text{ mole/l.}; \quad T_M = 1 \times 10^{-2} \text{ mole/l.}; \quad I = 0.1; \quad \lambda = 275 \text{ mI}; \quad l = 2 \text{ cm}; \]

\[ F/KT_M \text{ (starting value)} = 4.27; \quad D_0 = 0.510; \quad D_1 = 0.091; \quad D_2 = 0.121; \quad D_c = 0.167. \]

<table>
<thead>
<tr>
<th>ax10^4</th>
<th>bx10^4</th>
<th>cx10^2</th>
<th>D</th>
<th>\Delta h x10^6</th>
<th>cx10^6</th>
<th>y' x10^4</th>
<th>\Delta y' x10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>3.644</td>
<td>3.980</td>
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</tr>
<tr>
<td>9.090</td>
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<td>0.3880</td>
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<td>5.231</td>
<td>2.986</td>
<td>-0.146</td>
</tr>
<tr>
<td>9.090</td>
<td>6.902</td>
<td>3.980</td>
<td>0.4185</td>
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<td>3.923</td>
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<tr>
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<td>4.064</td>
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<td>0.4635</td>
<td>1.824</td>
<td>1.993</td>
<td>8.797</td>
<td>-0.234</td>
</tr>
</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 1.528; \quad \sigma_{F/KT_M} = \pm 0.021. \]

\[ K = 2.797 \times 10^2; \quad \sigma_K = \pm 0.039 \times 10^2. \]
TABLE 4.48 DETERMINATION OF THE ASSOCIATION CONSTANT OF

LANTHANUM 3-BROMO BENZOATE - ITERATION PROCEDURE No. 2

\( T_L = 9.817 \times 10^{-5} \text{ mole/l.} ; \ T_M = 1 \times 10^{-2} \text{ mole/l.} ; \ I = 0.1 ; \ \lambda = 242 \mu \text{m} ; \ \ell = 2 \text{cm}; \)

\( F/K_{T_M} \) (starting value) = 2.5; \ \( D_0 = 0.970; \ D_1 = 0.418; \ D_L = 0.5016; \ D_c = 0.762. \)

<table>
<thead>
<tr>
<th>( a \times 10^4 )</th>
<th>( b \times 10^4 )</th>
<th>( d \times 10^2 )</th>
<th>( D )</th>
<th>( \Delta h \times 10^6 )</th>
<th>( c \times 10^5 )</th>
<th>( y' \times 10^4 )</th>
<th>( \Delta y' \times 10^4 )</th>
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</thead>
<tbody>
<tr>
<td>9.090</td>
<td>9.968</td>
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<td>0.515</td>
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</tr>
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<td>3.978</td>
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<td>1.950</td>
<td>2.178</td>
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</tr>
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<td>9.090</td>
<td>9.393</td>
<td>3.978</td>
<td>0.5635</td>
<td>2.888</td>
<td>2.068</td>
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<td>+0.066</td>
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<tr>
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<td>9.074</td>
<td>3.978</td>
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<td>3.767</td>
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<td>8.754</td>
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<td>+0.057</td>
</tr>
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<td>9.090</td>
<td>8.435</td>
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<td>5.134</td>
<td>1.715</td>
<td>9.597</td>
<td>+0.106</td>
</tr>
</tbody>
</table>

\( F/K_{T_M} \) (final value) = 3.119; \ \( \sigma_{F/K_{T_M}} = \pm 0.014. \)

\( K = 1.370 \times 10^2; \ \sigma_K = \pm 0.006 \times 10^2. \)
TABLE 4.49 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM BENZOATE - ITERATION PROCEDURE No. 3

$T_L = 6.361 \times 10^{-5}$ mole/l.; $T_M = 1 \times 10^{-2}$ mole/l.; $I = 0.1$; $\lambda = 240$ mp; $l = 2$ cm;

$F/KT_M$ (starting value) = 0.4; $D_0 = 0.855$; $D_1 = 0.341$; $D_L = 0.492$; $D_c = 0.572$

<table>
<thead>
<tr>
<th>ax $10^k$</th>
<th>bx $10^k$</th>
<th>dx $10^2$</th>
<th>D</th>
<th>hx $10^5$ cx $10^5$</th>
<th>$x = 1 + \frac{hf^2}{K}$</th>
<th>$y = \frac{T_L - c}{c}$</th>
<th>$\Delta y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.075</td>
<td>9.491</td>
<td>4.006</td>
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<td>1.379</td>
<td>4.123</td>
<td>1.135</td>
<td>0.543</td>
</tr>
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<td>9.298</td>
<td>4.006</td>
<td>0.5075</td>
<td>3.034</td>
<td>3.976</td>
<td>1.297</td>
<td>0.600</td>
</tr>
<tr>
<td>9.075</td>
<td>9.106</td>
<td>4.006</td>
<td>0.5287</td>
<td>4.689</td>
<td>3.734</td>
<td>1.459</td>
<td>0.704</td>
</tr>
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</tr>
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<td>0.5757</td>
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<td>3.196</td>
<td>1.783</td>
<td>0.990</td>
</tr>
<tr>
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<td>8.465</td>
<td>4.006</td>
<td>0.5980</td>
<td>10.251</td>
<td>2.941</td>
<td>2.004</td>
<td>1.163</td>
</tr>
</tbody>
</table>

$F/KT_M$ (final value) = 0.532; $\Sigma_{F/KT_M} = \pm 0.020$.

$K = 8.039 \times 10^2$; $\Sigma_K = \pm 0.295 \times 10^2$. 
FIGURE 4.61 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM BENZOATE — ITERATION PROCEDURE 3.
TABLE 4.50 DETERMINATION OF THE ASSOCIATION CONSTANT OF
LANTHANUM 4-HYDROXY BENZOATE - ITERATION PROCEDURE No.3

\[ T_L = 4.218 \times 10^{-5} \text{ mole/l.}; \quad T_M = 1 \times 10^{-2} \text{ mole/l.}; \quad I = 0.1; \quad \lambda = 275 \mu; \quad \downarrow = 2 \text{cm}; \]

\[ F/KT_M \text{ (starting value)} = \frac{2}{7}; \quad D_o = 0.510; \quad D_1 = 0.091; \quad D_L = 0.121; \quad D_c = 0.167. \]

<table>
<thead>
<tr>
<th>ax10^4</th>
<th>bx10^2</th>
<th>dx10^2</th>
<th>D</th>
<th>hxi10^4</th>
<th>cx10^6</th>
<th>x=1+ \frac{hf^2}{K_1}</th>
<th>y = \frac{T_L-c}{c}</th>
<th>\Delta y</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>8.644</td>
<td>3.980</td>
<td>0.3210</td>
<td>0.662</td>
<td>8.103</td>
<td>2.516</td>
<td>0.421</td>
<td>-0.036</td>
</tr>
<tr>
<td>9.090</td>
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<td>0.3880</td>
<td>1.424</td>
<td>5.230</td>
<td>4.260</td>
<td>0.761</td>
<td>-0.055</td>
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<td>0.4185</td>
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<td>6.239</td>
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<td>-0.022</td>
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<td>5.870</td>
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<td>0.4360</td>
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<td>3.171</td>
<td>8.548</td>
<td>1.230</td>
<td>+0.077</td>
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<td>0.4497</td>
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<td>1.992</td>
<td>12.624</td>
<td>2.017</td>
<td>-0.087</td>
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</tbody>
</table>

\[ F/KT_M \text{ (final value)} = 1.529; \quad \sigma_{F/KT_M} = \pm 0.035. \]

\[ K = 2.795 \times 10^2; \quad \sigma_K = \pm 0.064 \times 10^2. \]
Determination of the association constant of lanthanum 4-hydroxy benzoate.

\[ 1 + \frac{h f_i^2}{K_i} \]

