Sorptive Separation
of
Simple Water Soluble Organics

by
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A Dissertation submitted for the degree of
Doctor of Philosophy

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University of Surrey
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England
1989
To my wife, Wahyun,

my mother, Saupeh and

my late father.
Acknowledgements

I would like to thank my supervisor Dr. Farhad A. Farhadpour for his guidance, encouragement and expert advice throughout the course of this thesis.

Thanks must also go to my colleagues Dr. Ajit Bansal and Mr. Yeow W. Fong for their assistance in the theoretical and experimental work.

Thanks are extended to the University staff, Ken George, Dave Arnall, Peter Pennington and Ron Brown for their help on the construction of the apparatus.

Finally, I would like to acknowledge the Biotechnology Directorate of the Science and Engineering Research Council for funding of the project and the research fellowship.
The primary objective of this thesis was to examine the major factors affecting the sorptive separation of simple water soluble organics, e.g., alcohols, aldehydes, ketones, carboxylic acids, with hydrophobic adsorbents. The model system considered is the separation of aqueous ethanol with an adsorbent formed by pelletizing micron sized hydrophobic silicalite crystals.

The structural characteristics of the bi-dispersed silicalite pellets are examined in Chapter 2. The size distribution of the crystals was measured by various techniques and fitted a log-normal distribution with a median size of $3.78 \mu m$. The macropore size distribution of the pellets was determined by mercury porosimetry and showed a unimodal distribution with a mean macropore diameter of $0.6 \mu m$. The pellets had a macropore volume of $0.202 \, cm^3/g$, a macropore voidage of 0.26 and a density of $1.285 \, g/cm^3$.

The sorption equilibria for the system (ethanol-water)/silicalite crystals is considered in Chapter 3. The basic difference between vapour and liquid phase sorption and the fundamental constraint caused by the inaccessibility of the adsorbed phase to direct measurement are considered first. This is followed by the development of a novel technique which for the first time enables the direct measurement of the individual adsorption isotherms for microporous solids. Comparison of the measured data with the predictions based on the available theories of adsorption from solution show considerable
discrepancy. This is traced to the inherent assumption of no volume change of mixing common to all the proposed theories. For the system {ethanol-water}/silicalite the adsorbed phase exhibits as much as 30% volume change of mixing. The packing density and the total number of molecules adsorbed is therefore a very strong function of composition.

Chapter 4 is devoted to a rigorous thermodynamic analysis of the adsorption equilibria for the system {ethanol-water}/silicalite. The relevant thermodynamic relationships are derived first without any a priori assumption other than the existence of a distinct adsorbed phase. The major significance of the analysis presented is that for the very first time it is based on measured rather than predicted adsorbed phase composition. For the {ethanol-water}/silicalite system, the behaviour of the adsorbed phase is shown to be radically different from that of the bulk solution. The bulk liquid exhibits strong positive deviation from Raoult’s law indicating that water-water and ethanol-ethanol molecular interactions dominate over that between unlike species. The adsorbed phase activity coefficients, however, show strong negative deviation from Raoult’s law; indicating that ethanol-water interactions overshadow that between the like molecules. The major practical consequence of this observation is that surface modification of the hydrophobic crystals is unlikely to alter the selectivity significantly. The analysis presented also enables a direct thermodynamic consistency test of the adsorption data which has not been previously reported.

The models proposed to describe intraparticle mass transfer are critically reviewed in Chapter 5 and the macropore-micropore diffusion
model is identified as the most realistic for silicalite pellets. The intracrystalline diffusion rates were measured directly and their analysis reveals fundamental differences between uptake of pure ethanol and pure water consistent with the observed equilibrium behaviour. This information is used to determine the controlling mechanism for mass transfer between a flowing fluid and silicalite pellets. The time constants for external film mass transfer, macropore diffusion and micropore diffusion are estimated at 2.72, 82.32 and 0.07 seconds respectively. The controlling mechanism is therefore macropore diffusion with intracrystalline diffusion playing an insignificant role. This a direct consequence of the small crystal size and the relatively rapid intracrystalline diffusivity of water and ethanol in silicalite.

The above information is pulled together in a mathematical model to describe the dynamics of adsorption of ethanol–water mixtures onto a fixed-bed of silicalite pellets. The model allows for axial dispersion, external film mass transfer and describes the intraparticle mass transfer in terms of a macropore diffusion model. The model partial differential equations are solved by the orthogonal collocation technique. A detailed sensitivity analysis is conducted which confirms axial dispersion and external film mass transfer coefficients can be confidently predicted from the available literature correlations. The isotherm is measured independently which leaves only the effective macropore diffusivity to be obtained by matching with experimental breakthrough curve. Such curves were obtained on a carefully designed small pilot adsorption unit with considerable attention to the distortions caused by the entrance and exit effects.
and the sampling procedures. The effective macropore diffusivity recovered is $4.0 \times 10^{-6}$ cm$^2$/s which suggests a tortuosity of 3.2 for the silicalite pellets. This model and the parameter values determined independently provides a valuable tool for future scale-up and design studies.
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<tr>
<td>(a)</td>
<td>Specific surface area ((\text{cm}^2/\text{cm}^3)).</td>
</tr>
<tr>
<td>(\left(B_{1}\right)_{m})</td>
<td>Mass transfer Biot number (K \frac{R}{(3 \pi D_{p} p_{p} p_{l})}).</td>
</tr>
<tr>
<td>(c_{i})</td>
<td>Fluid phase concentration of (i) ((\text{mol/ cm}^3)).</td>
</tr>
<tr>
<td>(c_{i}^I)</td>
<td>Interfacial fluid phase concentration of (i) ((\text{mol/ cm}^3)).</td>
</tr>
<tr>
<td>(c_{p_{l}})</td>
<td>Macropore fluid phase concentration of (i) ((\text{mol/ cm}^3)).</td>
</tr>
<tr>
<td>(c_{l_{0}}(t))</td>
<td>Fixed-bed inlet concentration of (i) ((\text{mol/ cm}^3)).</td>
</tr>
<tr>
<td>(c_{R})</td>
<td>Reference bulk liquid concentration ((\text{mol/ cm}^3)).</td>
</tr>
<tr>
<td>(D_{L})</td>
<td>Axial dispersion coefficient ((\text{cm}^2/\text{s})).</td>
</tr>
<tr>
<td>(D_{c_{i}})</td>
<td>Intracrystalline (solid) diffusion coefficient of (i) ((\text{cm}^2/\text{s})).</td>
</tr>
<tr>
<td>(D_{p_{l}})</td>
<td>Macropore diffusion coefficient of (i) ((\text{cm}^2/\text{s})).</td>
</tr>
<tr>
<td>(D_{s_{l}})</td>
<td>Surface diffusion coefficient of (i) ((\text{cm}^2/\text{s})).</td>
</tr>
<tr>
<td>(d)</td>
<td>Kinetic diameter (Å).</td>
</tr>
<tr>
<td>(d_{c})</td>
<td>Crystal or microsphere diameter ((\mu\text{m}) or cm).</td>
</tr>
<tr>
<td>(d_{mac})</td>
<td>Macropore diameter ((\mu\text{m}) or cm).</td>
</tr>
<tr>
<td>(d_{p})</td>
<td>Particle diameter (cm).</td>
</tr>
<tr>
<td>(f_{i}^{s})</td>
<td>Standard state fugacity of adsorbate (i).</td>
</tr>
<tr>
<td>(f_{l}^{0})</td>
<td>Fugacity of (i) in the adsorbed phase.</td>
</tr>
<tr>
<td>(f)</td>
<td>Fugacity of pure (i) in the adsorbed phase.</td>
</tr>
<tr>
<td>(\Delta g^{E})</td>
<td>Excess Gibbs free energy of the adsorbed phase (J/mol).</td>
</tr>
<tr>
<td>(G_{s})</td>
<td>Gibbs free energy of the adsorbed phase (J/mol).</td>
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<tr>
<td>(K',K)</td>
<td>Empirical constants [Eqs. 3.18, 3.19 and 3.20].</td>
</tr>
<tr>
<td>(K_{bl})</td>
<td>Overall mass transfer coefficient of (i), Eq. 5.2 ((\text{cm/s})).</td>
</tr>
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</table>
$K_{f1}$  External film mass transfer coefficient of $i$, Eq. 5.5 (cm/s).

$K_{p1}$  Overall mass transfer coefficient of $i$, Eq. 5.1 (cm/s).

$K_{s1}$  Pseudo-external film mass transfer coefficient of $i$, Eq. 5.3 (cm/s).

$M_i$  Molecular weight of $i$.

$m_t$  Solid uptake at time $t$ (mol/g).

$m_\infty$  Solid uptake at saturation (mol/g).

$N^s$  Total number of moles in the adsorbed phase (mol/g solid).

$n_a$  Number of "moles" of non-volatile adsorbent.

$n_{i0}^s$  Specific molar adsorption of pure $i$ (mol/g solid).

$n_i^s$  Specific molar adsorption of $i$ (mol/g solid).

$P_0^i$  Vapour pressure of pure $i$ (atm).

$P_i$  Partial pressure of $i$ (atm).

$\text{Pe}_L$  Axial peclet number ($vL/D_L$).

$\text{Pe}_p$  Particle peclet number ($v_d/D_p$).

$Q^s$  Total absolute adsorption (g/g solid).

$q_i$  Solid phase concentration of $i$ (mol/g solid).

$q_i^*$  Average solid phase concentration of $i$ (mol/g solid).

$q_{i1}^e$  Equilibrium solid phase concentration of $i$ (mol/g solid).

$q_{i1}^i$  Interfacial solid phase concentration of $i$ (mol/g solid).

$q_{Ri}$  Reference solid phase concentration (mol/g solid).

$q_{i1}^s$  Specific adsorption of $i$ from a mixture (g/g solid).

$q_{i1}^{0s}$  Specific adsorption of pure $i$ (g/g solid).

$R$  Universal gas constant.

$R_p$  Particle radius (cm).

$Re$  Particle Reynolds number ($\rho_d v_d/\nu$).

$S$  Selectivity of silicalite crystals.

$S_i$  Specific transfer rate of $i$ [Eq. 5.24] (mol/g/s).
Sc  Schmit number \( \nu / \rho_f \frac{D_m}{f_m} \).

\( \nu \)  Sherwood number \( 2K_f R_p / D_m \)

Specific micropore volume (cm\(^3\)/g of solid).

\( \nu_s^1 \)  Partial molar volume of \( i \) in the adsorbed phase (cm\(^3\)/mol).

\( \nu_{os}^1 \)  Molar volume of pure \( i \) in the adsorbed phase (cm\(^3\)/mol).

\( v \)  Interstitial velocity (cm/s).

\( v_R \)  Reference linear velocity (cm/s).

\( w_i \)  Weight fraction of \( i \) in liquid phase.

\( w_i^s \)  Weight fraction of \( i \) in adsorbed phase.

\( x_i \)  Mole fraction of \( i \) in liquid phase.

\( x_i^s \)  Mole fraction of \( i \) in adsorbed phase.

Greek symbols

\( \alpha \)  Tilt angle [Eq. 5.40].

\( \alpha_0, \beta_0 \)  Empirical constants [Eq. 3.16]

\( \beta_1 \)  Empirical constants [Eq. 3.17]

\( e \)  Fixed bed voidage.

\( e_p \)  Particle macropore voidage.

\( \phi \)  Three dimensional spreading pressure of mixed adsorbate (atm)

\( \phi_i \)  Three dimensional spreading pressure of pure adsorbate \( i \) (atm)

\( \Gamma_i \)  Specific molar excess adsorption of \( i \) (mol/g-solid).

\( \Gamma_i^w \)  Specific excess adsorption of \( i \) (g/g solid).

\( \gamma_i \)  Liquid phase activity coefficient of \( i \).

\( \gamma_i^s \)  Adsorbed phase activity coefficient of \( i \).

\( \mu \)  Mean particle size, \( \mu_m \) (Chapter 2 only).

\( \mu_a \)  Chemical potential of adsorbent.

\( \mu_{0a} \)  Chemical potential of clean adsorbent.

\( \mu_i \)  Liquid phase chemical potential of \( i \).
\[ \mu_s^i \] Adsorbed phase chemical potential of \( i \).
\[ \mu_v^i \] Vapour phase chemical potential of \( i \).
\[ \nu \] Liquid viscosity (Poise).
\[ \rho_a \] Molar density of adsorbed phase (mol/cm\(^3\)).
\[ \rho_c \] Mass density of crystalline solid (g/cm\(^3\)).
\[ \rho_f \] Molar density of bulk liquid (mol/cm\(^3\)).
\[ \rho_s, \rho_p \] Solid or particle density (g/cm\(^3\)).
\[ \sigma \] Standard deviation of particle sizes, \( \mu m \) (Chapter 2 only).
\[ \sigma_i \] Surface tension of pure \( i \) (dyne/cm).
\[ \tau_p \] Tortuosity of a porous particle.

**Superscripts**

- \( i \) Interfacial conditions
- \( o \) Pure component
- \( s \) Adsorbed phase
- \( v \) Vapour phase
- \( * \) Equilibrium conditions
- \( - \) Average conditions

**Subscripts**

- \( 1 \) Component \( 1 \)
- \( 2 \) Water (\( 1 = 2 \)).

\[ \dagger \] Other minor notations are described in the text.
CHAPTER 1

INTRODUCTION
1. INTRODUCTION

The efficient recovery of low molecular weight water soluble organics (e.g. alcohols, ketones, aldehydes, carboxylic acids etc.) presents considerable difficulty. This is because such molecules are relatively simple and lack suitable exploitable specific functional groups. Moreover such species are usually of low value and when produced by large scale fermentation are present at low concentration. The desired product is also frequently required in an anhydrous form and is often intended for internal consumption.

In this study we are mainly concerned with a fundamental investigation of the sorptive recovery of low molecular weight aqueous organics with the aid of hydrophobic adsorbents. The model system chosen is the recovery of aqueous ethanol. This system is of direct practical interest for the breakage of chemical azeotropes, the production of alternative fuels and the rapidly growing area of dealcoholized beverages. It is also a good model system in as far as the thermodynamic and diffusive behavior of the liquid phase is well documented and the hydrophobic nature of the adsorbent may lead to interesting behavior.

1.1 ALTERNATIVE SEPARATION TECHNIQUES

The development of an "ideal" separation process for dilute simple aqueous organics presents conflicting criteria. Such a process should:
be energy efficient
- require a low grade energy source
- have low capital costs
- be mechanically simple, easy to operate and simple to control
- avoid the use of toxic additives

In addition, in biological applications many of the desired products act as an end-inhibitor for the fermentation and should ideally be removed from the broth as soon as they are formed. The ideal separation process must therefore also be capable of interfacing with the fermenter to provide a high productivity fermentation-recovery system. Here, the most important requirement is for the separation to be operable at the temperature and pressure prevalent in the fermenter. With the above criteria in mind, the relative merits of the alternative separation techniques can now be briefly discussed:

(a) distillation

The most commonly used separation technique is distillation. Conventional distillation is, however, energy inefficient because large quantities of water need to be vapourised. For instance, recovery of an azeotropic product from a 4-10 vol% ethanol/water mixture requires between 1.4 -1.6 times more energy than the calorific value of the ethanol product [Hartline 1979]. The energy efficiency can be improved by the use of multiple columns and various heat recovery systems but at the expense of greatly increased capital costs. It is therefore not surprising that the development of alternatives to conventional distillation is of great interest.
(b) vacuum distillation

Distillation under vacuum offers certain advantages over conventional distillation. This is mainly because of the reduced energy required compared to conventional distillation; for example, in the case of aqueous ethanol a 75% energy saving over conventional distillation has been claimed [Swift 1983]. Vacuum columns are, however, more expensive and more difficult to operate. Vacuum distillation also offers an opportunity for integration with a fermenter also operated under vacuum to provide in-situ product recovery. The practicality of such an integrated system has been demonstrated for yeast fermentation by Wilke (1976). The fermentation was carried out at 35°C and 50 mm Hg, so that the ethanol produced appeared in the vapour stream along with water and carbon dioxide. This vapour stream was then vacuum distilled to produce high purity ethanol and water. The major problem with this scheme arises with the need to bring the non-condensable carbon dioxide to atmospheric pressure for discharge. Unfortunately, this process requires the use of expensive and thermodynamically inefficient vapour recompressors.

(c) solvent extraction

Recovery of aqueous organics by solvent extraction has also been intensively investigated [eg. Roddy 1981, Munson 1984]. The major problem here is that solvents with high capacity normally exhibit low selectivity whereas highly selective solvents possess minimal capacity. This is shown for example by the data in Table i extracted from the study by Roddy (1981) on extraction of ethanol.
In addition, highly selective organic solvents are frequently toxic and present difficulties when the product is required for internal consumption. Many solvents are also toxic to microorganisms which rules out combined fermentation-solvent extraction processes. The recovery of the solvent from the final product for recycle purposes also adds to the overall energy consumption.