Graph showing the relationship between \( \frac{1}{[L - C]} \times 10^4 \) and \( 1 + \frac{h f_i^2}{K_i} \).
### Table 4.51 Determination of the Association Constant of Lanthanum 3-Bromo Benzoate - Iteration Procedure No. 3

<table>
<thead>
<tr>
<th>$a \times 10^4$</th>
<th>$b \times 10^4$</th>
<th>$d \times 10^2$</th>
<th>$D$</th>
<th>$h \times 10^5$</th>
<th>$e \times 10^5$</th>
<th>$y = 1 + \frac{h}{K_1}$</th>
<th>$y = \frac{T_L - c}{c}$</th>
<th>$\Delta y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.090</td>
<td>9.968</td>
<td>3.978</td>
<td>0.5215</td>
<td>0.803</td>
<td>2.284</td>
<td>1.032</td>
<td>3.299</td>
<td>+0.083</td>
</tr>
<tr>
<td>9.090</td>
<td>9.713</td>
<td>3.978</td>
<td>0.5420</td>
<td>3.337</td>
<td>2.179</td>
<td>1.132</td>
<td>3.505</td>
<td>-0.023</td>
</tr>
<tr>
<td>9.090</td>
<td>9.393</td>
<td>3.978</td>
<td>0.5635</td>
<td>5.415</td>
<td>2.070</td>
<td>1.215</td>
<td>3.743</td>
<td>+0.043</td>
</tr>
<tr>
<td>9.090</td>
<td>9.074</td>
<td>3.978</td>
<td>0.5955</td>
<td>8.063</td>
<td>1.907</td>
<td>1.320</td>
<td>4.148</td>
<td>-0.035</td>
</tr>
<tr>
<td>9.090</td>
<td>8.754</td>
<td>3.978</td>
<td>0.6185</td>
<td>10.773</td>
<td>1.790</td>
<td>1.427</td>
<td>4.485</td>
<td>-0.038</td>
</tr>
<tr>
<td>9.090</td>
<td>8.435</td>
<td>3.978</td>
<td>0.6330</td>
<td>13.54</td>
<td>1.716</td>
<td>1.537</td>
<td>4.722</td>
<td>+0.068</td>
</tr>
</tbody>
</table>

$F/KT_M$ (final value) = 3.116; $\sigma_{F/KT_M} = +0.018$.

$K = 1.371 \times 10^2$; $\sigma_K = +0.008 \times 10^2$. 
FIGURE 4.63 DETERMINATION OF THE ASSOCIATION CONSTANT OF LANTHANUM -3-BROMO BENZOATE — ITERATION PROCEDURE 3.
summarised in table (4.52) which gives the values of $D_c$, the association constants and the corresponding standard deviations. It can be seen that in the case of the lanthanum salicylate, and the lanthanum 3-methyl, lanthanum 5-bromo and lanthanum 5-chloro salicylate ion pairs, all iteration methods yield results which agree not only with one another but also with the results obtained by the optimization procedure.

However, all three iteration procedures failed completely in the case of the lanthanum 5-nitro salicylate ion pair, while in the case of the lanthanum 3-nitro salicylate ion pair only iteration procedure No.1 gave a result; this is about 10% lower than that obtained by use of the optimization procedure. It is interesting to note that here, convergence occurred only after the value of $F/KT_{H}$ had been pinpointed to the second decimal place. The case of the lanthanum salicylate ion pairs again illustrates the importance of the two conditions for a successful application of iteration methods;

1. The choice of a suitable starting value for the iteration procedure.

2. Suitable form of the equations which underlie the iteration procedure.
<table>
<thead>
<tr>
<th>SALICYLIC ACID</th>
<th>ITERATION PROCEDURE No.1</th>
<th>ITERATION PROCEDURE No.2</th>
<th>ITERATION PROCEDURE No.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_c$</td>
<td>$K$</td>
<td>$D_c$</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>0.223</td>
<td>117.7 ± 0.6</td>
<td>0.223</td>
</tr>
<tr>
<td>3-methyl salicylic acid</td>
<td>0.239</td>
<td>120.0 ± 1.2</td>
<td>0.238</td>
</tr>
<tr>
<td>5-bromo salicylic acid</td>
<td>0.276</td>
<td>77.5 ± 0.7</td>
<td>0.276</td>
</tr>
<tr>
<td>5-chloro salicylic acid</td>
<td>0.217</td>
<td>88.9 ± 1.3</td>
<td>0.217</td>
</tr>
<tr>
<td>5-nitro salicylic acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-nitro salicylic acid</td>
<td>0.342</td>
<td>35.6 ± 4.8</td>
<td>-</td>
</tr>
</tbody>
</table>
SECTION V

CONCLUSIONS
To assess the significance of the results obtained, it will be convenient to recapitulate the main objectives of the present work, as set out in the introduction:

1. To study the efficacy and usefulness of spectrophotometric measurements in determining the association constants of complexes formed by the La$^{3+}$-ion with anions of weak acids.

2. To investigate substituent effects and the correlation of the stabilities of the metal complexes to those of the corresponding proton complexes.

The extent to which these objectives have been realised in the present work, will become apparent from the following discussion.

**REVIEW OF THE SPECTROPHOTOMETRIC METHODS FOR DETERMINING ASSOCIATION CONSTANTS DEVELOPED IN THE PRESENT WORK**

All the procedures evolved in the present work for the determination of the association constants, rely on spectrophotometric measurements alone. It will be remembered that an essential feature of the experimental method adopted for this purpose, is the comparison of the absorption curves of a pair of corresponding solutions, one of which contains both the ligand and the metal ion, and the other the ligand only. This method is very effective in detecting ion association, provided that the optical density of the experimental solutions is measured over a sufficiently wide wavelength range for significant differences in the two absorption curves to be observed.

Another important condition for the successful application of this procedure, is a judicious choice of the concentration of the metal ion
that of the ligand $L$, and the wavelength. To maximize the extent of complex formation and, at the same time, to minimize the formation of complexes containing more than one ligand per metal ion, it is important that the ratio $L$ to $^{3+}$-ion: ligand in the experimental solutions, be as large as possible.

In some cases, e.g. lanthanum salicylate, the method enables the value of $D_c$ to be estimated from the plot of $\Delta D$ against $h^0$, with a fair degree of accuracy. If such is the case, it is possible to calculate directly an approximate value of the association constant from equations (4.24), (4.31) and (4.23). Sometimes, a rough value of $D_c$ can be obtained by making use of the cross-over point exhibited by the plot of $D^0$ and $D$ against $h^0$. This type of behaviour was observed with the lanthanum nitro salicylates and lanthanum benzoate and lanthanum 3-bromo benzoate. In general, however, no direct information about $D_c$ can be obtained from the variation of $\Delta D$ with $h^0$. In such cases, it is necessary to resort to equations (4.54), (4.21), (4.31), and (4.23) which relate $D_L$ to $D_c$ and $K$.

It is possible to compute the association constant of a given ion pair using the data obtained for both series of solutions, (A and B); such treatment of data is employed in the optimization procedure and the first iteration method. Alternatively, the association constants of the ion pairs can be evaluated by using only the data associated with the solutions of series A. Such treatment of data lies at the basis of the second and third iteration methods. In view of the difference in the treatment of the experimental data, some discrepancy between the results found by the optimization and first iteration procedures on the one hand, and the second and third iteration methods on the other, is to be expected. For convenience,
the values of the association constants obtained in the present work by the various methods are summarised in table (5.1).

The results obtained from the optimization procedure indicate that the method has serious limitations, in that, it requires a knowledge of a fairly accurate value of $D_0$. However, even if such is the case, the results obtained by this method cannot be regarded as being reliable, unless the calculated value of $D_0$ agrees reasonably well with that found experimentally, or by other means. As already seen, this condition is satisfied in the case of all the lanthanum salicylate ion pairs. Consequently, the values obtained by this method for the association constants of these ion pairs can be treated with confidence. The reliability of these values is also enhanced by the fact that, with the exception of lanthanum 5-nitro salicylate, they all agree very well with the values obtained by the iteration methods.

The optimization procedure leads also to definite values for the association constants of lanthanum 4-hydroxy and lanthanum 3-bromo benzoate which however, differ considerably from those found by the three iteration methods, and have thus to be rejected. In the absence of confirmation from any of the iteration procedures, the value which the optimization procedure yields for lanthanum 4-nitro benzoate must be also considered as suspect.

The optimization procedure totally fails in the case of the lanthanum/salicylaldehyde and benzoic acid systems, in that, for each case the plot of $\sigma_\lambda$ against $D_0$ showed no minimum, which could be used to evaluate the best values of $D_0$ and $K$.

As already mentioned, one of the fundamental conditions for a successful application of the approximation procedures, is that the
TABLE 5.1. THE ASSOCIATION CONSTANTS OF THE LANTHANUM
ION PAIRS STUDIED IN THE PRESENT WORK

<table>
<thead>
<tr>
<th>ACID</th>
<th>OPTIMIZATION PROCEDURE</th>
<th>ITERATION PROCEDURE No.1</th>
<th>ITERATION PROCEDURE No.2</th>
<th>ITERATION PROCEDURE No.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic acid</td>
<td>118.8 ± 0.6</td>
<td>117.7 ± 0.6</td>
<td>118.3 ± 0.5</td>
<td>113.3 ± 0.6</td>
</tr>
<tr>
<td>3-methyl salicylic acid</td>
<td>119.7 ± 1.3</td>
<td>120.0 ± 1.2</td>
<td>119.8 ± 0.7</td>
<td>119.8 ± 0.9</td>
</tr>
<tr>
<td>5-bromo salicylic acid</td>
<td>76.4 ± 0.3</td>
<td>77.5 ± 0.7</td>
<td>77.2 ± 0.2</td>
<td>77.2 ± 0.2</td>
</tr>
<tr>
<td>5-chloro salicylic acid</td>
<td>84.1 ± 1.4</td>
<td>88.9 ± 1.3</td>
<td>88.2 ± 0.8</td>
<td>88.3 ± 0.8</td>
</tr>
<tr>
<td>5-nitro salicylic acid</td>
<td>43.5 ± 1.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-nitro salicylic acid</td>
<td>39.2 ± 1.4</td>
<td>35.6 ± 4.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4-hydroxy benzoic acid</td>
<td>459.8 ± 7.6</td>
<td>281.2 ± 9.8</td>
<td>279.7 ± 3.9</td>
<td>279.5 ± 6.4</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>-</td>
<td>-</td>
<td>807.9 ± 10.4</td>
<td>803.9 ± 3.0</td>
</tr>
<tr>
<td>3-bromo benzoic acid</td>
<td>169.6 ± 3.3</td>
<td>140.8 ± 3.0</td>
<td>137.0 ± 0.6</td>
<td>137.1 ± 0.8</td>
</tr>
<tr>
<td>4-nitro benzoic acid</td>
<td>69.1 ± 2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ACID</td>
<td>OPTIMIZATION PROCEDURE</td>
<td>ITERATION PROCEDURE No. 1</td>
<td>ITERATION PROCEDURE No. 2</td>
<td>ITERATION PROCEDURE No. 3</td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Salicylaldehyde</td>
<td>-</td>
<td>(3.53±0.00)x10^6</td>
<td>(3.52±0.00)x10^6</td>
<td>(3.99±0.05)x10^6</td>
</tr>
<tr>
<td>5-nitro salicylaldehyde</td>
<td>-</td>
<td>(2.69±0.03)x10^3</td>
<td>(2.69±0.02)x10^3</td>
<td>(2.71±0.17)x10^3</td>
</tr>
<tr>
<td>3-nitro salicylaldehyde</td>
<td>-</td>
<td>(3.24±0.02)x10^3</td>
<td>(3.24±0.02)x10^3</td>
<td>(3.26±0.16)x10^3</td>
</tr>
</tbody>
</table>
starting value of $F/\mathcal{K}_M$ should be as close to the true value as possible. Just how precarious the choice of a suitable starting value for the iteration process may become, can be illustrated by the application of the iteration procedure No. 1. to the case of lanthanum 3-bromo benzoate. Here, the iteration process fails to converge if the starting value of $F/\mathcal{K}_M$ is greater than 3.04 or less than 3.03. However, convergence is attained after only one cycle if the starting value is equal to the average value of these limits.

Even if the condition regarding the choice of a suitable starting value is satisfied, the iteration process may still fail to converge unless a second condition is fulfilled. According to Zaguskin [114] this condition requires that the sum of the elements of every row and every column of the matrix consisting of the partial derivatives of the functions underlying the approximation procedure, be less than unity. In the present work, failure to converge has been observed in the case of lanthanum 5-nitro salicylate with iteration procedures 1, 2, and 3, lanthanum 3-nitro salicylate with iteration procedures 2 and 3, lanthanum benzoate with iteration procedure 1 and lanthanum 4-nitro benzoate with iteration procedures 1, 2, and 3, (see table 5.1). Since, in all these cases, the starting value for the iteration process was varied over a very wide range, the conclusion must be drawn that the failure to converge here, is due to the second condition not being satisfied. As seen from table (5.1) in the majority of cases, however; studied in the present work, the iteration procedures lead to a successful conclusion, the results obtained by the three iteration methods agreeing remarkably well with one another.

In conclusion, it should be pointed out that whenever the conditions for convergence are satisfied, the iteration procedures, evolved in the
present work (on the basis of optical density measurements alone), lead to highly reliable results for the association constants of the ion pairs. The fact that in certain cases, one iteration procedure may fail while others succeed, shows that a further examination of the conditions for convergence is necessary.

The stability of an ion pair is governed by a number of factors, of which, the most important are -

1. The nature of the substituent on the ligand.
2. The magnitude of the electric charges on both metal ion and ligand.
3. The ionic radii of the metal ion and ligand.
5. Dielectric constant of the medium.

Of these, only the substituent effects, the size of the ligand and chelation need to be considered here, as only the ion pairs of the La$^{3+}$-ion in aqueous medium, are the subject of the present work.

It is reasonable to assume that the effect of a given substituent on the stability of the metal complex will be the same in nature as that on the corresponding proton complex but different in magnitude. This means that for a series of closely related ligands, (derived from weak acids), the stability of the metal complex should increase monotonically with increasing stability of the corresponding proton complex. This type of behaviour is, indeed, observed with all three groups of ion pairs studied in the present work. This can be seen from table (5,2) in which the ion pairs are arranged in three groups and which, in addition, to the dissociation constants of these acids, also gives the average values for the stability constants of the ion pairs found by the various methods.
<table>
<thead>
<tr>
<th>No.</th>
<th>ACID</th>
<th>$K_1$</th>
<th>$pK_1$</th>
<th>K</th>
<th>$\log_{10}K$</th>
<th>$\left(1/a\right) \times 10^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Salicylic acid</td>
<td>$1.064 \times 10^{-3}$</td>
<td>2.973</td>
<td>118.3</td>
<td>2.073</td>
<td>3.44</td>
</tr>
<tr>
<td>2</td>
<td>3-methyl salicylic acid</td>
<td>$1.135 \times 10^{-3}$</td>
<td>2.945</td>
<td>119.9</td>
<td>2.079</td>
<td>3.46</td>
</tr>
<tr>
<td>3</td>
<td>5-bromo salicylic acid</td>
<td>$2.20 \times 10^{-3}$</td>
<td>2.658</td>
<td>77.3</td>
<td>1.888</td>
<td>2.21</td>
</tr>
<tr>
<td>4</td>
<td>5-chloro salicylic acid</td>
<td>$2.23 \times 10^{-3}$</td>
<td>2.652</td>
<td>88.4</td>
<td>1.947</td>
<td>3.03</td>
</tr>
<tr>
<td>5</td>
<td>5-nitro salicylic acid</td>
<td>$7.57 \times 10^{-3}$</td>
<td>2.121</td>
<td>43.4</td>
<td>1.632</td>
<td>1.94</td>
</tr>
<tr>
<td>6</td>
<td>3-nitro salicylic acid</td>
<td>$13.4 \times 10^{-3}$</td>
<td>1.873</td>
<td>35.6</td>
<td>1.551</td>
<td>1.71</td>
</tr>
<tr>
<td>7</td>
<td>4-hydroxy benzoic acid</td>
<td>$2.692 \times 10^{-5}$</td>
<td>4.570</td>
<td>280</td>
<td>2.447</td>
<td>4.45</td>
</tr>
<tr>
<td>8</td>
<td>Benzoic acid</td>
<td>$6.295 \times 10^{-5}$</td>
<td>4.201</td>
<td>806</td>
<td>2.906</td>
<td>5.82</td>
</tr>
<tr>
<td>9</td>
<td>3-bromo benzoic acid</td>
<td>$1.553 \times 10^{-4}$</td>
<td>3.801</td>
<td>138</td>
<td>2.140</td>
<td>3.65</td>
</tr>
<tr>
<td>10</td>
<td>4-nitro benzoic acid</td>
<td>$3.61 \times 10^{-4}$</td>
<td>3.443</td>
<td>69</td>
<td>1.839</td>
<td>2.65</td>
</tr>
</tbody>
</table>