(d) membrane processes

Conceptually, membrane processes offer the best alternative for separation of water soluble biological organics. This is because such processes avoid costly phase changes and can operate under ambient temperature and pressure and therefore offer a potential for low energy bulk separation. The problem with membrane processes is similar to that for solvent extraction. Namely, membranes with high selectivity for organics offer low permeability whereas highly permeable membranes are non-selective. The hydrophobic membranes currently available [eg.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T °C</th>
<th>Initial [EtOH] mole/L</th>
<th>Partition Function</th>
<th>S.F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[EtOH]_org</td>
<td>[H2O]_org</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x 10^{-3}</td>
<td>x 10^{-5}</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>20</td>
<td>0.1</td>
<td>4.7</td>
<td>2.6</td>
</tr>
<tr>
<td>benzene</td>
<td>25</td>
<td>1.0</td>
<td>46.0</td>
<td>43.0</td>
</tr>
<tr>
<td>toluene</td>
<td>20</td>
<td>0.1</td>
<td>32.0</td>
<td>30.0</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>25</td>
<td>1.0</td>
<td>29.0</td>
<td>30.0</td>
</tr>
<tr>
<td>diethylbenzene</td>
<td>20</td>
<td>0.1</td>
<td>20.0</td>
<td>19.0</td>
</tr>
<tr>
<td>tri-n-butyl phosphate</td>
<td>25</td>
<td>1.0</td>
<td>540.0</td>
<td>6500.0</td>
</tr>
<tr>
<td>triisobutyl phosphate</td>
<td>25</td>
<td>1.0</td>
<td>650.0</td>
<td>6300.0</td>
</tr>
<tr>
<td>4-decanol</td>
<td>25</td>
<td>1.0</td>
<td>320.0</td>
<td>1400.0</td>
</tr>
</tbody>
</table>
silicone rubber, RC100 poly eth urea (UOP), FT-30 membrane (Film Tech.) only offer a moderate selectivity (S.F<3) at a low permeation rate (1.0 kg/m².hr) [Schissel and Orth 1984]. Hydrophobic membranes are, however, at an early stage of development and may well provide the ultimate separation technique in the future.

(e) sorptive processes

In contrast to membranes, hydrophobic adsorbents offering both a high selectivity and a reasonable capacity are now available. For example, the silicalite material used in this study has a separation factor of about 40 for a 10 mole % ethanol solution at a capacity of 0.11 g ethanol/g solid. Sorptive separations also offer several inherent advantages in as far as they

- are favoured by low temperature and can operate at atmospheric pressure
- are effective at low concentrations
- can recover the organics selectively and therefore avoid the need to vapourise the excess water
- for volatile products, low grade or waste heat can be used for product recovery
- the adsorbent can be regenerated and used over many cycles
- they are also mechanically simple and easy to operate.

On the negative side, sorptive separations are inherently transient processes and their design is substantially more complex than that of steady state processes. In the case of the separation of a specific
organic from multicomponent mixture, problems may also arise due to competitive adsorption.

On the positive side, it is also possible to interface the sorptive process with the fermenter to provide for the in-situ recovery of the end-inhibiting fermentation products. A schematic diagram of such a fermentation-adsorption system is shown in Figure 1. The fermenter effluent is first centrifuged or filtered to recover the cells which are returned back to the fermenter to maintain a high cell population. The clarified broth is then passed through a column packed with a suitable hydrophobic adsorbent. Initially, the effluent from the column contains no organics which gradually accumulate within the solid adsorbent. As saturation is approached, however, the organic concentration in the effluent rises and breakthrough is observed. At this time, the flow is diverted to a fresh parallel column and the organics are then recovered by draining the interparticle fluid, heating the column and condensing the ensuing organic vapours. For volatile solutes, low grade or waste heat may be sufficient for this purpose. In this study, the emphasis is placed on the separation process and questions arising from integration with the fermenter are left largely for future work.

1.2 HYDROPHOBIC ADSORBENTS

The success of the sorptive process depends primarily on the availability of a suitable adsorbent capable of the selective removal of the desired organic at a reasonably high capacity. The adsorbent
Fig. 1 Schematic of a combined adsorption-fermentation system.
should also possess mechanical strength, chemical and thermal stability and suitably fast kinetics for the uptake of the desired product.

Commercially available hydrophobic adsorbents include activated carbons, polymeric resins, carbon molecular sieves and recently developed high silica crystalline molecular sieves (zeolites). Activated carbons are widely used in industry for applications such as decolouring, deodourising, solvent recovery, water and effluent treatment and show good capacity for low molecular weight water soluble organics. Their use for separation of biologically produced organics can however present certain difficulties. This is because, such species are usually present in a broth also containing large organic molecules such as proteins and enzymes which are essential for the fermentation process. Carbon surfaces offer substantially higher selectivity for these larger organic molecules which can compete with the desired low molecular weight species. Hydrophobic polymeric resins also show good capacity but suffer from the same difficulty. In addition, they are also susceptible to swelling, (which can cause mechanical fragility) and are also thermally sensitive.

High silica hydrophobic molecular sieves, such as ZSM-5 and silicalite, offer the best potential for the recovery of low molecular weight species such as ethanol. These adsorbents are crystalline and have a well defined internal structure which can exclude the larger molecules by molecular sieving. In addition, they also possess good mechanical and thermal stability. For this study we chose to work with silicalite which contains no alumina or cations and offers excellent thermal and
chemical stability: it retains its internal structure at temperatures approaching 900 °C and resists attack by most chemicals except hydrofluoric acid. The properties and structural characteristics of silicalite are discussed in the next chapter. The following gives an overview of the influence of hydrodynamics, equilibria and kinetics of sorption in liquid phase applications.

1.3 MAJOR FACTORS AFFECTING SORPTIVE SEPARATION

Sorptive processes are characterised by the development and propagation of one or more concentration and temperature fronts through the bed of solids. The behaviour of such wave fronts is determined by the combined influence of:

- hydrodynamics and mode of contacting,
- solid/liquid phase equilibria, and
- interphase heat and mass transfer limitations,

all of which are more or less strongly influenced by the physical characteristics, surface properties and the internal structure of the adsorbent.

1.3.1 Hydrodynamics

Provided an adequate distribution of the liquid is achieved at the bed entrance, flow through industrial sorptive columns is relatively simple. The one dimensional axially dispersed plug flow model is adequate for all cases and for long columns ideal plug flow is often closely approached. This is to be expected since in full scale units the bed/particle diameter ratio normally exceeds 300, the particle size
is rarely below 1 mm and the bed length/particle diameter ratio is usually well in excess of 1000. Furthermore, liquid phase columns usually approach isothermal conditions, this is because the heat capacity of the liquid is sufficiently high to absorb the heat of adsorption. The majority of practical liquid columns are also usually operated with a particle Reynolds number in the range 0.1 to 10.

The influence of axial dispersion of mass and energy diminishes with column length. For the range of particle size and particle Reynolds number normally encountered, the particle Peclet number, $\text{Pe}_p = \nu D_p / D_L$, assumes a value of the order of 0.5 to 2 [Levenspiel 1972]. The axial Peclet number, $\text{Pe}_L = \nu L / D_L$, is therefore of the order of $L/D_p$. Evidently, unless the column is short, the contribution of axial dispersion of mass to overall performance is small. Care needs to be exercised, however, with small laboratory columns to ensure axial dispersion is suitably accounted for. For such columns, the axially dispersed plug flow model is sufficient and the extent of axial dispersion can be predicted from available empirical correlations with sufficient accuracy [Wakao et al., 1978, Ruthven 1984]. The major task in the analysis of sorptive columns is therefore the accurate measurement and description of the equilibria and the kinetics of sorption.

1.3.2 Sorption Equilibria

The accurate measurement and correlation of the solid/liquid equilibria is the most important step in the analysis of the sorptive process. In the majority of applications, the main driving force for mass transfer
is the local departure from equilibrium. In cases where equilibrium is not closely approached, a small error in the static equilibrium isotherm can lead to large error in the calculated breakthrough time and dynamic loading of the column. The measurement and interpretation of liquid phase adsorption isotherms require careful consideration and are important parts of this study.

The measurable quantity in any sorption system under equilibrium is the difference between the "amount" of material adsorbed in a given adsorption "space" (i.e. the pores and surfaces of the solid) and the amount of the bulk fluid which can be accommodated in the same "space". This is commonly referred to as the "excess" adsorption. In the case of a gas or a vapour at low pressure, the density of the bulk fluid is much smaller than that of adsorbed phase. The gas phase "excess" adsorption is then for all practical purposes equal to the "absolute" amount adsorbed. In the case of a liquid, however, the density of the adsorbed phase may be comparable to that of the bulk fluid. Consequently, the measurement of "excess" adsorption alone is not sufficient to establish the "absolute" amount of material held in the solid. Evidently, a second measurement is required to establish the "absolute" adsorption for liquid systems. This very simple point is often ignored in the literature, but has a crucial significance in the interpretation of liquid phase adsorption equilibria.

Excess adsorption is relatively easy to measure for liquid phase systems. The determination of the absolute adsorption, however, proves much more difficult. Consider contacting No moles of a binary liquid with a known initial mole fraction \( x \), with \( W \) g of adsorbent and let
$x_1$ be the mole fraction of the liquid at equilibrium. The easily measurable quantity is then the excess adsorption:

$$\Gamma_1 = \frac{N_0 (x_{10} - x_1)}{W_s}$$

with $\Gamma_1 = -\Gamma_2$ by definition. We also note that, the excess adsorption from a pure liquid is by definition zero, $(\Gamma_1)_{\text{pure}} = 0$. A simple mass balance can then relate the excess adsorption to the total amount of material adsorbed $N^s$ and the adsorbed phase mole fraction $x_1^s$:

$$\Gamma_1 = N^s (x_1^s - x_1)$$

Here we should note that Eq. (2) contains two unknowns: the total amount adsorbed $N^s$ and the concentration of the adsorbed phase $x_1^s$. Clearly, the measurement of excess adsorption alone cannot yield unique information on these two unknowns. Evidently, the determination of the absolute amount of individual species adsorbed also requires the independent measurement of the total adsorption $N^s$.

Unlike excess adsorption which can be measured with relative ease, the accurate determination of the total uptake of a solution by porous adsorbents presents a major challenge. The measurement of weight loss on direct desorption is ruled out by the insurmountable difficulties associated with the "clean" separation of the porous solid from the bulk liquid. From a purely thermodynamic viewpoint, the amount adsorbed from a solution must be the same as that adsorbed from the
saturated vapour in contact with the liquid. In principle, therefore, a classic gravimetric technique could be used to measure the total uptake from the saturated vapour [Kipling 1965]. In practice, however, this approach is severely impeded by the unavoidable capillary condensation of the saturated vapour. To eliminate capillary condensation, the measurements could of course be made from an unsaturated vapour. However, it would then be necessary to resort to a model isotherm and its attendant assumptions to extrapolate to the saturated conditions [Klein et al 1983, Kipling et al 1952]. A major objective of this study is the development of a technique (described in Chapter 3) for the direct measurement of the total uptake without removing the solid particles from the solution.

Here we should also note that in all the previously reported studies of the system examined in this thesis [Milestone et al 1981, Maddox 1982, Pitt et al 1983] the absolute amount of alcohol adsorbed is determined from:

\[
\frac{n^s}{1} = N^s x^s = \frac{\Gamma}{(1-x^s)}
\]

This amounts to the arbitrary assumption that water is nonadsorbed and the crystals are 100% selective towards alcohol which is clearly in error, particularly at low alcohol concentrations. Chapter 3 is devoted to the experimental measurement of the excess and absolute adsorption isotherms and a comprehensive thermodynamic treatment of the results obtained is given in Chapter 4. A major conclusion is that for aqueous organics the behaviour of the adsorbed phase within the
1.3.3 Interphase Mass Transfer Limitations

Heat and mass transfer between a flowing fluid and solid particles is influenced by resistances in the external film surrounding the particles and intraparticle diffusional resistances. Liquid phase adsorption systems usually approach isothermal conditions and the heat transfer limitation is therefore unimportant. The relative importance of extra and intra particle mass transfer is brought out by a classical argument. For a dilute system and a spherical particle with no accumulation at its external surface, the flux through the external film can be equated to that into the particle:

$$K_{fl} [c_{b1} - c_i(R_p,t)] = \varepsilon_p \frac{D_p}{\mu} \frac{\partial c_i}{\partial r} \bigg|_{r=R_p}$$

where $K_{fl}$ is the mass transfer coefficient through the film, $D_{p1}$ is the effective intraparticle diffusivity, $\varepsilon_p$ is the internal particle voidage, $c_{b1}$ and $c_i(R_p,t)$ are the concentration in the bulk fluid and at the particle surface respectively and $R_p$ is the particle radius. A measure of the internal to external concentration gradients is then given by the mass transfer Biot number $(Bi)_m$:

$$\frac{(Bi)_m}{3} = \frac{K_{fl} R_p}{3 \varepsilon_p D_{p1}} \frac{Sh_{m} D_{p1}}{6 \varepsilon_p D_{p1}}$$
Where \( D_{\text{mi}} \) is the molecular diffusivity and \( Sh \) is the Sherwood number (\( Sh = 2K_{R_p}/D_{\text{mi}} \)) which for a flowing system is greater than 2. For gaseous systems usually \( D_{\text{pi}} \ll D_{\text{mi}} \), so that \((Bi)_{\text{m}} \gg 1\) and mass transfer is dominated by intraparticle resistances. In liquid systems, however, the situation is less clear since \( D_{\text{pi}} \) may approach \( D_{\text{mi}} \) and extra particle mass transfer resistance may then play a significant role. There are numerous correlations available for the prediction of the overall mass transfer coefficient through the external film. Wakao and Funazkri (1978), after making due allowances for the porous nature of the solid, derived a relationship which can be used for both liquids and gases over a wide range of conditions:

\[
Sh = \frac{2K_{R_p}}{D_{\text{m}}} = 2.0 + 1.1 \frac{Sc^{1/3}Re^{0.6}}{} \quad 3 < Re < 10^4
\] (6)

Intraparticle diffusional resistances are not, however, open to prediction and must be determined experimentally. A major objective of this study is therefore the experimental determination of the intraparticle diffusivities which is covered in Chapters 5 and 6.

1.3.4 Fixed-Bed Column Dynamics

For practical purposes the combined influence of the above major factors must be expressed in terms of a mathematical model describing the dynamics of the sorption column. In general, a rigorous description of the behaviour of a liquid phase isothermal column requires the derivation of a differential model. For axially dispersed plug flow, such models will fall under the following general structure:
Fluid phase material balance

\[
\frac{\partial q_1}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial q_1}{\partial t} = D_L \frac{\partial^2 c_1}{\partial x^2} - \frac{\partial (\nu c_1)}{\partial x} \tag{7}
\]

Solid phase material balance

\[
\frac{\partial q_i}{\partial t} = f (q_1, \ldots, q_n, c_1, \ldots, c_n) \tag{8}
\]

The major difference between the proposed models is therefore in the manner in which the mechanism of intraparticle diffusion is approximated. For porous particles, the intraparticle mass transfer resistances are usually divided into contributions from a macro and a micro pore region. Diffusion through the macro and microporous regions could then be assumed to take place in parallel, in series, or by both mechanisms. The complexity and the detail of the model adopted will then depend on whether transport through a particular region is assumed to be controlling and whether a lumped or a distributed parameter (diffusion equation) model is used to describe the mass transfer.

Chapter 5 is devoted to a review of the intraparticle mass transfer mechanisms proposed in the literature and the description of experiments which allow the determination of the controlling mechanism for the system examined in this thesis. This is followed in Chapter 6 by the experimental determination of column breakthrough curves and the numerical solution of the model partial differential equations required to describe the dynamics of the column.
Recovery of low molecular weight water soluble organics from aqueous dilute mixtures presents conflicting requirements. Sorptive techniques offer several inherent advantages over other alternatives such as conventional distillation, vacuum distillation, solvent extraction and membrane processes. In this thesis we consider the sorptive separation of alcohol-water mixtures with the aid of a hydrophobic adsorbent, silicalite. The performance of the sorptive process is governed by the combined influence of:

1. hydrodynamics and mode of contacting,
2. solid/liquid sorption equilibria and
3. interphase heat and mass transfer limitations.