/continued.....
<table>
<thead>
<tr>
<th>No.</th>
<th>ACID</th>
<th>$K_1$</th>
<th>$pK_1$</th>
<th>$K$</th>
<th>$\log_{10}K$</th>
<th>$(1/a) \times 10^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Salicylaldehyde</td>
<td>$4.23 \times 10^{-9}$</td>
<td>8.374</td>
<td>$3.68 \times 10^6$</td>
<td>6.566</td>
<td>10.8</td>
</tr>
<tr>
<td>12</td>
<td>5-nitro salicylaldehyde</td>
<td>$4.676 \times 10^{-6}$</td>
<td>5.330</td>
<td>$2.70 \times 10^3$</td>
<td>3.431</td>
<td>6.30</td>
</tr>
<tr>
<td>13</td>
<td>3-nitro salicylaldehyde</td>
<td>$5.870 \times 10^{-6}$</td>
<td>5.231</td>
<td>$3.25 \times 10^3$</td>
<td>3.512</td>
<td>6.46</td>
</tr>
</tbody>
</table>
In some cases, e.g. ferric salicylate \([21]\) the difference in the standard free energy of formation of the metal and corresponding proton complexes is virtually independent of the nature of the substituent on the ligand. This condition can be expressed mathematically, by writing

\[
\Delta G^\circ_{LaL} - \Delta G^\circ_{HL} = \text{Constant}, \quad \text{(5.1)}
\]

where \(\Delta G^\circ_{LaL}\) and \(\Delta G^\circ_{HL}\) are the standard free energies of formation of the metal and proton complex, respectively.

Since, by definition

\[
\Delta G^\circ_{LaL} = -RT \ln K, \quad \text{(5.2)}
\]

and \(\Delta G^\circ_{HL} = -RT \ln K_1 = RT \ln K_1\), \(\text{(5.3)}\)

equation (5.1) becomes

\[
\Delta G^\circ_{LaL} - \Delta G^\circ_{HL} = -RT \ln K_1 = \text{Constant}. \quad \text{(5.4)}
\]

The last equation on rearranging takes the form

\[
\log K = pK_1 + \text{Constant}. \quad \text{(5.5)}
\]

Equation (5.5) predicts that a plot of \(\log K\) against \(pK_1\) should give a straight line with a slope equal to unity.

Such a plot is given in figure (5.1) for the ion pairs of the \(\text{La}^{3+}\)-ion with the salicylate and benzoate anions and in figure (5.2) for the ion pairs of the \(\text{La}^{3+}\)-ion with the salicylaldehyde anions. In the figures, the experimental points are numbered in the same way as the corresponding ion pairs are numbered in table (5.2). It can be seen that, in both cases, a reasonable straight line was obtained. In calculating the slope and intercept of these correlation plots, the method of least squares was used. The slopes and intercepts found by this means are \(0.386 \pm 0.083\) and \(0.847 \pm 0.210\) for figure \((5.1)\), and \(0.998 \pm 0.030\) and
-1.802 ± 0.196 for figure (5.2), respectively.

The fact that, in both cases, the slope is less than unity indicates that, on average, substitution affects the stability of the ion pairs to a smaller extent than the respective proton complexes. This type of behaviour is to be expected since the proton in the proton complexes is covalently bound and, consequently, is subject to stronger substituent effects than the La$^{3+}$-ion in the ion pairs.

To find to what extent the variates, in this case log $K$ and $pK_1$, are correlated to one another, the correlation coefficient $r$ [20] was calculated using the formula

$$r = \frac{n}{\sum_1^n (\log K - \overline{\log K})(pK_1 - \overline{pK_1})}/\left[\frac{n}{\sum_1^n (pK_1 - \overline{pK_1})^2} \frac{n}{\sum_1^n (\log K - \overline{\log K})^2}\right]^{1/2}, \hspace{1cm}(5.6)$$

where $n$ is the number of experimental points and the bar denotes the mean of the respective variables. In the limiting case, when the variates are fully correlated $r$ assumes the values +1 or -1. It is zero when the variates are not related at all.

The correlation coefficients, found in this way, are 0.851 for the ion pairs of the La$^{3+}$-ion with the salicylate and benzoate anions and 0.996 for the ion pairs of the La$^{3+}$-ion with the salicylaldehyde anions. It should be pointed out, however, that the coefficient of correlation for the La$^{3+}$/salicylaldehyde ion pairs is based on three points only and hence, is not very reliable. The present values for the correlation coefficients, are slightly smaller than found by Ernst and Menashi [21] for the ferric salicylates but are slightly larger than found by Ernst and Herring [22] for the ferric phenolates. The relatively high values of $r$ obtained in the present work, nevertheless, indicate that also, in the cases studied in the present work, a rough linear correlation exists between the stabilities of the metal complexes and those of the corresponding proton
complexes.

It appears, therefore, that linear substituent effects occur not only with covalent complexes but also with ion pairs. We are also led to the conclusion that since all the metal complexes studied in the present work, are due to ionic interaction alone, Williams' theory [12] regarding the significance of the slopes of correlation plots is not generally valid.

Further insight into the significance of the results found in the present work, may be obtained by considering them in the light of the Bjerrum theory of ion association [62].

The stability of an ion pair can be explained in terms of the standard free energy of formation by

$$\Delta G^0_{LaL} = -RT \ln K,$$

... (5.7)

where K is the association constant of the ion pair. Another measure of the stability of an ion pair is the interionic attraction energy

$$z_1 z_2 e^2 / a,$$

... (5.8)

where a is the distance of closest approach between the ions. It appears, therefore, that a plot of log K vs 1/a should yield a straight line. The distance of closest approach can be calculated using equations (1.4), (1.6) and (1.7) given in the Introduction.

The results of these calculations for the ion pairs are given in table (5.2). A plot of log K against 1/a as shown in figure (5.3) for the ion pairs of the La$^{3+}$-ion with the salicylate and benzoate anions and in figure (5.4) for the ion pairs of the La$^{3+}$-ion with the salicylaldehyde anions. In the figures, the experimental points are numbered in the same way as the corresponding ion pairs are numbered in table (5.2). It can be seen that, in both cases, the experimental points fall on good
FIGURE 5.1  CORRELATION PLOT FOR THE LANTHANUM SALICYLATES AND BENZOATES.
FIGURE 5.2. CORRELATION PLOT FOR THE LANTHANUM / SALICYLALDEHYDE ION PAIRS.
Figure 5.3: PLOT OF LOG K vs 1/a FOR THE LANTHANUM SALICYLATES AND BENZOATES.
FIGURE 5.4  PLOT OF LOG K vs $1/\alpha$ FOR THE LANTHANUM / SALICYLALDEHYDE ION PAIRS.
straight lines, thus indicating that the stability of the ion pairs studied in the present work, is inversely proportional to the distance of closest approach, as to be expected on the basis of the Bjerrum theory.

The correlation plot shown in figure (5.3) can be also used to draw some conclusions regarding the magnitude of the interaction of the La$^{3+}$-ion with the dipole of the -OH group in the lanthanum salicylate ion pairs.

It has been shown in the course of the present work that in the lanthanum salicylate ion pairs, the La$^{3+}$-ion associates with the carboxylate anion only, leaving the -OH group intact. This can be represented by the formula,

$$\text{C}_6\text{H}_5\text{COO}^- \cdots \text{La}^{3+} \cdots \text{OH}$$

Nevertheless, in view of the proximity of the -OH group, it is still possible for the La$^{3+}$-ion to interact with its dipole. However, the fact that, in constructing the correlation plot given in figure (5.3), it was possible to group together the lanthanum salicylate ion pairs with the lanthanum benzoate ion pairs suggests that in both types of complexes only the carboxylate group is involved and consequently that in the lanthanum salicylate ion pairs, the La$^{3+}$-ion dipole interaction is insignificant.

On the other hand, chelation through La$^{3+}$/dipole interaction appears to play some part in the formation of the La$^{3+}$/salicylaldehyde ion pairs. Some support for this conclusion can be drawn from the fact that the association constant of the La$^{3+}$/4-hydroxy benzaldehyde ion pair, where chelation of this type is not possible, was found to be too small for reliable measurements to be made.
Read in data;
$T_1, T_2, K_1, f_1, f_2, f_3$, initial trial value of $D_c$, increment of $D_c$, final trial value of $D_c$.
Sets of $(a-b), D^0, D$ values.

Calculate $h^0$ from equation (4.33)
Calculate $x, h^0 f_1^2, D^0 x$.
Apply least squares to equation (4.27); obtain $D_0$ and $D_1$.
Calculate standard deviations of $D_0$ and $D_1$.

Use initial trial value of $D_c$.
Set $\Delta h = 0$.
Calculate $c$ from equation (4.31)
Calculate $\Delta h$ from equation (4.21)
Test to see if previous value of $\Delta h$ differs by $\leq 0.01\%$.

NO YES

Calculate $(\Delta h x + T_1 K_1)/x$
Calculate $\Delta h(D_0 - D_1) - \Delta T_c + D_1 c$
Apply least squares to equations (4.23) and (4.32); obtain $K$ and $D_c^\#$, respectively.
Calculate standard deviations of $K$ and $D_c^\#$.

Print $h^0 x, h^0 f_1^2, D^0 x, D_0, D_1, \sigma_{D_0}, \sigma_{D_1}, c, \Delta h, y', y'', D_c, K, \sigma_K, D_c^\#, \sigma_{D_c^\#}$.

Add selected increment to $D_c$.
Test to see if new value of $D_c$ greater than final trial value of $D_c$ selected.

NO YES

STOP
Read in data.

\[ T_L, T_M, K_1, f_1, f_2, f_3, \] initial trial value of \( F/KT_M \),
selected increment of \( F/KT_M \), final trial value of \( F/KT_M \).
Sets of \((a - b), D^0, D\) values.

Calculate \( h^0 \) from equation (4.33).
Calculate \( x, h^0 f_1^2, D^0 x \).
Apply least squares to equation (4.27); obtain \( D_0 \) and \( D_1 \).
Calculate standard deviations of \( D_0 \) and \( D_1 \).

Use initial trial value of \( F/KT_M \). Print \( F/KT_M \).
Calculate \( D_c \) from equation (4.54).
Set \( \Delta h = 0 \).
Calculate \( c \) from equation (4.31).
Test to see if \( c < 0 \).

\[ \text{NO} \quad \text{YES} \]

Calculate \( \Delta h \) from equation (4.21).
Test to see if previous value of \( \Delta h \)
differs by \( < 0.01\% \).

\[ \text{NO} \quad \text{YES} \]

Calculate \( (\Delta h x + T_L K_1)/x \).
Apply least squares to equation (4.23);
obtain \( F/KT_M \). Print \( F/KT_M \).
Test to see if rate of change of \( F/KT_M \) with successive cycles is becoming smaller.

\[ \text{YES} \quad \text{NO} \]

Test to see if previous value of \( F/KT_M \)
differs by \( < 0.01\% \).

\[ \text{NO} \quad \text{YES} \]

Calculate standard deviation of \( F/KT_M \).
Print \( h^0, x, h^0 f_1^2, D^0 x, D_0, D_1, \sigma_{D_0}, \sigma_{D_1} \).
c, \( \Delta h, y, y'' \), \( D_0, K, F/KT_M, \sigma_{F/KT_M} \).

STOP

Add increment of \( F/KT_M \) to value of \( F/KT_M \).
Test to see if new value of \( F/KT_M \) is greater
than final trial value of \( F/KT_M \).
Print new value of \( F/KT_M \).

\[ \text{NO} \quad \text{YES} \]

STOP
FLOW DIAGRAM FOR ITERATION PROCEDURE No. 2.

Read in data.

- Initial trial value of \( \frac{F}{KT_M} \), increment of \( \frac{F}{KT_M} \), final trial value of \( \frac{F}{KT_M} \), \( D_0 \), \( D_1 \), \( D_L \).
- Sets of \((a - b)\) and \(D\) values.

Calculate \( h^0 \) from equation (4.33).

Calculate \( x \).

Use initial trial value of \( \frac{F}{KT_M} \). Print \( \frac{F}{KT_M} \).

Calculate \( c \) from equation (4.59).

Calculate \( \Delta h \) from equation (4.21).

Test to see if \( c < 0 \).

- NO
- YES

Calculate \( \frac{(\Delta h x + T_L K)}{x} \).

Apply least squares to equation (4.23); obtain \( \frac{F}{KT_M} \). Print \( \frac{F}{KT_M} \).

Test to see if rate of change of \( \frac{F}{KT_M} \) with successive cycles is becoming smaller.

- YES
- NO

Test to see if previous value of \( \frac{F}{KT_M} \) differs by \(< 0.01\%\).

- NO
- YES

Calculate standard deviation of \( \frac{F}{KT_M} \).

Calculate \( D_0 \) from equation (4.54).

Print \( h^0 \), \( x \), \( c \), \( \Delta h \), \( D_0 \), \( K \), \( \frac{F}{KT_M} \), \( \sigma_{\frac{F}{KT_M}} \).

STOP

Add increment of \( \frac{F}{KT_M} \) to value of \( \frac{F}{KT_M} \). Test to see if new value of \( \frac{F}{KT_M} \) is greater than final trial value of \( \frac{F}{KT_M} \).

- NO
- YES

STOP
FLOW DIAGRAM FOR ITERATION PROCEDURE No. 3

Read in data.

- Initial trial value of \( F/\theta T_M \), increment of \( F/\theta T_M \), final trial value of \( F/\theta T_M \), \( D_0, D_1, D_L \).
- Sets of \( (a - b) \) and \( D \) values.

Calculate \( h^0 \) from equation (4.33).

Use initial value of \( F/\theta T_M \). Print \( F/\theta T_M \).

Calculate \( c \) from equation (4.59).

Test to see if value of \( c < 0 \).

- YES: Calculate \( h \) from equation (4.61).
  Calculate \( (T_L-c)/c \) and \( 1 + hf_1^2/K_1 \).
  Apply least square to equation (4.62); obtain \( F/\theta T_M \). Print \( F/\theta T_M \).
  Test to see if rate of change of \( F/\theta T_M \) with successive cycles is becoming smaller.