All of the above factors are influenced by the physical characteristics, surface properties and the internal structure of the adsorbent which are examined in Chapter 2. The measurement and interpretation of the sorption equilibria for the system (ethanol-water)/silicalite are examined in Chapters 3 and 4. In particular, an experimental technique is developed which enables the direct determination of the individual isotherms for the crystalline solid. This information is then used in a rigorous thermodynamic analysis which confirms that the behaviour of the adsorbed phase is radically different from that of the bulk liquid. This is followed in Chapter 5 by a review of the intraparticle mass transfer mechanisms and the independent experimental determination of the controlling mechanism for the system (ethanol-water)/silicalite. The above factors are
incorporated in a suitable mathematical model in Chapter 6 to describe the overall performance of the sorptive process. The proposed model is validated against experimental breakthrough curves obtained on a small scale pilot plant. Finally, the methods developed are of a generic nature and their application to other systems is described in Chapter 7 together with suggestions for future work.
CHAPTER 2

PHYSICAL AND STRUCTURAL CHARACTERISTICS OF THE ADSORBENT
2. PHYSICAL AND STRUCTURAL CHARACTERISTICS OF THE ADSORBENT

2.1 INTRODUCTION

The successful sorptive recovery of low molecular weight aqueous organics depends largely on the availability of a hydrophobic solid capable of the selective adsorption of the desired product at a reasonable capacity. Evidently, the adsorbent should possess a highly developed internal structure to provide a large capacity per unit volume. In addition, the solid adsorbent should be thermally and chemically stable, be easily regenerated, and have sufficient resilience to repeated usage. Well known porous hydrophobic adsorbents include polymeric resins, activated carbons and porous silicas which have been thermally and chemically treated to remove the sites for hydrogen bonding and polar and acid-base interactions [Meisel et al. 1976, Flanigen et al. 1978]. Potential hydrophobic adsorbents suitable for the recovery of alcohols include activated coconut charcoal, carbon molecular sieves, divinylbenzene cross-linked polystyrene beads and recently developed high silica hydrophobic molecular sieves such as ZSM-5 [Meisel et al 1976] and silicalite [Flanigen et al 1978]. Based on exploratory experiments and published data [Flanigen et al 1978] silicalite was chosen for further investigation.

The surface properties and the structural characteristics of the adsorbent exert a significant influence on the ultimate performance of the adsorption process. The manufacture and internal structure of silicalite crystals will be briefly discussed in the next section. For
the moment we note that the crystals have a highly regular microporous structure with pores of approximately 6Å. Silicalite crystals, in common with other molecular sieves, cannot be easily grown beyond 2-5 μm. Such small particles cannot be fluidized and also offer an unacceptable pressure drop in packed bed operation. It is therefore necessary to bind the crystals into larger pellets in the mm size range for packed bed applications. The silicalite pellets will therefore have a bi-modal pore structure with 6Å selective micropores of the crystals and larger non-selective macropores consisting of the voids between the crystals. Diffusion through such bi-dispersed pellets can be controlled either by the micropores or by the macropores or by both types of pore. The determination of the controlling mechanism therefore requires an adequate knowledge of the size distribution of the crystals as well as the size distribution of the macropores. The size distribution of the crystals was determined by various techniques and is described in section 2.3. The macropore size distribution of the pellets was determined by mercury porosimetry to establish the (macropore) voidage and a mean (macro) pore size. This information (crystal and pore size distributions) will be used for the determination of the controlling mechanism and the investigation of the column dynamics in Chapters 5 and 6.

2.2 MANUFACTURE AND INTERNAL STRUCTURE OF SILICALITE

2.2.1 Manufacture of Silicalite

Silicalite is a microporous crystalline form of silicon oxide which was first produced by Union Carbide [Flanigen et al. 1978]. The silicalite precursor is produced by hydrothermal crystallisation in a closed
system containing tetrapropylammonium (TPA) cations, hydroxyl ions, and a reactive form of pure amorphous silica at 100-200 °C. The organic TPA cations are believed to act as a template around which the silica tetrahedra are formed during crystallisation [Flanigen et al 1978, Price et al 1983]. The silicalite crystals are activated by calcining the precursor in air at around 600 °C to decompose and remove the TPA ions. The activated crystals have a mean refractive index of 1.39 and a measured density of 1.76 g/cm³. The calcined crystals have a (micro) voidage of 33 % and retain their structure at temperatures up to 900 °C, and also resist attack by most mineral acids except hydrogen fluoride [Flanigen et al. 1978].

More significantly, unlike the hydrophilic aluminosilicate zeolites, the surface of the activated silicalite crystal (which does not contain alumina or cations) is hydrophobic and organophilic [Flanigen et al 1978, Price et al 1983]. The organophilic nature of silicalite is manifested in the selective vapour and liquid phase adsorption of organic molecules with a kinetic diameter smaller than the limiting channel dimensions.

2.2.2 Structure and Surface Properties of Silicalite Crystal

The crystal structure of silicalite and other related compounds have been determined by X-Ray diffraction data from the precursor crystals [Flanigen et al. 1978, Price et al 1983, Kokotailo et al 1980]. The idealised structure of the silicalite precursor is shown in Figure 1 and is composed of straight elliptical channels (free aperture 5.8 x 5.2 Å) cross-linked by near circular...
zig-zag channels (free aperture 5.4 ± 0.2 Å) with both types of channels defined by 10-rings of oxygen. The removal of the organic cation during calcination could possibly affect the pore sizes to a certain extent. The calcined crystals act as a molecular sieve rejecting molecules larger than 6 Å in diameter.

The organophilic nature of the surface as well as the molecular sieving capabilities of silicalite are well demonstrated by the following data extracted from Flanigen et al (1978). Water (\(d=2.65\) Å) is slightly adsorbed whereas methanol (\(d=3.8\) Å) is strongly adsorbed. Moreover benzene (\(d=5.85\) Å) is strongly adsorbed whereas the organic molecule neopentane (\(d=6.2\) Å) is strongly excluded.
Table 1. Adsorption of molecules with various kinetic diameters onto silicalite [Flanigen et al 1978].

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Temperature °C</th>
<th>Kinetic Diameter, d (Å)</th>
<th>Amount Adsorbed (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20</td>
<td>2.65</td>
<td>0.047</td>
</tr>
<tr>
<td>Methanol</td>
<td>20</td>
<td>3.8</td>
<td>0.152</td>
</tr>
<tr>
<td>n-Butane</td>
<td>20</td>
<td>4.3</td>
<td>0.110</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>20</td>
<td>4.3</td>
<td>0.131</td>
</tr>
<tr>
<td>Benzene</td>
<td>20</td>
<td>5.85</td>
<td>0.119</td>
</tr>
<tr>
<td>Neo-pentane</td>
<td>20</td>
<td>6.2</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Figure 2 shows scanning electron microscope (SEM) photographs of the silicalite crystals taken at various magnifications. The photograph at high magnification shows that the crystals are essentially cubic with rounded edges and have a smooth external surface with an occasional crack running down one side. The determination of the controlling diffusion mechanism in silicalite pellets requires a knowledge of the crystal size distribution, which is considered next, as well as a knowledge of the macropore size distribution which is discussed in section 2.4.

2.3 SIZE DISTRIBUTION OF SILICALITE CRYSTALS

The separate evaluation of the macro and micro pore contributions to the intraparticle mass transfer requires the independent measurement of the resistance within the silicalite crystals. The micropore resistance is usually determined from an uptake curve which is influenced by the shape and size distribution of the crystals. This is because for a wide size distribution, the smaller crystals saturate
Fig. 2 Scanning electron micrographs of silicalite crystals.
more rapidly than the larger ones which complicates the analysis. The SEM photographs shown in Figure 2 indicate that the crystals may be assumed to be cubic. The determination of the size distribution of the crystals however requires careful consideration. This is because various measurement techniques often yield conflicting distributions in the micron size range [Seville et al 1983]. Consequently, a fairly detailed study of several techniques was made to establish the crystal size distribution with confidence. The size distribution obtained by electronic image analysis (Quantimet), electrical sensing zone method (Coulter counter) and forward lobe light scattering (Malvern) showed good agreement and are presented below.

2.3.1 Electronic Image Analysis (Quantimet)

Quantimet equipment consists of an electronic microscope linked to computerised scanning and monitoring units. Representative sections from each specially prepared specimen slide were examined at random under the microscope to determine the crystal sizes. Quantimet measures the maximum projected area of individual crystals in random orientation. The resulting data is two dimensional and gives rise to a number based size distribution. The size of the particle is calculated from the diameter of the sphere with the same projected area as that of the particle, 

$$d = \sqrt{\frac{4 \times \text{area}}{\pi}}$$

A typical size distribution obtained with Quantimet is plotted in Figure 3 as the percentage number of crystals against size. The distribution appears multi-modal with a mean of 2.24 μm and a standard
The Quantimet data also indicated that only 2% of the total number of the crystals lie below 0.8 μm and that none are smaller than 0.6 μm. This was also confirmed by filtration tests: a 0.8 μm filter produced a very slightly cloudy filtrate whilst a 0.45 μm filter practically removed all the particles.

![Histogram of crystal size distribution](image.png)

**Fig. 3** Silicalite crystal size distribution measured by electronic image analysis technique

### 2.3.2 Electrical Sensing Zone method (Coulter Counter)

The electrical sensing zone method relies on the passage of the particles suspended in an electrolyte solution through a small orifice.
Electrodes are mounted on either side of this orifice and the passage of each particle disrupts the electrical field. The resultant change in resistance generates a voltage pulse which has been shown to be proportional to the volume of the particle [Allen 1981]. A size distribution is obtained by counting the number of voltage pulses within specified limits over a period of time. The choice of the orifice size presents some difficulty. For proper operation of the instrument the particle diameter must lie between 2 and 40% of the orifice diameter [Allen 1981]. For silicalite particles ($2 < d < 10 \, \mu m$) a 30 \, \mu m orifice was found to be adequate. The results obtained were, however, also checked by using different orifice sizes with the scale factors recommended by the manufacturer to confirm the measurements made with a single orifice.

Figure 4 shows a typical number distribution of the particle diameters obtained with the Coulter Counter. The particles were found to have a mean diameter of 2.43 \, \mu m with a standard deviation of 1.09 \, \mu m. This is in good agreement with the electronic image analysis results which is to be expected as the silicalite particles are not far from spherical. The size distribution is often required on weight or volume rather than a number basis. Figure 5 shows the volumetric size distribution of the silicalite crystals generated from the number distribution in Figure 4. Evidently, the volumetric size distribution will be biased towards the larger sizes and shows a mean value of 4.85 \, \mu m with a standard deviation of 2.95 \, \mu m.
**Fig. 4** Silicalite crystals size distribution measured by electrical sensing zone method (Coulter Counter).

\[ \mu = 2.43 \, \mu m \]
\[ \sigma = \pm 1.09 \, \mu m \]

**Fig. 5** Silicalite crystals size distribution measured by electrical sensing zone method (Coulter Counter).
2.3.4 Forward Lobe Light Scattering Technique (Malvern)

The Malvern particle size analyser uses a single monochromatic light beam to illuminate a sample cell containing a suspension of the particles at high dilution. A schematic of the instrument is shown in Figure 6. The light rays falling on a particle are scattered at an angle which depends on the projected area of the particle. Smaller particles scatter light at larger angles in the forward direction than larger particles. The light scattered by the particle assembly is passed through a Fourier lens of prescribed focal length and is focused onto a plane detector which consists of a series of concentric photosensitive rings. The particle size distribution is obtained through an iterative optimization procedure which matches the theoretical energy distribution falling on the detector elements with that measured experimentally [Farhadpour 1987]. The volumetric size distribution determined by the Malvern analyser is shown in Figure 7 and has a mean of 4.55 μm with a standard deviation of 2.48 μm. This is

![Fig. 6 Schematic of the light scattering technique](image-url)
in good agreement with the data obtained by the electrical sensing zone method (i.e. 4.85 and 2.95 μm).

The results obtained from electrical sensing zone method and forward lobe light scattering are compared in Figure 8 and are in good agreement. The distributions appear to be multimodal, but for our purposes it is sufficient to correlate the data in terms of a log-normal distribution. Figure 9 shows the results of such a correlation for the volumetric distribution which will be required for

![Graph](attachment:image.png)

**Fig. 7** Silicalite crystal size distribution measured by Malvern light scattering technique.

2.3.5 Correlation of the Crystal Size Distribution
Fig. 8  Comparison of the crystal size distribution obtained by (a) Light scattering technique (Malvern) and (b) Electrical sensing zone method (Coulter Counter).
the interpretation of the uptake curves in Chapter 5. The data appears
to be adequately described by the following distribution:

$$f(d_c) = \frac{1}{\sqrt{2\pi} \sigma_{ln(d_c)}} \exp \left( -\frac{(\ln(d_c)-\ln(d_c)^m)^2}{2\sigma_{ln(d_c))^2}} \right)$$

with a median size of $d_c = 3.78 \times 10^{-4}$ cm
and a standard deviation of $\sigma_{ln(d_c)} = 0.44$

Fig. 9 Log-normal volumetric size distribution of silicalite crystal,
$\ln (d_c) = -7.88$ and $\sigma_{ln(d_c)} = 0.44$, [● light scattering technique,
o Coulter Counter technique].
The activated silicalite crystals are too small and offer excessive pressure drop in packed bed operation. To avoid unacceptable pressure drop, the crystals are bound together using a dealuminised clay binder to form approximately millimeter sized pellets. This is achieved by making a paste containing approximately 80 wt% crystals and 20 wt% of the binder. This paste is then extruded to form long cylindrical extrudate with a diameter of approximately 1.5 mm. The internal structure of the extrudates is shown in Figure 10 and consists of large non-selective macropores giving access to the selective micropores of the embedded crystals. For our applications, the cylindrical extrudates supplied by Union Carbide were crushed and sieved to provide irregular pellets in the 0.5-1.0 mm diameter size range. The pellet density, packed bed density and packed bed voidage were measured and found to be 1.285 g/cm$^3$, 0.798 g/cm$^3$ and 0.38 respectively.

2.4.1 Macro Pore Size distribution of Silicalite Pellets

The macropore size distribution of the silicalite pellets was determined by mercury porosimetry. This method is based on the fact that an external pressure is required to force a non-wetting fluid into a narrow pore. Assuming the pore is cylindrical, the pressure required is related to the pore diameter by the Washburn equation [Gregg and Sing 1982],

\[
p = \frac{\sigma \cos \theta}{d_{mac}}
\]
where $\sigma$ is the surface tension and $\theta$ the contact angle between the solid and the non-wetting fluid. The values normally adopted for mercury are $\theta=141.3$ and $\sigma=480$ dyne/cm which lead to:

$$\frac{36979.92}{P \text{ (atm)}}$$

The range of operation of the instrument available to us (Carlo Erba) was between 0.33 and 2000 atm which corresponds to pores ranging from 11 $\mu$m down to 70 \AA\ diameter after allowing for compressibility of mercury.

The porosimetry results are presented in Figure 11 as cumulative and differential distributions. The silicalite pellets appear to have an essentially unimodal macropore size distribution with a mean macropore size of 0.3 $\mu$m which is consistent with the size of the individual crystals forming the pellets. The specific macro pore volume of the pellets was found to be 0.202 cm$^3$/g.

![Figure 11: Pore size distribution of silicalite pellets measured by mercury porosimetry.](image)
2.5 SUMMARY

The structural characteristics of the silicalite adsorbent in crystalline and pellet form was carefully investigated. The size distribution of the crystals was measured with good agreement by various technique and found to be well fitted by a log-normal size distribution with a (volumetric) median size of 3.78 μm. The macropores within the bi-dispersed silicalite pellets were found to lie predominantly in the range 0.1 to 1.0 μm with a mean value of 0.3 μm. Other relevant structural data are summarized in Table 2 for the crystals and in Table 3 for the pellets.

Table 2. Structural Characteristic of Silicalite Crystals

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>density</td>
<td>1.76 g/cm³</td>
</tr>
<tr>
<td>micropore volume</td>
<td>0.19 cm³/g</td>
</tr>
<tr>
<td>micropore voidage</td>
<td>0.33</td>
</tr>
<tr>
<td>elliptical channels</td>
<td>5.2 x 5.6 Å</td>
</tr>
<tr>
<td>cylindrical channels</td>
<td>5.4 Å</td>
</tr>
</tbody>
</table>

Table 3. Structural Characteristics of Silicalite Pellets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet density</td>
<td>1.285 g/cm³</td>
</tr>
<tr>
<td>Macro pore volume</td>
<td>0.202 cm³/g</td>
</tr>
<tr>
<td>macroporosity</td>
<td>0.26</td>
</tr>
<tr>
<td>mean macro pore radius</td>
<td>0.3 μm</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL MEASUREMENT OF LIQUID PHASE SORPTION EQUILIBRIA
3. EXPERIMENTAL MEASUREMENT OF LIQUID PHASE SORPTION EQUILIBRIA

3.1 BACKGROUND

The accurate measurement of sorption equilibria is by far the most important initial step in the analysis of any sorptive separation. This is because in the majority of separations of commercial interest the driving force for separation is the local departure from equilibrium. Consequently, in cases where equilibrium is not closely approached, small errors in the measurement of the static isotherm can lead to substantial errors in the dynamic loading and breakthrough time. An accurate knowledge of the saturation capacity and selectivity of the adsorbent is therefore of crucial importance.