- NO: Test to see if previous value of \( F/\theta T_M \) differs by \(< 0.01\% \).

- NO: Calculate standard deviation of \( F/\theta T_M \). Calculate \( D_c \) from equation (4.54).

- YES: Print \( h, x, c, (T_L-c)/c, 1 + hf_1^2/K_1 \).

- STOP

Add increment of \( F/\theta T_M \) to value of \( F/\theta T_M \).

Test to see if new value of \( F/\theta T_M \) is greater than final trial value of \( F/\theta T_M \). Print \( F/\theta T_M \).

- NO: STOP
- YES: STOP
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SPECTROPHOTOMETRIC DETERMINATION OF ASSOCIATION CONSTANT OF LANTHANUM SALICYLATE
Spectrophotometric Determination of Association Constant of Lanthanum Salicylate

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Spectrophotometric evidence has been obtained for the formation of the ion-pair LaHSal$^{2+}$ in aqueous solution of lanthanum salicylate. A new spectrophotometric method of determining association constants of ion-pairs of metal ions with anions of weak acids is described. The method, which dispenses with pH-measurements, has been applied to determine the association constant $K = \frac{[\text{LaHSal}^{2+}]}{[\text{La}^{3+}][\text{HSal}^-]}$ for the LaHSal$^{2+}$ ion-pair; at 25°C its value is $1.19 \times 10^2$.

The stability constants of the complexes of the Fe$^{3+}$-ion with some substituted salicylic acids have been reported and the correlation function relating the stabilities of these complexes to those of the corresponding proton complexes was discussed. In general, the form of such correlation functions depends on many factors, such as the ionization potential of the metal ion, polarization of the ligand by the metal ion, and in particular $\pi$-bonding which plays such an important part in the ferric salicylate complexes. It seemed desirable, therefore, to extend these studies to metal ions which are unlikely to enter into $\pi$-bonding with the salicylate anions, as e.g., the La$^{3+}$-ion. Since the absorption spectra of aqueous solutions of salicylic acid have been studied it was decided to adopt the spectrophotometric method. In this paper we present a method of determining association constants of ion-pairs (involving anions of weak acids) which dispenses with pH-measurements and relies solely on spectrophotometric measurements.

EXPERIMENTAL

REAGENTS

All reagents were of a.r. grade unless otherwise stated. Salicylic acid and NaClO$_4$ (B.D.H. laboratory grade) were purified as previously described. The method of preparing solutions of NaOH, NaClO$_4$, HClO$_4$ and salicylic acid has also been reported. A stock-solution of La(ClO$_4$)$_3$ was made up by dissolving 99.5% La$_2$O$_3$ (Johnson and Matthey) in a HClO$_4$ solution. The resulting solution was analyzed for lanthanum using a solution of EDTA which has been standardized against spectroscopically pure zinc (Johnson and Matthey). The concentration of free HClO$_4$ in the La(ClO$_4$)$_3$ stock-solution was found by passing an aliquot of the solution through a cation-exchange resin (Zeocarb 225) and titrating the eluant with a standard CO$_2$-free NaOH solution using methyl red as the indicator.

OPTICAL DENSITY MEASUREMENTS

Optical density measurements were carried out at 250 ± 0.1°C by means of a Unicam S.P. 500 spectrophotometer using matched silica cells (of 4-cm optical path length). The instrument was calibrated as previously described. To test the reproducibility of the measurements duplicate solutions were used throughout. All calculations were carried out on a Ferranti Sirius computer.
SPECTROPHOTOMETRIC EVIDENCE FOR ION-PAIRING

The symbol H$_2$L represents salicylic acid. Also, to distinguish solutions of La-salicylate from those of salicylic acid, the symbols associated with the latter solutions are written, where appropriate, with the superscript zero. For the first constant of salicylic acid the value $K_1 = 1.064 \times 10^{-3}$ is used.

The experimental procedure involved measurements of the optical density of two series of solutions. Solutions of series A were prepared by mixing fixed amounts of a standard La(ClO$_4$)$_3$-solution, and varying amounts of a standard HClO$_4$-solution; to each mixture a calculated amount of a standard NaClO$_4$-solution and a requisite amount of water were added so that the stoichiometric concentration $T_M$ of La(ClO$_4$)$_3$, the stoichiometric concentration $T_L$ of salicylic acid, and the ionic strength $I$ of the final solutions were maintained constant throughout, at $T_M = 10^{-2}$ mole/l, $T_L = 2.5 \times 10^{-4}$ mole/l, and $I = 0.1$. The stoichiometric concentration of La(ClO$_4$)$_3$ was 40 times greater than that of salicylic acid, this large excess of La$^{3+}$-ions being used to minimize the formation of ion pairs containing more than one ligand per metal-ion. Solutions of series B were prepared in the same way except that the La(ClO$_4$)$_3$ was replaced by NaClO$_4$ the amount of which was adjusted so as to keep the ionic strength constant. The H$^+$-ion concentration of the solutions ranged from $5 \times 10^{-2}$ to $10^{-5}$ mole/l, in which region only the first stage of ionization of salicylic acid occurs appreciably; accordingly, the only light-absorbing species which are considered are H$_2$L, HL$^-$ and any complexes that may be present.

To obtain spectrophotometric evidence for the occurrence of ion-association in the La-salicylate solutions the absorption curves of the two types of solutions were recorded at various pH-values (in the range 1-5-5) and the wavelength region 240-350 m$\mu$. In this region, in which neither NaClO$_4$ nor La(ClO$_4$)$_3$ absorbs light, the effect of the La$^{3+}$-ions on the absorption curves of salicylic acid was relatively small except at $\lambda = 326 m\mu$ at which the pH-variations of the optical density were the most pronounced. This wavelength, therefore, was adopted for the study of complex formation in the La-salicylate solutions. At this wavelength and throughout the pH-region employed the optical density $D$ of the La-salicylate solutions (series A) is always smaller than the optical density $D^0$ of the salicylic acid solutions (series B). The results of these experiments, are given in table 1 which shows the variation of both $D$ and $D^0$ with the H$^+$-ion concentration $h^o$ of the latter solutions. The difference $\Delta D = D^0 - D$ increases at first with increasing $h^o$, reaches a maximum at $h^o \sim 10^{-3}$ mole/l, and then decreases.

Since, in the pH-region corresponding to this maximum, the $\Delta D$ values are significantly larger than the experimental error involved in the optical density measurements we conclude that some complex formation takes place in the La-salicylate solutions. On the left-hand side of the maximum, the quantities $D$ and $D^0$ approach each other as $h^o$ decreases until at $h^o \sim 10^{-5}$ mole/l, when more than 99% of the

| Table 1.—VARIATION OF $\Delta D$ WITH $h^o$ |
| $T_L = 2.509 \times 10^{-4}$ mole/l; $T_M = 1.002 \times 10^{-2}$ mole/l; $\lambda = 326 m\mu$; $I = 4 cm$; $I = 0.1$ |
| $h^o \times 10^2$ | 0.010 | 0.123 | 0.228 | 0.642 | 1.300 | 2.596 | 3.593 | 6.062 | 10.04 | 49.32 |
| $D^0$ | 0.228 | 0.237 | 0.261 | 0.351 | 0.426 | 0.507 | 0.542 | 0.586 | 0.620 | 0.683 |
| $D$ | 0.228 | 0.232 | 0.251 | 0.332 | 0.399 | 0.479 | 0.516 | 0.565 | 0.607 | 0.679 |
| $\Delta D$ | 0.000 | 0.005 | 0.010 | 0.019 | 0.027 | 0.028 | 0.026 | 0.021 | 0.013 | 0.004 |

The values of $h^o$ at which the optical density of La-salicylate solutions (series A) is maximum at $\lambda = 326 m\mu$ are given in table 2.
salicylic acid has dissociated, they become virtually equal, at a value of about 0.23. On the right-hand side of the maximum, $D$ and $D^*$ converge as $h^0$ increases and approaches the value 0.690. The two limiting values 0.690 and 0.23 coincide with the values which we obtained at $I = 0.1$ for the quantities

$$D_0 = \varepsilon_0 T_L l, \quad D_1 = \varepsilon_1 T_L l,$$

respectively, in which $\varepsilon_0 =$ extinction coefficient of the undissociated salicylic acid molecules, $\varepsilon_1 =$ extinction coefficient of the HL$^-$-ion, and $l =$ length of the optical path.