The measurement and interpretation of liquid phase adsorption equilibria presents a number of difficulties which are perhaps not always fully recognized, particularly by those more familiar with gas adsorption. From a purely thermodynamic point of view, there is no difference between adsorption from a solution and adsorption from the saturated vapour in contact with the solution. From an experimental point of view, however, the measurement and interpretation of gas and liquid phase adsorption equilibria demand alternative treatment. Such practical differences have given rise to some confusion regarding the treatment of pure and multicomponent liquid phase adsorption. To appreciate the basic differences it is advantageous to consider single and multicomponent adsorption separately.
The measurable quantity in any adsorption system is the "excess adsorption". This is defined as the additional amount of "adsorbate" held in the adsorption space (ie the pores and surface of the solid) compared to the amount of the "fluid" which can be accommodated in the same space. In the case of a pure component, therefore, the excess adsorption is normally defined as:

\[ n^e = \nu (\rho_a - \rho_f) = n^S - \nu \rho_f \]  

where \( \nu \) denotes the adsorption space, \( n^S = \nu \rho_a \) is the absolute adsorption and \( \rho_a \) and \( \rho_f \) are the densities of the adsorbed and bulk fluids respectively.

For a pure gas or a pure vapour at low pressure, the density of the adsorbate is much higher than that of the bulk fluid; the excess adsorption then closely corresponds to the "absolute" amount adsorbed. At low pressures, therefore, the absolute adsorption of a pure gas can be measured with relative ease either by classical static gravimetric or volumetric techniques [Sorial et al., 1983] or by dynamic chromatography methods [Ruthven et al., 1980]. For gases at high pressure, however, the density of the bulk fluid approaches that of the adsorbed phase and the (measurable) excess adsorption deviates significantly from the absolute adsorption. This is reflected in the occurrence of a maximum in the pure gas excess isotherm at sufficiently high pressures [Menon 1968].
For a pure liquid, the densities of the bulk fluid and the adsorbate are comparable and the measurement of the excess adsorption does not yield the "absolute" adsorption directly. For a pure liquid or a pure gas at high pressure, therefore, the basic problem is reduced to that of measuring the density of the pure adsorbate $\rho_a$. Since the adsorbed phase is not open to direct measurement, this presents considerable practical difficulties. The definition of the excess adsorption by Eq.(1) is therefore of little practical utility for a pure liquid. Indeed, experimental values of absolute adsorption or adsorbate density for a pure liquid are hardly ever reported in the literature. Instead, the absolute adsorption of a pure liquid is normally calculated on the basis of the arbitrary assumption that the density of the adsorbate and the pure liquid are identical. In this case, the excess adsorption as defined by Eq.(1) is identically zero but the absolute adsorption can be calculated from $n^a = \rho_a v = \rho_f v$, which requires a knowledge of the adsorption space $v$. There is in fact no theoretical justification for this arbitrary assumption and the density of the pure adsorbate may differ radically from that of the bulk fluid. A suitable technique for the direct measurement of the adsorbate density in microporous crystalline solids will be presented in Section 3.3. The application of this technique for (ethanol-water)/silicalite system confirms that the pure adsorbate density may differ radically from that of the bulk fluid. We shall return to this topic later, for now we need to consider the alternative definition of excess adsorption normally used for binary and multicomponent liquids.
Liquid phase adsorption normally involves a solution containing two or more components. Consider contacting $N_0$ moles of a solution with initial composition $x_{i0}$ with $W_s$ grams of an adsorbent and let $x_i$ denote the bulk liquid composition after equilibrium has been achieved. The easily measurable quantity is then:

$$\Gamma_i = \frac{N_0 (x_{i0} - x_i)}{W_s}$$  \hspace{1cm} \text{(2)}$$

The quantity $\Gamma_i$ indicates the relative strength of adsorption and is positive for a preferentially adsorbed species. A suitable name for this quantity would be \textit{relative adsorption}. In the liquid phase adsorption literature, however, the quantity $\Gamma_i$ is normally referred to as \textit{excess adsorption}. It should be recognized, however, that this definition of excess adsorption for a multicomponent liquid is different from that in Eq.(1) for a pure substance.

Two consequences of the definition of the excess adsorption $\Gamma_i$ by Eq.(2) should be clearly understood. First, for a pure component $\Gamma_i=0$ by definition. This does not, however, imply that the bulk and adsorbed phases have an identical density but is merely a consequence of the definition of $\Gamma_i$. Second, for an $N$-component solution, the sum of the $\Gamma_i$ is identically zero,

$$\sum_{i=1}^{N} \Gamma_i = \sum_{i=1}^{N} \frac{N_0 (x_{i0} - x_i)}{W_s} = 0$$  \hspace{1cm} \text{(3)}$$

which implies that only $N-1$ of the $\Gamma_i$ are independent.
A simple material balance serves to establish the connection between the excess adsorption $\Gamma_i$ and the absolute amounts of the individual species adsorbed:

$$\Gamma_i = N^s (x_i^s - x_i) = n_i^s - x_i \sum n_i^s$$

where $N^s = \Sigma n_i^s$ is the total absolute amount of all species adsorbed, $x_i$ and $x_i^s$ are the composition of the bulk liquid and adsorbed phase respectively and $n_i^s = N^s x_i^s$ is the absolute adsorption of component $i$.

The liquid phase excess adsorption isotherms assume various shapes which were first classified by Ostwald and Izaguirre in 1922 [Oscik 1982]. The isotherms shown in Figure 1a and 1b are frequently

![Classification of excess isotherms](image)

Fig. 1 Classification of excess isotherms by Ostwald and Izaguirre [Oscik 1982].

44
encountered. The U shaped isotherm in Figure 1a arises when one component is preferentially adsorbed across the entire concentration range. The S shaped isotherm in Figure 1b is obtained when the adsorbent shows selectivity reversal. In this case the crossing point of the x axis corresponds to an adsorption azeotrope where the adsorbed and bulk phases have identical composition. Adsorption azeotropes can arise for both gases and liquids but are more common in the latter case. The linear isotherm in Figure 1c arises when only one component is adsorbed and the other is excluded, as for example with molecular sieves. A more detailed classification of the first two type isotherm was presented by Schay and Nagy (1960) [Oscik 1982] and is shown in Figure 2.

Fig. 2 Classification of excess isotherms by Schay and Nagy [Oscik 1982].
3.1.3 Interpretation of Liquid Phase Adsorption

The theoretical interpretation of liquid phase adsorption is normally based on the easily measured experimental excess adsorption isotherm \( \Gamma_i = \Gamma_i^r(T, x_i) \). A brief look at Eq.(4), however, reveals that for an \( N \) component system there are \( N \) unknown quantities \( n_i^s \), \( i=1,\ldots,N \) but only \( (N-1) \) of the \( \Gamma_i^r \) are independent. The experimental measurement of the excess adsorption alone cannot, therefore, yield the absolute adsorption of the individual species uniquely. Evidently, an additional independent relationship is required for this purpose.

For a binary mixture, the excess isotherm Eq.(4) can be rewritten as:

\[
\Gamma_1 = (1 - x_1) n_1^s - x_1 n_2^s
\]

where \( n_i^s = N_i^s x_i^s \) denotes to absolute amount of component \( i \) adsorbed per unit mass of solid. It is clear that in general the single relationship (5) cannot determine the two unknowns \( n_1^s \) and \( n_2^s \) uniquely. The exception to this general rule is for very dilute solutions, \( x_1 n_2^s \ll (1-x_1)n_1^s \), in which case:

\[
\frac{n_1^s}{n_1^s} \approx \frac{\Gamma_1}{(1-x_1)} \quad \text{dilute system}
\]

Here we should note that Eq.(6) does not yield any information on the adsorption of component 2, all that can be said is that at very low concentrations the amount of component 2 adsorbed is practically constant. Unfortunately, Eq.(6) is frequently and erroneously used for systems which are not dilute. This is in fact the case for all the
previously reported studies of the (ethanol-water)/silicalite system considered in this thesis [Milestone et al 1981, Maddox 1982, Pitt et al 1983]. The use of Eq.(6) for a non-dilute system amounts to the arbitrary assumption that component 2 is non-adsorbed and the solid has a 100% selectivity towards component 1, which is clearly in error.

Evidently, for a non-dilute system a second relationship is required to establish $n_1^s$ and $n_2^s$ unambiguously. In previous analyses of liquid phase adsorption, this extra relationship has invariably been obtained at the expense of a *priori* theoretical assumptions about the nature of adsorption. This is an unsatisfactory procedure since the validity of the assumptions *inherent* in the proposed theories cannot be tested against directly measured experimental data. As a result, such inherent assumptions may be self-fulfilling and the proposed theories, although capable of fitting the excess isotherm accurately, may be grossly in error as far the absolute capacity and the selectivity of the adsorbent is concerned. This is demonstrated for two such theories in Sections 3.4.1 and 3.4.2 which fit the excess adsorption isotherm for the (ethanol-water)/silicalite system accurately but overestimate the selectivity of the solid for ethanol by as much as 60%.

To avoid *a priori* theoretical assumptions and to determine the capacity and selectivity of the solid directly it is necessary (and sufficient) to measure the total adsorption isotherm:

$$N^s = n_1^s + n_2^s$$  \hspace{1cm} (7)

as well as the excess isotherm. The composition, absolute adsorption
and the selectivity of the solid can then be obtained by combining Eqs. (5) and (7):

\[ x_1^s = x_1 + \frac{\Gamma_1}{N^s} \]  

(8)

\[ n_1^s = N^s x_1^s \]  

(9)

\[ s_{ij} = \frac{x_i^s / x_j^s}{x_i / x_j} = \frac{x_j (x_i^s + \Gamma_i / N^s)}{x_i (x_j^s + \Gamma_j / N^s)} \]  

(10)

Unlike the excess isotherm which can be measured with relative ease, the accurate experimental measurement of the total adsorption presents a major challenge. A suitable technique for microporous adsorbents is described in Section 3.3 and for the very first time enables the direct measurement of the extent and composition of the adsorbed phase independent of a priori theoretical assumptions. Comparison of the directly measured values with those predicted on the basis of proposed theories of adsorption from solution is presented in this chapter and serves to highlight the limitations of such theories. The availability of experimentally determined individual adsorption isotherms also enables a rigorous model independent thermodynamic treatment of adsorption from solution which will be described in the next chapter.

3.2 EXPERIMENTAL MEASUREMENT OF EXCESS ADSORPTION

The conventional technique for the measurement of the excess isotherm involves contacting a known weight \(W_0\) of a solution with an initial weight fraction \(w_{i0}\) in a closed vessel with a measured mass of
adsorbent $W_s$ and determining the free liquid weight fraction $w_f$ after equilibrium has been achieved. The excess adsorption on a weight basis $\Gamma^w$ is then simply given by:

$$\Gamma^w = \frac{W_0 \ (w_f - w_{10})}{W_s}$$

The excess isotherms for the system (ethanol(l)- water(2))/silicalite were determined by the conventional technique at 25 and 60 °C. The solutions were made up by weight using Anal-R grade ethanol (>99.7%) and double distilled deionised water degassed by the method of Van Ness and Abbot (1978). Prior to contact with the liquid, the crystals were dried and activated for at least 4 hours at 400 °C and 10⁻³ Torr and their dry weight $W_s$ determined. The crystals were then cooled and a known weight $W_0$ of a liquid with an initial weight fraction $w_{10}$ was added and the suspension was equilibrated for minimum of 18 hours in a thermostated shaker bath controlled to ± 0.05 °C. At equilibrium, samples of the free liquid were withdrawn through a septum using a gas-tight syringe fitted with a detachable 0.45 μm microfilter cartridge and the equilibrium mass fraction $w_f$ was measured by a differential refractometer (Waters R400).

The experimental excess isotherm at 25 and 60 °C are shown by the open circles in Figure 3. The isotherms conform to the type 2 classification of Schay and Nagy (1960) which is to be expected for a microporous adsorbent such as silicalite. The isotherms do not show selectivity reversal and the adsorbed phase, unlike the bulk liquid, does not exhibit an azeotrope. Moreover, temperature has a relatively
Fig. 3 Specific excess adsorption isotherms for the system (ethanol(l)-water(2))/silicalite. (o conventional technique, • pycnometer technique).

Excess adsorption, \( \Gamma^M \) g/g dry crystals.

Liquid mass fraction, \( w_1 \)
small influence and lowers the excess adsorption slightly between 25 and 60 °C.

The accuracy of the experimental procedure was determined by duplicate and triplicate experiments and a maximal error analysis which indicates that:

\[
\Gamma^w_1 \pm \delta(\Gamma^w_1) \approx \frac{W_0 [(w_{10} - w_1) \pm 2\delta w]}{W_s}
\]

where \(\delta w\) indicates the accuracy with which the composition of the free liquid can be measured. The maximum error is shown for each individual point by the error bars in Figure 3. It is evident that the critical factor is the ratio \(\delta w/(w_{10}-w_1)\) and to improve the accuracy the solid/liquid loading must be increased to increase the change in concentration \((w_{10}-w_1)\). There is, however, a practical upper limit on the solid concentration in the suspension beyond which stirring and sampling become difficult. For our system, which has a relatively high capacity, a solid/liquid ratio of 1/3 was sufficient to provide acceptable accuracy. For systems with a much lower uptake, as well as for a more comprehensive study of the influence of temperature, one must resort to more sophisticated apparatus (e.g Ash et al 1973).

In a previous examination of the (ethanol - water)/silicalite system [Pitt et al 1983] it was claimed that the adsorption isotherms were not reversible and exhibited a hysteresis with composition. The reversibility of the isotherms was examined by first contacting the crystals for prolonged periods with one pure adsorbate and then
diluting with the other. In all cases where sufficient time (>18 hours) was allowed for final equilibration, the excess adsorption was independent of the order of contacting. This is in contrast to the anomaly reported by Pitt et al (1983); most probably because their contact time of 1 hour was insufficient to ensure equilibrium.

3.3 EXPERIMENTAL MEASUREMENT OF TOTAL ADSORPTION

The excess adsorption $\Gamma_1^w$ is related to the total adsorption $Q^s$ and the weight fraction of the adsorbed phase $w_1^s$ by following the material balance,

$$\Gamma_1^w = Q^s (w_1^s - w_1)$$

To determine the adsorbed phase composition without resorting to a priori theoretical assumptions it is therefore necessary (and sufficient) to measure the total adsorption $Q^s$ in addition to the excess adsorption $\Gamma_1^w$.

Unlike the excess adsorption which can be measured with relative ease, the accurate determination of the total uptake of a solution by small microporous adsorbents presents major difficulties. The measurement of the weight loss on direct desorption is ruled out by the insurmountable difficulties associated with the "clean" separation of the micron sized particles from the bulk liquid. From a thermodynamic viewpoint, the amount adsorbed from a solution must be the same as that adsorbed from the saturated vapour in equilibrium with the solution [Kipling 1965]. In principle, therefore, a classic gravimetric technique could be used to measure the total uptake from the saturated vapour [Kipling 1965].
In practice, however, this approach is severely impeded by the unavoidable capillary condensation of the saturated vapour in between the individual micron-sized crystals. To eliminate capillary condensation, the measurements could of course be made from an unsaturated vapour. However, it would then be necessary to resort to a model isotherm and its attendant assumptions to extrapolate to the saturated conditions. This procedure was used by Kipling and Tester (1952) for the (benzene-ethanol)/charcoal and (Klein and Abraham (1983) for (ethanol-water)/silicalite system. The major objection is that the a priori assumption inherent in the model isotherm chosen cannot be validated.

To avoid the above difficulties, a pycnometric technique was developed to allow the direct measurement of total adsorption without removing the solid particles from the solution. A similar technique has been used by Dubinin et al (1980) for the measurement of the density of pure adsorbates within zeolitic crystals. A schematic of the apparatus is shown in Figure 4 and consists of a pycnometer calibrated to better than $4 \times 10^{-4}$ cm$^3$ and fitted with a magnetic stirring device. The temperature in the pycnometer was controlled to better than $\pm 0.05 \, ^\circ C$ through a thermostated water bath. The solutions were made up by weight using Anal-R grade ethanol (>99.7%) and double distilled deionised water degassed by the method of Van Ness and Abbott (1978). The use of a degassed liquid is of some importance in this measurement to avoid the formation of air bubbles in the liquid. The degassing technique of Van Ness and Abbott is described in Chapter 5 in connection with diffusion measurements where the use of a degassed liquid is of critical importance. Prior to each experiment, a batch of
silicalite crystals was placed in the pycnometer bulb and dried and activated at 400 °C for minimum of 4 hours and the dry weight $W_s$ was measured. The crystals were then cooled and sufficient solution of known mass fraction $w_{1o}$ was introduced to half fill the bulb and the suspension was equilibrated for 3 hours in a bath controlled to ±0.05 °C. This initial step was necessary to allow any residual air issued from the crystals to either escape or redissolve in the liquid. The pycnometer capillary was then connected, the liquid level was brought up into its graduated section, and the suspension was allowed to equilibrate for a further 18 hours. At equilibrium, the total weight $W_p$ and the total volume $V_p$ of the suspension in the pycnometer were measured. A sample of the solid free liquid was then withdrawn with a gas-tight syringe fitted with a microfilter cartridge and its
density $\rho_f$ and equilibrium mass fraction $w_1$ were determined. The excess adsorption $\Gamma_1^w$ and total absolute adsorption $Q_s$ were then calculated from:

$$
\Gamma_1^w = \frac{[W_p - W_s](w - w_1)}{W_s}
$$

$$
Q_s = \frac{W_p - [V_p - W_s/\rho_c] \rho_f - W_s}{W_s}
$$

where $\rho_c$ refers to the density of the crystals. The excess adsorption data measured by this procedure are shown by the full circles in Figure 3 and are in keeping with the data measured by the conventional batch technique. Figure 5 shows the influence of temperature on the total uptake of the pure adsorbates and the isothermal data for the

Fig. 5 Influence of temperature on adsorption of pure ethanol and pure water on silicalite.
The error bars in these figures reflect the accuracy and reproducibility of the measurements which were established by a detailed error analysis and experiments run in duplicate and triplicate.

**Fig. 6** Total adsorption isotherms for the system (ethanol(1)-water(2))/silicalite.
3.3.1 Calculation of the Individual Adsorption Isotherm

A simple material balance shows the excess isotherm $\Gamma_1^w$ is related to the individual absolute adsorption on a weight basis $q_1^s$ by

$$\Gamma_1^w = q_1^s - w_1 Q^s$$  \hspace{1cm} (14)

The individual absolute adsorption of component $i$ can therefore be determined directly from a knowledge of the excess and total adsorption:

$$q_1^s = \Gamma_1^w + w_1 Q^s$$  \hspace{1cm} (15)

The point values of the absolute individual adsorption for the system {ethanol-water}/silicalite calculated through Eq. (15) are shown in Figure 7 together with an estimate of the maximum error at each point. The solid lines on this figure were based on the following empirical formulae used to smooth the excess and total adsorption data in Figures 3 and 6:

$$\Gamma_1^w = \alpha \frac{w_1 (1 - w_1)}{1 + \alpha w_1}$$  \hspace{1cm} (16)

$$Q^s = q_2^{os} + (q_1^{os} - q_2^{os}) \frac{(1 + \beta_0) w_1}{1 + \beta_0 w_1^\beta}$$  \hspace{1cm} (17)

where $q_1^{os}$ and $q_2^{os}$ represent the independently measured absolute adsorption from the pure components. The parameters $\alpha_0$, $\alpha$, $\beta_0$, and $\beta$
Fig. 7 Experimental individual adsorption isotherms for system (ethanol(1)-water(2))/silicalite. (— based on smooth data Figs. 3 and 6).
were obtained by a maximum likelihood nonlinear regression technique [Prausnitz et al 1980, Law et al 1963] taking full advantage of the error estimates at each individual data point:

Empirical parameters for Eqs.(16) and (17)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$</td>
<td>0.1085</td>
<td>0.0923</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>89.9680</td>
<td>93.9860</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>103.5920</td>
<td>92.7290</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.0053</td>
<td>1.0016</td>
</tr>
</tbody>
</table>

The selectivity of silicalite towards ethanol was also calculated directly from the experimental excess and total adsorption data points and is presented in Figure 8. Here again, the solid lines were obtained through the empirical smoothing formulae (16) and (17) used to fit the data in Figures 3 and 6. As far as we are aware this is the very first time that sufficient measurements have been taken to enable the direct calculation of the individual adsorption isotherms and the composition of the adsorbed phase on the basis of experimental measurement without recourse to any a priori theoretical assumptions.
Fig. 8 Experimental distribution diagram for the system (ethanol(1)-water(2))/silicalite. (— based on smoothed data Figs. 3 and 6).
The simultaneous measurement of the excess and total adsorption enables the direct calculation of the absolute individual adsorption without any \textit{a priori} assumption. This information can then be used to test the validity of the various theories for the prediction of the absolute individual adsorption from a knowledge of the excess isotherm alone. Such theories invariably involve \textit{a priori} theoretical assumptions whose validity has not been previously verified.

### 3.4.1 Pseudo-Ideal Adsorption

Adsorption within microporous solids can be analysed under various levels of detail. On the simplest level, binary adsorption can be viewed as an exchange reaction,

\[
(1)^1 + (2)^s \rightleftharpoons (1)^s + (2)^1
\]

with the added stipulation that the adsorption space is always fully covered. The exchange reaction envisaged therefore implies that the same total number of molecules is adsorbed irrespective of composition. Under these assumptions we can follow an analysis analogous to that used in the classical monolayer theory of surface adsorption [Kipling 1965, Everett 1965, Everett 1964, Everett 1983]. This is possible because, as pointed out by Everett (1964), the actual location of the adsorbed molecules or adsorption sites (whether on the surface or in the body of the solid) is largely immaterial to the theoretical development of the "monolayer" model. The equilibrium constant for the above exchange reaction can be defined as [Everett 1964, Everett 1983];
\[ K(T) = \frac{x_1^s x_2}{x_1 x_2^s} \left( \frac{\gamma_1^s \gamma_2}{\gamma_1 \gamma_2^s} \right) \]  

(18)

where \( \gamma_1 \) and \( \gamma_1^s \) denote the activity coefficients in the bulk and adsorbed phases respectively. Clearly, pseudo-ideal Langmuir type behaviour with an apparent equilibrium constant \( K'(T) = K(T)[\gamma_2^s \gamma_1 / \gamma_1^s \gamma_2] \) will be observed whenever the bracketed term in Eq. (18) remains a constant. This could occur if the activity coefficient in the bulk and adsorbed phases are identical or if \( \gamma_2^s / \gamma_1 \) has a fixed ratio with \( \gamma_1^s / \gamma_2 \) across the entire concentration range. In either case, combination of Eqs. (4) and (18) leads to the following (Langmuir-type) expression [Everett 1964, Everett 1983],

\[ \frac{x_1 x_2}{\Gamma_1} = \frac{1}{N^s} \left[ x_1 + \frac{1}{K' - 1} \right] \]

(19)

which can be tested against experimental excess adsorption data to determine \( K' \) and \( N^s \). The apparent conformity of the (ethanol(l)-water(2)/silicalite) system to pseudo-ideal adsorption behaviour is demonstrated in Figure 9. The excess isotherms for pseudo-ideal adsorption can be calculated from

\[ \Gamma_1 = N^s \frac{(K' - 1)x_1 (1-x_1)}{1 + (K' - 1)x_1} \]

(20)

and fit the experimental data well at both 25 and 60 °C, see Figure 10.
Fig. 9 Apparent conformity of the system (ethanol(1)-water(2))/silicalite to pseudo-ideal adsorption.
Fig. 10 Comparison of the excess adsorption for the system of (ethanol(1)-water(2))/silicalite with curves predicted by pseudo-ideal adsorption.
This is rather surprising since the interaction between ethanol and water molecules within the hydrophobic confines of silicalite micropores is unlikely to remain the same as that in the bulk liquid. Further doubt arises because the theoretical $N^s$ value, as well as being temperature dependent, is smaller than the total adsorption measured for either pure component:

<table>
<thead>
<tr>
<th>Adsorption (mmol/g)</th>
<th>T °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>$N^s$</td>
<td>2.38</td>
</tr>
<tr>
<td>$n_1^{0s}$</td>
<td>2.87</td>
</tr>
<tr>
<td>$n_2^{0s}$</td>
<td>2.67</td>
</tr>
</tbody>
</table>

The inadequacy of the above analysis is clearly brought out in Figures 11 and 12 which compare the predicted individual adsorption and the composition of the adsorbed phase with the corresponding experimentally determined values. Clearly, despite the apparent fit of the excess isotherm, the \textit{a priori} adoption of pseudo-ideal adsorption behaviour leads to substantial error in estimation of both the capacity and the selectivity of the silicalite crystals.

The above behaviour is not limited to the system studied in this thesis and a large number of the reported (surface) excess isotherms are also apparently well fitted by pseudo-ideal behaviour [Everett 1983]. This has led to assertions that activity coefficients in the bulk and adsorbed phases are identical [Everett 1983, Everett 1965] or that the adsorbed phase is ideal even the bulk liquid is nonideal [Myers and
Fig. 11 Comparison of the experimental individual adsorption isotherms for the system (ethanol(1)-water(2))/silicalite with prediction based on (a) pseudo-ideal adsorption (b) volume filling mechanism.
Fig. 12 Comparison of the experimental adsorbed phase composition for the system (ethanol(1)-water(2))/silicalite with prediction based on (a) pseudo-ideal adsorption, (b) Langmuir adsorption from vapour and (c) volume filling mechanism.
Everett (1983) has criticised such speculation on the grounds that conformity to Langmuir-like behaviour could also arise when $\gamma_1^s/\gamma_1$ has a fixed ratio with $\gamma_2^s/\gamma_2$. The activity ratios calculated subsequently in Chapter 4 show that apparent pseudo-ideal behaviour can arise even when the activity ratio $\gamma_2^s/\gamma_1^s \gamma_2$ varies with composition. This confirms Everett's view [Everett 1983] that Eq. (19) is an insensitive test of the ideal behaviour of the system. Put another way, the apparent conformity of the excess isotherm to pseudo-ideal behaviour [i.e Eq. (19)] could arise as a consequence of nothing more than a fortuitous curve fit.

3.4.2 Comparison of Vapour and Liquid Phase Adsorption

At this point it is also of some interest to compare the predicted selectivity based on adsorption from solution with that based on adsorption from vapour. Klein and Abraham (1983) have examined vapour-phase adsorption of ethanol and water vapours and their mixtures at 60 and 115 °C. To avoid capillary condensation, the vapour-phase measurements were made at conditions far removed from saturation [Klein and Abraham 1983] and cannot therefore be directly compared to the saturated liquid-phase adsorption data reported in this Chapter. An indirect comparison is, however, possible if both sets of data are analysed under similar ideal (Langmuir type) assumptions.

Adsorption from ethanol-water vapour mixtures can be described by the familiar multicomponent Langmuir isotherm:
where \( P_1 \) and \( P_2 \) are the partial pressure of ethanol and water respectively, \( k_i \) is a characteristic constant for component i, and \( n_{i}^{os} \) is the saturation capacity of component i. The constant \( n_{i}^{os} \) and \( k_i \) can be obtained by fitting Eqs. (21) and (22) to the experimental vapour phase adsorption isotherms. To determine the adsorption from the solution in contact with the vapour we note that:

\[ P_i = \gamma_i x_i P^o \]  

(23)

and Eqs. (21) and (22) can be written as

\[
\begin{align*}
\hat{n}_1^s &= \frac{n_1^{os}k_1P^o}{1 + k_1P + k_2P^2} \\
\hat{n}_2^s &= \frac{n_2^{os}k_2P^o}{1 + k_1P + k_2P^2}
\end{align*}
\]

Thus, given the liquid phase composition \( x_i \) and activity coefficients \( \gamma_i \), the individual adsorption \( \hat{n}_1^s \) and \( \hat{n}_2^s \) can be calculated. The selectivity of the adsorbent on a weight basis is then given by:
where \( M_i \) denotes the molecular weight of component \( i \). The result obtained is compared with that based on liquid phase data in Figure 12 presented previously.

As expected, the selectivity predicted from vapour phase Langmuir isotherms [Klein and Abraham 1983] is practically the same as that based on liquid phase pseudo-ideal adsorption. In both cases, however, the predicted selectivity deviates significantly from that measured experimentally. This goes a long way in establishing the accuracy and the correspondence of both sets of data. It also confirms that similar serious errors are incurred when either vapour or liquid phase adsorption data are analysed under unjustified \textit{a priori} theoretical assumptions.

### 3.4.3 Volume Filling Mechanism

As an alternative to pseudo-ideal adsorption we could assume that adsorption within the microporous solid occurs by a simple volume filling mechanism [Hansen and Hansen 1954]. If we let \( \nu_1^s \) and \( \nu_2^s \) denote the partial molar volume of the components and further assume that the adsorbed molecules are distributed within the entire micropore volume \( v \), it follows that:

\[
S_{12} = \frac{n_1^s M_1 / n_2^s M_2}{w_1 / w_2}
\]

where \( n_i^s \) denotes the number of moles of component \( i \).
\[ \nu = n_1^{os} \nu_1^{os} + n_2^{os} \nu_2^{os} \] 

(24)

Similarly, for each pure component we may write,

\[ \nu = n_i^{os} \nu_i^{os}, \quad i = 1, 2 \] 

(25)

where \( n_i^{os} \) and \( \nu_i^{os} \) refer to the amount and molar volume of pure component \( i \) adsorbed. If, following Hansen and Hansen (1954), it is assumed that there is no volume change of mixing within the adsorbed phase, i.e. \( \nu_1^{os} = \nu_1^{os} \) irrespective of the adsorbed phase composition, we may combine Eq. (24) and (25) to give

\[ \frac{n_1^{os}}{n_1} + \frac{n_2^{os}}{n_1} = 1 \] 

(26)

The individual amounts adsorbed and the composition of the adsorbed phase can now be calculated by combining Eqs. (5) and (26). The results presented in Fig. 11 and 12 reveal that the predictions based on the simple volume filling mechanism are significantly better than those based on pseudo-ideal adsorption. The individual adsorption predicted for ethanol is in fact surprisingly accurate. Those for water are, however, in significant error particularly at low alcohol concentrations.

The superiority of the simple volume filling mechanism over pseudo-ideal adsorption is easily explained. In the latter case, the total number of molecules adsorbed is assumed constant irrespective of the adsorbed phase composition. The volume filling mechanism, however,
allows for a linear variation between the respective number of molecules adsorbed from each pure component. The wider applicability of Eq.(26), which is often referred to as the Lewis relationship [Lewis et al 1950], has also been empirically demonstrated for a wide variety of binary vapour mixtures adsorbing onto silica gel and activated carbon adsorbents [Lewis et al 1950]. This is to be expected, since while Eq.(26) can itself be derived from the Langmuir isotherm, the converse is not true and many other binary model isotherms also conform, at least approximately, to Eq.(26).

3.4.4 Molar Volume of the Adsorbed Phase

If it is assumed that the entire micropore volume \( v \) is accessible to the adsorbed molecules, an average value can be assigned to the molar volume \( v^s = v/(n_1^s + n_2^s) \) of the adsorbed phase. The independent measurement of the excess and total adsorption therefore enables the calculation of \( v^s \) as a function of the adsorbed phase composition and temperature. Much is learnt about the nature of the adsorbed phase if we compare the mean molar volume of the pure adsorbates with the corresponding values for pure liquid and vapour. Figure 13 contrasts the data obtained for silicalite with that reported by Dubinin et al (1980) for the highly polar 5A zeolite. For silicalite, the mean molar volume of the adsorbed ethanol falls between the molar volume of liquid ethanol and the van der Waals volume of ethanol vapour but is considerably closer to the liquid molar volume. This indicates that within the "hydrophobic" pore structure of silicalite, adsorbed ethanol is in a "condensed" state somewhat less dense than liquid ethanol. In
Fig. 13 Mean molar volume of pure ethanol and pure water adsorbed within (a) — o — hydrophobic silicalite crystals, (b) — e — hydrophilic NaA zeolite crystals [Dubinin et al., 1980]. (— liquid molar volume, ▼ van der Waals volume of vapour).

contrast, the molar volume of ethanol adsorbed within the strongly hydrophilic and more open structure of 5A zeolite is consistently smaller than that of the bulk liquid.