This type of behaviour can be best explained by assuming that in the La-salicylate solutions complex formation takes place mainly between the La$^{3+}$- and the HL$^-$-ions, and that the extinction coefficient of the species LaHL$^{2+}$ is not appreciably different from that of the HL$^-$-ion. At pH-values, at which most of the salicylic acid is in the undissociated form, little complex formation occurs; the optical density of both A- and B-solutions is then approximately equal to $D_0$ and $\Delta D$ is very small. As $h^0$ decreases the degree of dissociation of salicylic acid and, consequently, the extent of complex formation in the La-salicylate solutions increases; as a result the concentrations of both HL$^-$ and H$_2$L in these solutions will be less than in the corresponding salicylic acid solutions which do not contain lanthanum. Since the extinction coefficient of the species LaHL$^{2+}$ does not differ much from that of HL$^-$ the optical density of the A-solutions will be less than the optical density of the B-solutions by an amount which is roughly proportional to the decrease in the concentration of H$_2$L brought about by complex formation. Finally, at pH-values at which most of the salicylic acid has dissociated the contribution of H$_2$L to the total absorbance will be small and the optical densities of both A and B solutions will be approximately equal to $D_1$.

Therefore, under the experimental conditions employed, ion-pairing occurs between La$^{3+}$- and HL$^-$-ions.

**THEORY**

In accordance with the spectrophotometric evidence we assume that in the La-salicylate solutions ion-association mainly occurs between the La$^{3+}$- and HL$^-$-ions. Calculations based on data reported on ion-association in salts of sodium and some univalent anions suggest that at the total concentrations of Na$^+$-ions and salicylic acid employed in the present investigation the extent of ion-pairing between the Na$^+$- and HL$^-$-ions would be much too small to be spectrophotometrically detectable; the species NaHL can thus be disregarded. Since, in our pH-range the terms [OH$^-$], [L$^2$-], and [LaOH$^{2+}$]$^8$ are negligible the only equilibria considered for the La-salicylate solutions are

$$K_1 = \frac{h[HL^-]}{[H_2L]} f_1^2,$$

$$K = \frac{cf_2}{[La^{3+}][HL^-] f_1 f_3}$$
where \( h = [\text{H}^+] \), \( c = [\text{LaHL}^{2+}] \) and \( f_1, f_2, \) and \( f_3 \) are the activity coefficients of the singly, doubly, and triply, charged species, respectively. The concentration terms \( c, [\text{La}^{3+}], [\text{HL}^-], \) and \( [\text{H}_2\text{L}] \) are related to one another by the expressions

\[
T_L = c + [\text{HL}^-] + [\text{H}_2\text{L}],
\]

\[
T_M = [\text{La}^{3+}] + c \approx [\text{La}^{3+}],
\]

since \( T_M \gg T_L \), and hence \( T_M \gg c \).

By combining (2.3) with (2.1),

\[
[\text{HL}^-] = (T_L - c)K_1/(K_1 + hf_1^2),
\]

\[
[\text{H}_2\text{L}] = (T_L - c)hf_2^2/(K_1 + hf_1^2),
\]

From the electroneutrality principle,

\[
h = a + c + [\text{HL}^-],
\]

where \( a \) is the stoichiometric concentration of \( \text{HClO}_4 \) added.

For solutions of salicylic acid which do not contain lanthanum, eqn. (2.3) (2.5), (2.6) and (2.7) simplify to

\[
T_L = [\text{HL}^-]^o + [\text{H}_2\text{L}]^o,
\]

\[
[\text{HL}^-]^o = T_LK_1/x,
\]

\[
[\text{H}_2\text{L}]^o = T_lh^of_1^2/x,
\]

\[
h^o = a + [\text{HL}^-]^o,
\]

where

\[
x = K_1 + h^of_1^2.
\]

Hence,

\[
c = [\text{H}_2\text{L}]^o - [\text{H}_2\text{L}]^o - [\text{HL}^-],
\]

\[
\Delta h = c - ([\text{HL}^-]^o - [\text{HL}^-]),
\]

\[
\Delta h = [\text{H}_2\text{L}]^o - [\text{H}_2\text{L}],
\]

where

\[
\Delta h = h - h^o.
\]

Substituting for \([\text{HL}^-] \) and \([\text{HL}^-]^o \) from (2.5) and (2.9) into (2.14),

\[
\Delta h^2xf_1^2 + \Delta h(x^2 + T_lK_1f_1^2 - cx^2f_1^2) - cxh^of_1^2 = 0.
\]

Since, in our pH-range the term \( \Delta h^2xf_1^2 \) is negligibly small, eqn. (2.17) becomes

\[
\Delta h = cxh^of_1^2/(x^2 + T_lK_1f_1^2 - cx^2f_1^2).
\]

Substituting for \([\text{HL}^-] \) from (2.14) into (2.2) and rearranging,

\[
(\Delta hx + T_lK_1)/c = ax,
\]

where

\[
\alpha = 1 + (f_2/KTMf_1f_3),
\]

Thus a plot of \( y' = (\Delta hx + T_lK_1)/c \) against \( x \) should yield a straight line with a slope equal to \( \alpha \).

The optical density of the solutions of salicylic acid which do not contain lanthanum is given by

\[
D^o = e_0[H_2L]^o + e_1[HL^-]^o,
\]
where \( l \) is the length of the optical path in cm. In view of (1.1), (1.2), (2.9), and (2.10) the last equation can be also written in the form

\[
D^o x = D_1 K_1 + D_0 h^o f_1^2,
\]

For solutions of La-salicylate the Lambert-Beer law takes the form

\[
D = e_0[H_2L]l + e_1[HL^-]l + e_cl,
\]

where \( e_c \) is the extinction coefficient of LaHL\(^{2+}\).

Upon substituting for [HL\(^-\)] and [H\(_2\)L] from (2.5) and (2.6) into (2.23) and solving for \( c \),

\[
c = \frac{D_1 K_1 + h f_1^2 D_0 - D(K_1 + h f_1^2)}{D_1 K_1 + h f_1^2 D_0 - D(K_1 + h f_1^2)} T_l,
\]

where

\[
D_c = e_c T_l l,
\]

Combination of (2.24) with (2.22) gives

\[
c = \frac{\Delta D x + \Delta h f_1^2(D_0 - D)}{(D^o - D_x)x + \Delta h f_1^2(D_0 - D_c)} T_l.
\]

Finally, subtraction of (2.23) from (2.21), and use of (2.14) and (2.15), gives

\[
\Delta h(D_0 - D_1) - \Delta DT_l + D_1 c = D_c c,
\]

from which if \( y^* = \Delta h(D_0 - D_1) - \Delta DT_l + D_1 c \) is plotted against \( c \) a straight line should be obtained with a slope equal to \( D_c \).