The influence of the surface properties and pore structure is more pronounced for water. The water adsorbed by silicalite has a mean molar volume more than twice the van der Waals volume of water vapour. The adsorbed water is therefore in a highly mobile state with either individual water molecules or perhaps small cluster of water molecules.
effectively excluding a volume much larger than that indicated by the molecular dimensions of water. The mean molar volume of water within the hydrophilic 5A zeolite is, on the other hand, consistently smaller than that of liquid water. Indicating that within the 5A zeolite the water molecules are highly localised and can pack more densely than in the bulk liquid.

Considering the radically different nature of pure water and pure ethanol adsorbed within silicalite, we could expect significant volume changes to occur in binary adsorption of ethanol and water mixtures. Figure 14 is an attempt to quantify the magnitude of such changes based on the smoothed data of Figures 3 and 6. Here, we should point out that the molar volume of the adsorbed phase is plotted as a function of the experimentally determined adsorbed phase composition, $x^*$, but the corresponding bulk liquid composition is also shown for comparison. The excess and the total adsorption values measured simultaneously by the pycnometer technique enable the direct calculation of point values of $v^*$ and these are also shown for comparison purposes.

The shape of the mean molar volume curve at low ethanol concentrations is sensitive to the initial slope of the smoothing lines drawn through the data in Figures 3 and 6. Clearly further experimental values at very low liquid ethanol concentrations are necessary to establish the shape of this curve with greater confidence. Nevertheless, despite the tentative nature of the mean molar volume curve at low ethanol concentrations, we are led the following general observations. Unlike the bulk liquid, the adsorbed phase shows considerable volume changes with composition. The packing density and the total number of
Fig. 14 Mean molar volume of mixed adsorbate for the system (ethanol(1)-water(2))/silicalite. [ o experimentally measured, —— smoothed data, ▲ molar volume of liquid and ▼ Van der Wall volume of vapour].
molecules accommodated within the micropores of silicalite is therefore strongly dependent on composition. The straight line in Figure 14 corresponds to the assumption of no volume change of mixing inherent in the simple pore filling mechanism. The failure of this theory therefore appears to be due to the erroneous a priori assumption of no volume change of mixing within the adsorbed phase.

3.5 CONCLUSION

The theoretical analysis of adsorption from solution of nonelectrolytes is normally based on the interpretation of the excess adsorption isotherm alone. Such analyses are, however, burdened with a priori assumptions whose validity can only be directly verified by the measurement of the total as well as the excess adsorption isotherm. A pycnometric technique was developed which for the first time enables the experimental determination of the extent and the composition of substances adsorbed from solution by microporous adsorbents. For the system ethanol-water/silicalite, considerable discrepancies were observed between the experimental individual adsorption isotherms and the corresponding values predicted by the available theories of adsorption from solution. Such discrepancies can be traced to the basic assumption of no volume (or area) change of mixing inherent in all the proposed theories of adsorption from solution. Within the hydrophobic pore structure of silicalite, ethanol is localised onto the surface at its organic end whereas water is in a highly mobile state.
The experimental results obtained suggest that for the system (ethanol-water)/silicalite considerable interaction occurs between the hydrophilic end of the localised ethanol and the mobile water molecules. These interactions are of sufficient strength to cause as much as 30% volume change of mixing within the adsorbed phase and alter the thermodynamic character of the adsorbed phase radically from that of the bulk liquid. Such differences are quantified in the next chapter which presents a model independent thermodynamic analysis of adsorption from solution based on the directly measured individual adsorption isotherms.
CHAPTER 4

THERMODYNAMIC ANALYSIS OF SORPTION EQUILIBRIA
4. THERMODYNAMIC ANALYSIS OF SORPTION EQUILIBRIA

4.1 INTRODUCTION

The thermodynamic analysis of adsorption from solution of non-electrolytes has received considerable attention over the past three decades. A lucid survey of this theoretical development, which has been largely concerned with surface adsorption, has been given by Everett (1983) and includes the simple mono- and multi-layer models with a sharp interface [Everett (1964, 1965), Larionov and Myers 1971], multilayer and lattice models accounting for the gradual decay of the potential field of the solid surface [Lane 1983, Ash 1968, Ash et al. 1970, Lane 1968] and, more recently, pure thermodynamic analyses independent of a specific molecular model for the adsorbed phase. All of these theories share the Gibbsian premise of an adsorbed phase with distinct physical properties. The derivation of the physical properties, for instance the activity coefficients, of the adsorbed phase is however invariably obtained under restrictive \textit{a priori} assumptions whose validity has not been directly verified. This state of affairs exists because a direct measurement of both the composition and the extent of the adsorbed phase is not normally available. The proposed thermodynamic theories of adsorption from solution have therefore been largely appraised against their ability to match the excess adsorption isotherms alone. This, as was demonstrated in Chapter 3, can result in significant error in the predicted selectivity and capacity of the solid. The primary purpose of this chapter is to
present a thermodynamic analysis based on the directly measured individual adsorption isotherms which avoids a *priori* assumptions about the nature of adsorption. Comparison of the results of this analysis with those based on the proposed theories of adsorption from solution serves to highlight the limitation of such theories and also leads to a clear picture of the molecular interactions within the microporous adsorbent.

In the absence of directly measured adsorbed phase composition, the evidence offered in support of the proposed theories is of an indirect nature. For monolayer models, it is based on the conformity of the projected molecular area calculated from liquid phase adsorption data with that measured by standard nitrogen gas adsorption technique [Everett 1983]. For lattice models, the argument is based on the ability of the same regular solution parameter to describe the behaviour of either phase [Everett 1983, Lane 1983]. Everett (1983) is careful to point out the limitation of such evidence and also presents examples where agreement is not observed. The evidence derived from immersion calorimetry and heat capacity measurements [Everett 1981, Myers et al 1971] in support of the structural change predicted by pure thermodynamic analysis of adsorption data, although much stronger, is still indirect. Moreover, the facilities for such measurement are not readily available and their interpretation in the case of heterogeneous adsorbents and multicomponent mixtures is complicated. The direct measurement of the individual adsorption isotherms enables *for the first time* a direct appraisal of the proposed theories of adsorption from solution. In particular, it allows the calculation of the adsorbed phase activity coefficients with no major assumption other
than the existence of a distinct adsorbed phase. This serves to show conclusively that the thermodynamic behaviour of ethanol–water mixtures within the hydrophobic confines of the silicalite micropores is radically different from that in the bulk liquid.

The lack of directly measured individual adsorption isotherms has imposed a fundamental restriction on the formulation of all of the proposed theories of liquid phase adsorption. To the best of the author’s knowledge, the proposed theories of liquid phase adsorption have in common an initial assumption regarding the total number of molecules confined to the adsorption space. For molecules of equal size, this amounts to the total coverage of the adsorption space with a fixed number of molecules irrespective of the adsorbed phase composition [Everett 1964]. For binary mixtures of molecules of unequal size, it is assumed that the total number of the adsorbed molecules varies linearly between the respective amounts adsorbed from the pure components. This, as was pointed out by Larionov and Myers (1971), is equivalent to the assumption of no area change of mixing on a two dimensional adsorption surface. Evidently, the analogous assumption for a three dimensional adsorption space is no volume change of mixing within the adsorbed phase. In either case, as we shall demonstrate, this assumption implies that the excess Gibbs free energy of the adsorbed phase is a function of composition alone; whereas in reality it may also depend on the spreading pressure.

Although some doubt about the validity of the above assumptions has been raised previously [Everett 1964, Everett 1983], a direct experimental verification has not yet been attempted. Since other
thermodynamic properties ascribed to the adsorbed phase are derived from the excess Gibbs free energy, the initial assumption that this quantity is a function of composition alone can exert a significant influence on the thermodynamic properties of the adsorbed phase. This is confirmed by the thermodynamic analysis presented here which shows that for the \{ethanol-water\}/silicalite system the excess Gibbs free energy of the adsorbed phase is indeed a very strong function of spreading pressure. In addition, the adsorbed phase exhibits a large volume change of mixing and the total number of molecules adsorbed is a strong function of composition.

4.2 THE GIBBS ADSORPTION ISOTHERM

The first step in the thermodynamic analysis is the derivation of the Gibbs adsorption isotherm which relates the properties of the bulk and adsorbed phases. In the case of a bulk fluid, vapour or liquid, three variables (e.g. pressure, temperature and volume) are sufficient to completely establish the thermodynamic state of the fluid. In the case of an adsorbed phase, however, four rather than three variables are needed to define the thermodynamic state. This additional variable is of course the amount of adsorbent over which the adsorbate molecules are spread. The derivation of the Gibbs adsorption isotherm therefore requires careful attention.

We consider the adsorbed phase as a solution of \(n_1^s, n_2^s, \ldots, n_N^s\) moles of sorbate and \(n_a^s\) "moles" of non-volatile adsorbent. The fundamental differential equation summarising the first and second law of thermodynamics for the entire system can then be written in any one of
the following entirely equivalent forms [Ruthven 1984, Hill 1950],

\[
dU = T dS - P dV + \mu_a \, dN_a + \sum \mu_i^s \, dN_i^s
\]  

(1a)

\[
dH = T dS - V dP + \mu_a \, dN_a + \sum \mu_i^s \, dN_i^s
\]  

(1b)

\[
dF = -S dT - P dV + \mu_a \, dN_a + \sum \mu_i^s \, dN_i^s
\]  

(1c)

\[
dG = -S dT + V dP + \mu_a \, dN_a + \sum \mu_i^s \, dN_i^s
\]  

(1d)

where \(U, H, F\) and \(G\) refer respectively to the internal energy, enthalpy, Helmholtz free energy and Gibbs free energy of the system.

For the work described in this thesis Eq.(1d) is chosen as the basic relationship for the analysis.

For a clean adsorbent, the Gibbs free energy may be written as:

\[
dG_{\text{oa}} = - S_{\text{oa}} \, dT + V_{\text{oa}} \, dP + \mu_{\text{oa}} \, dN_a
\]  

(2)

Subtraction of Eq.(2) from (1d) yields:

\[
dG_s = - S_s \, dT + V_s \, dP - \Omega dN_a + \sum \mu_i^s \, dN_i^s
\]  

(3)

where \(G_s = G - G_{\text{oa}}, S_s = S - S_{\text{oa}}, V_s = V - V_{\text{oa}}, -\Omega = \mu_a - \mu_{\text{oa}}\)

If we now adopt the Gibbsian viewpoint and consider the \(N_a\) "moles" of the adsorbent as thermodynamically inert, the quantities \(G_s, V_s, S_s\) and \(\Omega\) become the properties of the adsorbed phase in the potential
field of the adsorbent. Any contribution from the \( n_a \) "moles" of the adsorbent is eliminated in the subtraction. For instance the variable \( G_s \) now refers to the Gibbs free energy of the sorbate in the potential field of the adsorbent. The physical meaning of the thermodynamic variables \( \Omega \) and \( \mu_1^s \) is therefore clear. The variable \( \Omega \) is defined by

\[
\Omega = \mu_{oa} - \mu_a = \left( \frac{\partial G_{oa}}{\partial n_a} \right)_{T,P} - \left( \frac{\partial G_a}{\partial n_a} \right)_{T,P,n_j^s}
\]

and therefore represents the change in the Gibbs free energy per unit "amount" of the adsorbent caused by the spreading of the sorbate over the clean adsorbent. Similarly the variable \( \mu_1^s \) is defined by

\[
\mu_1^s = \left( \frac{\partial G_s}{\partial n_1^s} \right)_{T,P,n_a, n_j \neq 1}
\]

and represents the change in the Gibbs free energy caused by a change in the number of molecules adsorbed on a fixed amount of the solid. From Eq.(3) we also note that an extra variable is required to define the thermodynamic state of an adsorbed phase unambiguously. This additional variable is the "amount" of adsorbent \( n_a \) over which the sorbate molecules are spread.

Now, for adsorption on a two dimensional surface, the total surface area \( A \) is directly proportional to the "amount" of adsorbent \( n_a \). Similarly, for three dimensional adsorption within a microporous
adsorbent, the total micropore volume $v$ is directly proportional to the "amount" of adsorbent $n_a$. Without any loss of generality, therefore, we may define two new thermodynamic variables $\pi$ and $\phi$ such that

$$\Omega d_n = \pi dA = \phi dv$$

where

$$\pi = -\left( \frac{\partial G^s}{\partial A} \right)_{T,P,n_1^s} \quad \text{and} \quad \phi = -\left( \frac{\partial G^s}{\partial v} \right)_{T,P,n_1^s}$$

Defined in this way, $\pi$ corresponds to the difference in the two dimensional spreading pressure between a clean surface and one covered with the adsorbate. Similarly, the variable $\phi$ represents the difference between the "three dimensional spreading pressure" between a clean microporous adsorbent and one filled with sorbates. The physical meaning of the three dimensional spreading pressure is therefore at least as clear as that for the two dimensional spreading pressure. In fact, within the Gibbsian viewpoint, there is a formal relationship between the thermodynamic relationship based on $(\Omega$ and $n_a)$, $(\pi$ and $A)$ and $(\phi$ and $v)$. Essentially the same relationships based on $(\pi$ and $A)$ for two-dimensional adsorption can be derived for three-dimensional adsorption but based on $(\phi$ and $v)$. For our analysis we choose to work with $(\phi$ and $v)$.

At this point it is worthwhile to comment on the relationship between the two dimensional spreading pressure and surface tension. From the definition

$$\pi = -\left( \frac{\partial G^s}{\partial A} \right)_{T,P,n_1^s}$$

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it is clear that $\pi$ is effectively the negative of surface tension. We should note that whereas for a vapour/liquid interface the surface tension (hence spreading pressure) can be measured directly, the spreading pressure at a solid/liquid interface is not open to measurement. This fact should not, however, worry us unduly. All that is needed for the thermodynamic analysis is that the spreading pressure is well defined. We shall also show subsequently that although absolute values of $\Phi$ or $\pi$ cannot be measured, the relative changes in of $\Phi$ or $\pi$ can be calculated from liquid phase adsorption data.

We can now turn to the derivation of the Gibbs adsorption isotherm. Using Eq.(6), we may rewrite Eq.(3) in terms of ($\phi$ and $v$) rather than ($\Omega$ and $n_s$):

$$dG = - S dT + V dP - \Phi dv + \sum \mu_i^n s d n_s \tag{9}$$

Integration of this equation, whilst holding all intensive variables ($T,P,\phi,\mu_i^s$) constant, gives:

$$G_s = G_s(T,P,v,n_1^s) = -\Phi v + \sum \mu_{i_1}^s n_1^s \tag{10}$$

Now, at constant pressure and temperature we have from Eq.(9)

$$dG = - \Phi dv - vd\Phi + \sum \mu_i^n s d n_1^s + \sum n_1^s d\mu_i^s \tag{11}$$

Differentiation of Eq.(10) yields on the other hand

$$dG_s = - \Phi dv - vd\Phi + \sum \mu_i^n s d n_1^s + \sum n_1^s d\mu_i^s \tag{12}$$
Comparison of Eqs. (11) and (12) yields the Gibbs adsorption isotherm used as the starting point for our thermodynamic analysis.

\[ \nu d\Phi = \sum n_1^s d\mu_1^s \quad \text{(13)} \]

This equation can be rewritten in terms of the fugacity of component \( i \) in the adsorbed phase \( f_1^s \) which is defined as:

\[ d\mu_1^s = RT \ln (f_1^s) \quad \text{(14)} \]

Eq. (13) therefore takes the form:

\[ \nu d\Phi = RT \sum n_1^s \ln (f_1^s) \quad \text{(15)} \]

### 4.2.1 Standard States

In order to proceed with the analysis we must evaluate the fugacity \( f_1^s \), which raises the question of standard states. The fundamental equilibrium relationship between a vapour in contact with a liquid which is contact with the adsorbent can be stated as:

\[ d\mu_1^s = d\mu_1 = d\mu_1^v \quad \text{(16)} \]

or in terms of fugacity

\[ df_1^s = df_1 = df_1^v \quad \text{(17)} \]
The above differential equation is valid irrespective of the standard states chosen in any of the phases. To integrate this equation, however, a definite choice must be made for the standard state of component i. Put another way, the definition of fugacity by Eq. (14) is incomplete without a specific choice for the standard state.

There is no "standard" method of defining the standard state for adsorption from solution and various approaches have been reported. For example, Everett (1965) chose the standard state as the fugacity of component i in a perfect monolayer. The advantage of this choice is that the properties of the adsorbed phase are then referred to that of a perfect monolayer. The disadvantage is that at equilibrium the fugacities of component i in the bulk and adsorbed phases are not numerically equal. Larionov and Myers (1971) on the other hand chose the pure adsorbate but at the same temperature and spreading pressure as the mixed adsorbate (T and $) for the standard state. This has the advantage that at equilibrium the numerical value of the fugacity of component i is identical in each phase. The basic equilibrium condition can then, and only then, be stated as:

\[ f_s^i = f_1 = f_v^i \]  

(18)

We should, however, note that the pure adsorbate does not exist at the spreading pressure of the mixture but at a spreading pressure $\phi_1^0$. It is therefore necessary to make a correction for the spreading pressure by integrating the Gibbs adsorption isotherm for the pure component between the conditions experienced by the pure adsorbate i (T and $\phi_1^0$).
and that felt by the mixed adsorbate ($T$ and $\Phi$) to arrive at the standard state $f_{1}^{s}$ [Larionov and Myers 1971]:

\[
\int_{\Phi_{1}^{0}}^{\Phi} v \, d\Phi = n_{1}^{os}RT \int_{f_{1}^{os}}^{f_{1}^{s}} \frac{d\ln f_{1}}{f_{1}^{os}}
\]

(19)

where $n_{1}^{os}$ is the (measurable) amount of pure $i$ adsorbed at temperature $T$ and $f_{1}^{os}$ is the fugacity of pure adsorbate $i$ which for an ideal vapour phase can be equated to vapour pressure $f_{1}^{os} = P_{1}^{o}(T)$. The result takes the following form

\[
f_{1}^{s} = f_{1}^{os} \exp \left( \frac{v(\Phi - \Phi_{1}^{0})}{n_{1}^{os}RT} \right)
\]

(20)

and referred to the above standard state, the fugacity of component $i$ in the adsorbed phase is given by

\[
f_{1}^{s} = P_{1}^{o} \exp \left( \frac{v(\Phi - \Phi_{1}^{0})}{n_{1}^{os}RT} \right) \gamma_{1}^{s} x_{1}^{s}
\]

(21)

where $\gamma_{1}^{s}$ is the activity coefficient of $i$ in the adsorbed phase and the exponential term accounts for the influence of spreading pressure on the fugacity of pure adsorbate $i$ [Larionov and Myers 1971]. The equilibrium condition can therefore be stated as

\[
f_{1}^{s} = P_{1}^{o} \exp \left( \frac{v(\Phi - \Phi_{1}^{0})}{n_{1}^{os}RT} \right) \gamma_{1}^{s} x_{1}^{s} = f_{1} = P_{1}^{o} x_{1} \gamma_{1}
\]

(22)
With the derivation of the Gibbs adsorption isotherm and the choice of a suitable standard state for the adsorbed phase, we only require a knowledge of the bulk liquid activity coefficients to calculate the thermodynamic properties of the adsorbed phase. The activity coefficients for ethanol-water mixtures are readily available in the literature and thermodynamically consistent data at 25 and 60 °C were taken from Jones et al [1943] and Hansen et al [1954]. Some care must be exercised, however, in defining the size of the adsorption space \( v \) required in the calculations. This is because for very small microporous particles, adsorption on the external surface could make a significant contribution to the total uptake and must be accounted for.

The size distribution of the silicalite crystals used in this study was measured by several methods and the results were reported in Chapter 2. On a number basis, the predominantly cubic crystals had mean size of 2.4 \( \mu \text{m} \) with less than 2% of the crystals below 0.8 \( \mu \text{m} \) and none less than 0.6 \( \mu \text{m} \). Calculations based on the measured size distribution and the measured saturation capacities reported in Chapter 3 confirm that less than 0.5% of the total number molecules adsorbed can be accommodated in a close packed monolayer on the external surface of the crystals. For silicalite crystals, therefore, the Gibbsian dividing surface between the bulk and adsorbed phases effectively coincides with the physical boundary of the particles and the adsorbed molecules are virtually totally confined within the (measurable) micropore volume, \( v \).

Here we also note that this also implies that the silicalite crystals do not expand or contract on adsorption.
4.3.1 Calculation of the Spreading Pressure

The absolute value of the spreading pressure is not open to direct measurement. Relative changes in the spreading pressure can, however, be calculated by relating $\frac{vd\phi}{RT}$ to the directly measurable quantities $\Gamma_j$, $\gamma_j$ and $x_j$. Substitution of the individual adsorption $n^s_j$

$$n^s_j = N^s x^s_j = N^s x_j + \Gamma_j \quad (\text{cf Eq. 8 Chapter 3})$$

(23)

and the equilibrium condition

$$f^s_j = f_j = p_j^0 \gamma_j x_j$$

(24)

into the Gibbs adsorption isotherm $vd\phi = RT \sum n^s_i \ln (f^s_i)$ leads to

$$\frac{vd\phi}{RT} = \sum_j \Gamma_j \ln (\gamma_j x_j) + N^s \sum_j x_j \ln (\gamma_j x_j)$$

(25)

Assuming that the volume change of mixing in the bulk liquid is negligible, the activity coefficients $\gamma_j$ must satisfy the restricted Gibbs-Duhem equation:

$$\sum_j x_j \ln (\gamma_j) = 0$$

(26)

The last term in Eq.(25) is therefore identically zero and $vd\phi/RT$ is directly related to the measurable quantities $\Gamma_j$, $\gamma_j$ and $x_j$:

$$\frac{vd\phi}{RT} = \sum_j \Gamma_j \ln (\gamma_j x_j)$$

(27)
Further expansion of Eq.(27) for a binary system leads to

\[ \frac{d\Phi}{RT} = \Gamma_1 \left[ \frac{d(y_1 x_1)}{y_1 x_1} - \frac{d(y_2 x_2)}{y_2 x_2} \right] \]  

Noting that \( dx_2 = -dx_1 \), we have from Eq. (26),

\[ -d\ln \gamma_2 = \frac{x_1 d\ln \gamma_1}{x_2} \]  

Substituting the above expression into (28) leads to:

\[ \frac{d\Phi}{RT} = \frac{\Gamma_1 d(y_1 x_1)}{y_1 x_1 x_2} \]  

The relative changes in \( \Phi \) can therefore be obtained by the numerical integration of Eq.(30):

\[ \frac{\nu(\Phi - \Phi_1^0)}{n_1^{os}RT} = \frac{1}{n_1^{os}} \int_1^{x_1} \frac{\Gamma_1}{y_1 x_1 x_2} d(y_1 x_1) \]  

\[ \frac{\nu(\Phi - \Phi_2^0)}{n_2^{os}RT} = \frac{1}{n_2^{os}} \int_0^{x_1} \frac{\Gamma_1}{y_1 x_1 x_2} d(y_1 x_1) \]  

To perform the above integrations requires only a knowledge of the measurable quantities \( \Gamma_1, \gamma_1, x_1 \) across the entire concentration range. The integrand in Eqs.(31) and (32) is indefinite at both \( x_1=0 \) and \( x_1=1 \). However, the application of the L'Hopital rule reveals that

\[ \lim_{x \to 0} \frac{\Gamma_1}{y_1 x_1 x_2} = \frac{d\Gamma_1}{dx} \bigg|_{x_1=0} \]  

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where the limiting slopes of the excess isotherm can be evaluated from
the experimental data (eg. Eq.(16) in Chapter 3). Using the
experimentally measured excess isotherm and its limiting slopes, the
experimentally determined pure component adsorption $n_1^{os}$ and $n_2^{os}$, and
the bulk liquid activity data presented in Figure 1, Eqs.(31) and (32)
were integrated numerically and the result is presented in Figure 2 as
a function of the adsorbed phase composition $x_i^s$; the corresponding
liquid phase composition $x_i$ is also shown for clarity. It is evident
that the influence of the spreading pressure on the fugacity of the
pure adsorbate is significant and must be taken into account.

The above development is frequently used to check the thermodynamic
consistency of liquid phase adsorption data. If the integration in
Eq.(32) is carried out between $x = 0$ to $x = 1$, the result is

$$ (\Phi^0 - \Phi^0) = \frac{RT}{v} \int_0^1 \frac{\Gamma_1}{\gamma_1 x_1 x_2} d(\gamma_1 x_1) $$

Thus, for a three component mixture the quantities $(\Phi^0 - \Phi^0)_1$, $(\Phi^0 - \Phi^0)_2$, and $(\Phi^0 - \Phi^0)_3$ can all be calculated from the respective binary excess
isotherm data. Thermodynamic consistency of the data then requires
that [Everett 1983, Sircar et al., 1971].

$$ (\Phi^0 - \Phi^0)_1 + (\Phi^0 - \Phi^0)_2 + (\Phi^0 - \Phi^0)_3 = 0 $$
Fig. 1: Liquid phase activity coefficients for ethanol(1)-water(2) mixtures [Jones et al., 1943, Hansen et al., 1954].
Fig. 2  Influence of spreading pressure on the fugacity of the pure adsorbate for the system (ethanol(1)-water(2))/silicalite.

(a) $-n(\phi - \phi_1^o)/n_1^{os}$ RT and (b) $n(\phi - \phi_2^o)/n_2^{os}$ RT.
We should, however, note that this procedure does not allow for a direct thermodynamic consistency test of each individual binary pair. It is conceivable that the data for the respective binary pairs may be thermodynamically inconsistent but such that when added the errors compensate and Eq.(36) is fulfilled fortuitously. In section 4.3.5 we shall present a procedure for a direct thermodynamic consistency test which can be applied to each binary pair individually.

4.3.2 Derivation of the Gibbs-Duhem Equation for the Adsorbed Phase

In the case of bulk liquids, the volume change of mixing is normally sufficiently small and the general Gibbs-Duhem Equation at constant temperature

$$\sum_{1} x_{i} \ln \gamma_{i} = \frac{\Delta V}{RT} dP$$  

may be safely approximated by the restricted Gibbs-Duhem equation

$$\sum_{1} x_{i} \ln \gamma_{i} = 0$$  

The Gibbs-Duhem equation for an adsorbed phase is in analogy with bulk liquids often quoted as

$$\sum_{1} x_{i}^{s} \ln \gamma_{i}^{s} = 0$$  

This, however, implies that the volume change of mixing is also negligible in the adsorbed phase. The experimental results presented
in Chapter 3 show that this is not necessarily true and the adsorbed phase can exhibit significant volume change of mixing. It is therefore necessary to establish the Gibbs-Duhem equation for the adsorbed phase without the arbitrary neglect of the volume change of mixing.

Taking the total derivative of the logarithm of Eq.(21)

$$\frac{d\ln f_i^s}{n_1^{os}RT} = \frac{vd\Phi}{n_1^{os}RT} + d\ln(\gamma_i^s x_1^s)$$  \hspace{1cm} (40)

and substituting the result into the Gibbs adsorption isotherm $vd\Phi/RT = \Sigma n_1^{os}d\ln(f_i^s)$ leads after some manipulation to the unrestricted Gibbs-Duhem equation for the adsorbed phase:

$$\frac{d\Phi}{RT} \left[ v \left( \frac{1}{N^s} - \sum \frac{x_i^s}{n_1^{os}} \right) \right] = \sum x_i^s d\ln(\gamma_i^s)$$  \hspace{1cm} (41)

The bracketed term in Eq.(41) represents the volume change of mixing within the adsorbed phase. The equivalent expression derived for the area change of mixing by Everett (1964, 1965, 1983) and by Larionov and Myers (1971) is arbitrarily set to zero. It is clear that under the assumption of no volume (or area) change of mixing, the activity coefficients in the adsorbed phase are constrained to obey a relationship similar to the restricted Gibbs-Duhem equation normally employed for bulk liquids, cf Eq. (39). The experimental data on the volume change of mixing presented in Figure 14 of Chapter 3 show that the restricted Gibbs-Duhem type relationship (39), although generally applicable to bulk liquids, does not necessarily hold for the adsorbed phase. Retaining the general form of the Gibbs-Duhem equation (41) for
the adsorbed phase and expanding it for a binary system leads to the unrestricted form applicable to a binary adsorbed phase

\[ x_1^s \ln \gamma_1^s + x_2^s \ln \gamma_2^s = \nu \frac{d\Phi}{RT} \left[ \frac{1}{N^s} \left( \frac{x_1^s}{n_1^{os}} + \frac{x_2^s}{n_2^{os}} \right) \right] \]  

(42)

4.3.3 Activity Ratio and Selectivity

It is of some interest to compare the experimentally measured selectivity of the silicalite crystals towards ethanol with the values predicted through the proposed theories of adsorption from solution. The selectivity of silicalite toward ethanol is defined as

\[ S = \frac{[x_1^s/x_2^s]}{[x_1/x_2]} \]  

(43)

and its value can be calculated given the adsorbed phase composition as a function of the bulk liquid composition. Figure 3 compares the results obtained on the basis of experimentally determined adsorbed phase composition with those based on psuedo-ideal and volume filling mechanisms. It is clear that the theoretical predictions are in poor agreement with the measured data.

To understand the reason for this disagreement, we can note that the selectivity is given by (see Eq. 22):

\[ S = \frac{x_1^s/x_2^s}{x_1/x_2} = \frac{\gamma_2^s/\gamma_1^s}{\gamma_2/\gamma_1} \exp \left[ \frac{\nu(\phi - \phi_2^0)}{n_1^{os}RT} - \frac{\nu(\phi - \phi_1^0)}{n_2^{os}RT} \right] \]  

(44)

and is a function of both the adsorbed phase activity coefficients $\gamma^s_1$. 

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Fig. 3 Comparison of the selectivity for the system (ethanol(1)-water(2))/silicalite based on: (1). Experimental data, (2). Volume filling mechanism and (3). Pseudo-ideal adsorption.
and the spreading pressure $\phi$. In the case of pseudo-ideal adsorption, the selectivity is a priori assumed constant whereas for volume filling mechanism the selectivity may vary with composition but in an undefined manner.

The contribution of spreading pressure to selectivity can be obtained from the values of $(\phi - \phi_1^0)$ and $(\phi - \phi_2^0)$ at different composition. The data presented in Figure 2 show that at 25 °C, the bracketed term in Eq.(44) varies almost linearly between 3.4 at $x = 0$ to 3.7 at $x = 1$. The contribution of the exponential term (i.e. the spreading pressure variation) to selectivity therefore falls from 30 at $x = 0$ to 40 at $x = 1$. Similar comments can also be made for the data at 60 °C. For the (ethanol-water)/silicalite system, therefore, the contribution of the changes in spreading pressure to variations in selectivity is relatively small. The selectivity may, however, vary considerably if the activity ratio ($\gamma_2^s / \gamma_1^s$) has a strong concentration dependence. It is therefore instructive to compare the values of the activity ratio based on the experimental data with those predicted by the proposed theories.

The activity ratio is obtained by rearranging Eq.(44),

$$\frac{\gamma_2^s / \gamma_1^s}{\gamma_2 / \gamma_1} = \frac{x_2^s x_1}{x_2 x_1} \exp \left[ \frac{\nu(\phi - \phi_1^0)}{n_1^{os} RT} - \frac{\nu(\phi - \phi_2^0)}{n_2^{os} RT} \right]$$

and its value can be calculated from a knowledge of the excess and total adsorption which together establish all the variables on the right hand side. To make a valid comparison, the excess experimental isotherm data was used to calculate the exponential term in Eq.(45).
independently of the adsorbed phase composition. The activity ratio was then obtained by substituting, in turn, the values of the adsorbed phase composition measured experimentally, that predicted from pseudo-ideal adsorption and that obtained from the volume filling mechanism. The result of this calculation is summarized in Figure 4 and demonstrates that the activity ratio varies between 7 and 0.1 at 25°C and between 11 and 0.1 at 60°C. The sharp variation in the selectivity is therefore largely due to the concentration dependence of the activity ratio.

In the case of pseudo-ideal adsorption, the calculated activity ratio remains constant across the entire concentration range which is to be expected from the a priori assumptions inherent in this theory. Clearly, despite the apparent fit of the excess isotherm, the inherent assumptions of pseudo-ideal analysis are self-fulfilling and can lead to substantial errors. The activity ratio calculated on the basis of volume filling mechanism varies with composition. However, there are substantial quantitative differences between the activity ratio calculated on the basis of the volume filling mechanism and that based on the experimentally determined individual adsorption isotherms. It is clear that such differences are related to the inherent inability of the volume filling mechanism to account for the volume change of mixing in the adsorbed phase.

An interesting feature of the (ethanol-water)/silicalite system is brought out by comparing the selectivity at very low liquid ethanol concentrations as a function of temperature. At sufficiently low liquid concentrations, the adsorbed phase approaches ideal behaviour.
Fig. 4 Activity ratio \( \frac{y_1^s}{y_2^s} \) for the (ethanol(1)-water(2))/silicalite calculated from (a) pseudo-ideal adsorption, (b) volume filling mechanism and (c) experimental individual adsorption isotherms.
and the selectivity as a function of the adsorbed phase composition must approach a straight line. This is confirmed by Figure 5 which show that at liquid mole fractions below about 0.01, which corresponds to an adsorbed phase mole fraction of 0.5, the experimentally determined selectivity does indeed appear to follow a straight line.