**DISCUSSION**

**DETERMINATION OF \( D_0 \) AND \( D_1 \)**

The evaluation of the association constant \( K \) requires a knowledge of \( e_0, e_0, \) and \( e_1 \) at the selected wavelength \( \lambda = 326 \text{ m} \mu \). For the last two coefficients Ernst and Menashi\(^4\) have found the values \( e_0 = 717 \) at \( I = 0.8 \) and \( e_1 = 200 \) at \( I = 10^{-3} \); however, as all solutions employed in the present work were maintained at \( I = 0.1 \) we redetermined these quantities by means of eqn. (2.22). This predicts that a plot of

<table>
<thead>
<tr>
<th>( a \times 10^3 ) mole/l.</th>
<th>( b \times 10^2 ) mole/l.</th>
<th>( D^o )</th>
<th>( h f_1^2 \times 10^3 )</th>
<th>( x \times 10^3 )</th>
<th>( y = D^o x \times 10^3 )</th>
<th>( \Delta y \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.459</td>
<td>9.950</td>
<td>0.351</td>
<td>0.395</td>
<td>1.459</td>
<td>0.512</td>
<td>+0.005</td>
</tr>
<tr>
<td>1.157</td>
<td>9.888</td>
<td>0.426</td>
<td>0.801</td>
<td>1.865</td>
<td>0.795</td>
<td>+0.002</td>
</tr>
<tr>
<td>2.496</td>
<td>9.736</td>
<td>0.507</td>
<td>1.600</td>
<td>2.664</td>
<td>1.351</td>
<td>-0.003</td>
</tr>
<tr>
<td>3.511</td>
<td>9.644</td>
<td>0.542</td>
<td>2.214</td>
<td>3.278</td>
<td>1.776</td>
<td>-0.004</td>
</tr>
<tr>
<td>4.490</td>
<td>9.553</td>
<td>0.566</td>
<td>2.809</td>
<td>3.873</td>
<td>2.192</td>
<td>-0.009</td>
</tr>
<tr>
<td>6.006</td>
<td>9.400</td>
<td>0.586</td>
<td>3.735</td>
<td>4.799</td>
<td>2.812</td>
<td>+0.009</td>
</tr>
</tbody>
</table>

\( D_0 = 0.690; \sigma_{D_0} = \pm 0.003 \); \( e_0 = 688 \); \( \sigma_{e_0} = \pm 3 \).

\( D_1 = 0.229; \sigma_{D_1} = \pm 0.005 \); \( e_1 = 228 \); \( \sigma_{e_1} = \pm 5 \).

\( D^o x \) against \( h f_1^2 \) should give a straight line with a slope and intercept equal to \( D_0 \) and \( D_1 K_1 \), respectively.

The quantity \( h^o \) was calculated using eqn. (2.11) expressed as a quadratic equation and solved by standard methods. The activity coefficients were evaluated by means of the Davies equation, with a probable error not exceeding 3%.

The results are given in table 2 where \( b \) is the concentration of NaClO\(_4\) and \( \Delta y \) the residual
The precision of the results was assessed by computing the standard deviations of the sloped and intercept \( ^9 \) and hence the standard deviations \( \sigma_{D_0} \) and \( \sigma_{D_1} \) of \( D_0 \) and \( D_1 \), respectively.

The values \( \varepsilon_0 = 688 \) and \( \varepsilon_1 = 228 \) found in the present work at \( I = 0.1 \) differ significantly from the corresponding values obtained by Ernst and Menashi.\(^4\) Since (as shown by our calculations not reported here) these differences cannot be completely accounted for by the inaccuracy of the Davies equation, it appears that \( \varepsilon_0 \), and to a much greater extent \( \varepsilon_1 \) vary with changing ionic strength. Also in the evaluation of the association constant \( K \) the present values for \( \varepsilon_0 \) and \( \varepsilon_1 \) give much more consistent results than those obtained by Ernst and Menashi.\(^4\)

**DETERMINATION OF ASSOCIATION CONSTANT**

An inspection of eqn. (3.1), (2.18), (2.19), (2.26) and (2.27) shows that if \( D_c \) were known the values of \( \Delta h \) and \( c \), corresponding to any given value of \( h^o \), could be calculated by solving eqn. (2.18) and (2.26). It would then be possible to evaluate the association constant \( K \) by plotting \( y' = (\Delta h + T_1 K_1)/c \) against \( x \) and measuring the slope \( \alpha \) of the straight line so obtained.

Since only the approximate value of \( D_c \) (obtained from the variation of \( \Delta D \) with \( h^o \)) was known beforehand, the value of \( K \) was calculated by varying the value of \( D_c \) in the range 0.21-0.24 and finding the best value of the slope \( \alpha \). The values of \( h^o \) and \( x \) were first obtained from eqn. (3.1); next, the values of \( \Delta h \) and \( c \), corresponding to any given value of \( D_c \), were computed by means of eqn. (2.18) and (2.26) using the method of successive approximations. The values of \( y' \) were then found and the slope of the plot of \( y' \) against \( x \) determined by applying the method of least squares. The goodness of fit attained at a given value of \( D_c \) was assessed by calculating the standard deviation \(^{10} \sigma_{\alpha} \) of \( \alpha \). The variation of \( \sigma_{\alpha} \) with \( D_c \) is given in fig. 1; as \( D_c \) increases \( \sigma_{\alpha} \) decreases, passes through a minimum and then increases. The values of \( \alpha \) and \( D_c \) which correspond to this minimum, and which enable the experimental data to be best fitted into equation (2.19) are \( \alpha = 4.597 \) and \( D_c = 0.226 \). The results are summarized in table 3 where the precision of the experimental data is expressed in terms of the residuals \( \Delta y' \) and \( \Delta y^o \), and of the standard deviations \( \sigma_{\alpha} \), \( \sigma_{\alpha}^c \), and \( \sigma_K \). In computing the value \( K = (1.188 \pm 0.008) \times 10^2 \) for the association constant the values
ASSOCIATION CONSTANT OF LANTHANUM SALICYLATE

\[ \alpha = 4.597 \pm 0.024, \text{ and } D_e = 0.226 \pm 0.001 \] were used; for the activity coefficients the values \( f_1 = 0.785 \), \( f_2 = 0.380 \), and \( f_3 = 0.113 \), obtained from the Davies equation (and, according to Davies,\(^8\) subject to a probable error of \( \pm 3\% \)) were employed. The standard deviation of \( K \) is less than \( 1\% \), thus indicating that satisfactory precision has been attained. The present value \((1.188 \pm 0.008) \times 10^2\) for \( K \) is appreciably lower than that obtained by Cefola, Tompa, Celiano, and Gentile at 30°C using the glass electrode.\(^{11}\)

<table>
<thead>
<tr>
<th>Table 3.—Association constant of lanthanum salicylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_L = 2.509 \times 10^{-4} \text{ mole/l.} ); ( T_M = 1.002 \times 10^{-2} \text{ mole/l.} ); ( I = 0.1 ); ( \lambda = 326 \text{ m\mu} ); ( l = 4 \text{ cm} ); ( D_e = 0.226 )</td>
</tr>
<tr>
<td>( \alpha \times 10^3 )</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>0.201</td>
</tr>
<tr>
<td>1.241</td>
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<tr>
<td>2.238</td>
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<tr>
<td>3.253</td>
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<tr>
<td>4.232</td>
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<tr>
<td>5.748</td>
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</tbody>
</table>

\( \alpha = 4.597 ; \sigma_\alpha = \pm 0.024 ; \) \( D_e^* = 0.228 ; \sigma_\alpha = \pm 0.001 ; \) \( K \) (present work) = \((1.188 \pm 0.008) \times 10^2\); \( K \) (previous work) = \(4.37 \times 10^2 \ [\text{ref. (11)}]\).

As a further test of the reliability of these calculations the value of \( D_e \) was computed by means of eqn. (2.27); values of \( y'' \) were calculated using the values of \( \Delta h \) and \( c \) shown in table 3, and the slope of the plot of \( y'' \) against \( c \) was obtained by applying the method of least squares. The value 0.228 of \( D_e \), shown in table 3 as \( D_e^* \), is in good agreement with the value 0.226 obtained from the plot of \( \sigma_\alpha \) against \( D_e \).

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