Fig. 5 Comparison of selectivity for the system (ethanol(l)-water(2))/silicalite at low concentration (--- straight line fitted to the data $x^s_1 < 0.5$).
We can now turn to the calculation of the adsorbed phase activity coefficients which has been the subject to considerable debate in the literature [see Everett 1983]. A fundamental constraint in the theoretical interpretation of adsorption from solution arises because only the bulk liquid is open to direct measurement. The composition and the properties ascribed to the adsorbed phase have therefore been inferred from such measurements under restrictive \textit{a priori} theoretical assumptions. This has led to considerable speculation about the nature of adsorption, the thickness of the adsorbed layer, and the properties of the adsorbed phase. For instance, it has variously been assumed that the activity coefficients in the bulk and adsorbed phases are identical [Everett 1965], that an empirical relationship exists between them [Lane 1983], or that the adsorbed phase is ideal even when the bulk liquid is non-ideal [Myers and Sircar 1971].

Now, if (and only if) both the specific excess adsorption $\Gamma_1$ and the specific total adsorption $N^s$ are measured across the concentration range, will the evaluation of the composition, the volume change of mixing, and the activity coefficients in the adsorbed phase remain unambiguous. The purpose of this section is to calculate the adsorbed phase activity coefficients for the system (ethanol-water)/silicalite without recourse to \textit{a priori} and at times unjustified theoretical assumptions.

An expression for the adsorbed phase activity coefficients can be obtained by rearranging Eq.(42) as,
and integrating to give

\[
\ln \gamma_2^s = x_1 \ln \left[ \frac{\gamma_2}{\gamma_1^s} \right] - \int_0^{x_1} \ln \left[ \frac{\gamma_2}{\gamma_1^s} \right] dx_1 + \int_0^{x_1} \left[ \frac{1}{N_s} - \left( \frac{x_1}{n_1} + \frac{x_2}{n_2} \right) \right] \frac{vd\phi}{RT} 
\]

(47)

with a similar expression for \( \gamma_1^s \).

The major difference between Eq.(47) and the corresponding expression derived in previous analyses (e.g. Everett 1965, Larionov and Myers 1971) is the last term which accounts for the volume change of mixing and the influence of the spreading pressure on the Gibbs free energy of the adsorbed phase.

Given the excess and total adsorption isotherms, \( \Gamma_1 \) and \( N_s^s \), and the liquid phase activity data, the calculation of the activity coefficient \( \gamma_1^s \) can therefore proceed as follows. The composition \( x_1^s \) is obtained from Eq.(3.8) and the volume change of mixing can then be calculated from \( v(1/N_s^s - \Sigma x_j^s/n_j^s) \). The ratio,

\[
\frac{\gamma_2^s}{\gamma_1^s} = \frac{x_1^s \gamma_2 x_2}{x_2 \gamma_1 x_1} \exp \left[ \frac{v(\phi - \phi_1^o)}{n_1^o RT} - \frac{v(\phi - \phi_2^o)}{n_2^o RT} \right] 
\]

(48)

is obtained by first integrating Eqs.(31) and (32) to give the exponential term and substituting the result along with \( x_1^s \) and \( \gamma_1 \) into Eq.(47). Using this ratio and Eq.(30) the integrations in Eq.(47)
can then be performed numerically to yield the value of $\gamma_2^s$. A similar procedure furnishes the value of $\gamma_1^s$.

The above procedure differs from those reported previously (e.g. Everett 1983, Everett 1965, Larionov and Myers 1971 and Lane 1983) in two important respects. First, no assumptions are made regarding the volume change of mixing or the excess Gibbs free energy of the adsorbed phase. Second, the evaluation of the activity coefficients is based on the experimentally measured adsorbed phase composition. In the procedure suggested by Everett (1964,1983) for molecules of (approximately) equal size, the adsorbed phase composition is predicted under the a priori assumption $N^s = n_1^{os} = n_2^{os} =$ constant. Similarly, in the analysis of Larionov and Myers (1971) for molecules of different size, the composition of the adsorbed phase is predicted under the a priori assumption of no area change of mixing, i.e.,

$$\left\{1/N^s - \left[x_1^{s}/n_1^{os} + x_2^{s}/n_2^{os}\right]\right\} = 0.$$  

In contrast, the procedure adopted here uses the experimentally determined adsorbed phase composition and makes no a priori assumptions other than the existence of a distinct adsorbed phase. As far as we are aware, this is the first time in the study of adsorption from solution that sufficient measurements have been made to enable the direct calculation of the thermodynamic properties of the adsorbed phase.

The adsorbed phase activity coefficients calculated from Eq.(47) are shown in Figure 6 and exhibit substantial negative deviation from ideality. This is in contrast to the behaviour of the bulk liquid which shows strong positive deviation from ideality (see Fig. 1). The behaviour of the adsorbed phase is therefore radically different from
Fig. 6 Adsorbed phase activity coefficients for the system ethanol(l)-water(2)/silicalite based on the experimental individual adsorption isotherms.

Liquid Phase Mole Fraction, $x_1$

Adsorbed Phase Mole Fraction, $y_1$

Activity Coefficient, $\gamma$

$T = 60^\circ C$

$T = 25^\circ C$
that in the bulk liquid. The positive deviations in the bulk liquid indicate that water–water and ethanol–ethanol molecular interactions dominate over the interaction between unlike molecules. In contrast, within the hydrophobic confines of the silicalite micropores, the ethanol–water interactions overshadow those between like molecules. This indicates that the adsorbed water is largely associated with the adsorbed ethanol. The selectivity of the crystals towards ethanol is therefore severely limited by ethanol–water interactions within the hydrophobic micropores. A major practical consequence of this is that improvements in the surface properties of the crystals is unlikely to improve the selectivity significantly. A better and practically simpler alternative appears to be the addition of a third component to structure the water sufficiently to retain it in the bulk liquid.

4.4.5 Thermodynamic Consistency Test

Finally, we should also point out that the experimental determination of the excess and total adsorption also enables for the first time a direct thermodynamic consistency test of the binary adsorption data. The molar excess Gibbs free energy of the adsorbed phase can be defined as

$$\frac{\Delta g^E}{RT} = x_1^s \ln \gamma_1^s + x_2^s \ln \gamma_2^s$$

and its point values can be calculated without recourse to the Gibbs-Duhem relationship (42). The adsorbed phase activity coefficients, $\gamma_i^s$, can be determined from the equilibrium relationship
The exponential term in the above expression can be determined from a knowledge of the excess adsorption alone, and the adsorbed phase composition can be obtained from the experimentally measured excess and total adsorption. The only remaining unknown in Eq.(50) is then \( \gamma_i^s \) which can be calculated directly using the actual experimental points prior to smoothing. Comparison of the point values of the molar excess Gibbs free energy of the adsorbed phase with the values calculated through the Gibbs-Duhem relationship (41) will then serve to test the thermodynamic consistency of experimental data. It follows from Eqs.(47) and (49) that the different contributions to the excess Gibbs free energy of the adsorbed phase are given by

\[
\frac{\Delta g^E}{RT} = \int_0^{x_1^s} \ln \left( \frac{\gamma_2^s}{\gamma_1^s} \right) dx_1^s + \int_0^{x_1^s} \left[ \frac{1}{N^s} - \left( \frac{x_1^s}{n_1^{os}} + \frac{x_2^s}{n_2^{os}} \right) \right] \frac{vd\phi}{RT}
\]

where the first integral represents the influence of composition and the second integral the influence of spreading pressure. The different contributions calculated according to Eq.(51) are shown in Figure 7 together with the point values of the molar Gibbs free energy of the adsorbed phase. It is clear that the point values coincide with the curve predicted through the Gibbs-Duhem equation which confirms the thermodynamic consistency of the data. Evidently, the assumption of negligible volume change of mixing which leads to the restricted Gibbs-Duhem equation is justified only at adsorbed ethanol mole fraction below 0.15 which corresponds to a liquid mole fraction as
Fig. 7 The molar excess Gibbs free energy of the adsorbed phase for the system (ethanol(1)-water(2))/silicalite.

- point values and contributions from (a) composition and (b) spreading pressure.
small as 0.001. At higher ethanol concentrations, the contribution from the volume change of mixing and spreading pressure is comparable to that of composition and must be accounted for in any predictive theory.

4.4 CONCLUSION

The successful experimental measurement of the individual (absolute) adsorption isotherms has for the first time enabled the direct calculation of the activity coefficients and the molar excess Gibbs free energy of the adsorbed phase without any major assumption other than the existence of a distinct adsorbed phase. The limitations of the available theories of adsorption from solution, all of which share the inherent assumption of no volume or area change of mixing, is clearly highlighted by comparing the various contributions to the excess Gibbs free energy of the adsorbed phase, see Figure 7.

For the system (ethanol-water)/silicalite, the adsorbed phase, in complete contrast to the bulk liquid, exhibits strong negative deviations from ideality. Within the hydrophobic confines of silicalite, ethanol-water molecular interaction are sufficiently strong to limit the selectivity of the "hydrophobic" crystals toward ethanol. A major practical consequence of this is that improvements in the surface properties of the crystals are unlikely to improve the selectivity significantly. A better and simpler alternative appears to be the addition of a third component to structure the water sufficiently to retain it in the bulk liquid.
Furthermore, for the system (ethanol-water)/silicalite, the molar excess Gibbs free energy of the adsorbed phase is found to be a strong function of the spreading pressure as well as the composition of adsorbed phase. This indicates that the arbitrary assumption of no volume (or area) change of mixing inherent in all the proposed theories of adsorption from solution is not necessarily justified. A major theoretical consequence of this observation is that the adsorbed phase obeys the more general Gibbs-Duhem equation (41) and the restricted form (39) commonly adopted in the proposed theories of adsorption from solution is not applicable. This may well be a general characteristic of the behaviour of water-soluble organics within hydrophobic adsorbents which must be accounted for in predictive theories of adsorption from solution.

Evidently, much remains to be done with other model systems before accurate and reliable predictive theories allowing for the volume change of mixing and the influence of spreading pressure on the excess Gibbs free energy of the adsorbed phase can be formulated. This very interesting problem is not pursued further in this thesis but is a fertile ground for future work. To this end, further studies on adsorption of binary and ternary solutions of the other members of the homologous series of aliphatic alcohols within silicalite will be particularly advantageous. For the practical purposes of the work at hand, the experimental measurement of the individual adsorptions isotherms has freed us from theoretical assumptions about equilibria and thus allows a closer look at the kinetics of adsorption.
CHAPTER 5

KINETICS OF INTRAPARTICLE MASS TRANSFER
5. KINETICS OF INTRAPARTICLE MASS TRANSPORT

The performance of sorptive separations is governed by the combined influence of:

- hydrodynamic flow conditions
- sorption equilibria, and
- interphase heat and mass transfer limitations;

all of which are more or less strongly influenced by the structural characteristics of the solid. The internal structure of silicalite pellets was examined in Chapter 2 and a detailed analysis of the sorption equilibria for the system {ethanol-water}/silicalite was presented in Chapters 3 and 4. This chapter is devoted to a general description of interphase mass transfer in porous materials and the determination of the controlling diffusional resistance within silicalite pellets. The conclusions reached in this chapter will be used in Chapter 6 to examine the dynamics of fixed-bed recovery of ethanol on a bed of silicalite adsorbent.

Mass transfer between a porous particle and a flowing fluid involves diffusion across the external film to the surface of the particle followed by transport within the porous structure of the particle. External mass transfer occurs by molecular diffusion and is therefore amenable to prediction from a variety of semi-empirical correlations (e.g. Wakao and Funazkri 1978, Wilson and Geankopolis 1966). Intraparticle transport on the other hand is much more complex and can proceed by many different diffusional mechanisms. The major problem is
therefore the identification of the controlling diffusion mechanism (if any), the theoretical description of the intraparticle transport in terms of a suitable model and the measurement of the diffusional parameters contained in the model.

5.1 THEORETICAL DESCRIPTION OF INTRAPARTICLE MASS TRANSFER

Many mathematical models have been developed to represent diffusion into porous adsorbents and these may be broadly classified into "lumped parameter" and "diffusion" models. In the case of lumped models, all resistances to mass transfer are lumped into a single parameter and the driving force for transport is expressed in terms of the average concentration within the particles. Diffusion models are on the other hand much more complex and describe the transport in terms of one or more assumed diffusional mechanisms. The appropriate choice of the model will depend on the particular case at hand and the level of detail required. In practice, however, we are forced to seek a compromise between the level of theoretical detail and the practicality of measuring the model parameters reliably and accurately. The following review provides a critique of the proposed lumped and diffusional models reported in the literature.

5.1.1 Lumped Parameter Models

In the simplest description of intraparticle mass transfer, the driving force is based on the average conditions within the particle and the resistances to mass transfer are accordingly "lumped" into an overall mass transfer coefficient. In one such model, the driving force is
taken as the difference between the (volume) averaged adsorbate concentration $\bar{q}_1$ within the solid and that which would be in equilibrium with the bulk fluid $\bar{q}_1^*$ (Fleck et al. 1973, Harwell et al. 1980, Sircar et al. 1983). All extra and intraparticle mass transfer resistances are then lumped into a single overall mass transfer coefficient, $K_p l$ for each individual component:

$$\frac{\partial \bar{q}_1}{\partial t} = K_p^{il} (\bar{q}_1^* - \bar{q}_1)$$

Another related model is based on a driving force taken as the difference between the bulk fluid concentration and that which would be in equilibrium with the average solid loading (Aguwa et al. 1984, Needham et al. 1966, Sircar et al. 1983):

$$\rho_s \frac{\partial \bar{q}_1}{\partial t} = K_b^{il} a (c^*_1 - c_1)$$

Another single parameter linear rate model uses a driving force based on the difference between the adsorbate concentration at the particle surface and the mean concentration within the solid (Glueckauf 1955, Colins et al. 1973, Liaw et al. 1979):

$$\frac{\partial \bar{q}_1^i}{\partial t} = K_s^{il} a (q_1^i - \bar{q}_1^i)$$

where the superscript "i" refers to conditions at the external surface of the particle and $K_{s1}^{il}$ is a pseudo-film mass transfer coefficient. The model is completed by coupling the fluid and solid concentrations at the particle surface through the adsorption isotherm. Glueckauf
(1955) has shown that for spherical particles the above equation with 
\[ K_{sl} = \frac{5D_p}{R_p} \] 
gives a surprisingly accurate approximation of Fickian diffusion for adsorbates with linear or mildly nonlinear isotherms. 
A two parameter lumped model is simply obtained by combining the Glueckauf model with an external film mass transfer resistance. The model equations therefore consist of:

\[
\frac{\partial \bar{q}_l}{\partial t} = K_{sl} a (q^I_l - \bar{q}_l) \tag{4}
\]

and a lumped parameter linear driving force equation for the external film transfer:

\[
\rho_s \frac{\partial \bar{c}_l}{\partial t} = K_{r1} a (c^I_l - \bar{c}_l) \tag{5}
\]

where \( K_{r1} \) is the external film mass transfer coefficient and the surface concentration \( c^I_l \) and \( \bar{q}_l \) are coupled through the adsorption isotherm.

Lumped parameter models describing intraparticle heat and mass transfer in terms of linear functions of overall driving force have been applied with reasonable success using constant values of the overall transport coefficients to a number of complex adsorption systems (i.e Harwell et al 1980, Wong and Niedzwiecki 1982, Liapis and Crosser 1982, Litchfield et al 1982). It should be remembered, however, that approximate models based on constant-value lumped transport coefficients can only be extrapolated across a relatively small range of operating conditions. Therefore, to use such models over a large range of operating conditions it becomes necessary to establish the influence of the
operating conditions on the lumped transport coefficients either theoretically or preferably using suitable small scale experimentation.

In several cases involving bi-dispersed adsorbents, lumped parameter models have been shown to exhibit a systematic deviation from experimental observation. In an attempt to model this situation, Famularo et al (1980) arbitrarily divided the solid particle into an outer "macro shell" containing the macropores and an inner "micro core" in which all the micropores reside. Intraparticle mass transfer was then characterised by three linear driving forces involving transfer from the bulk fluid to the surface of the macro shell, from the particle surface through the macro shell and from the macro shell into the micro core region. The major drawback to this model is the artificial division of the porous structure into the macro shell and micro core regions. This requires a more or less arbitrary assignment of volumes and average pore sizes to the macro and micro pore regions. Consequently, a better fit of experimental data is obtained only at the expense of introducing additional parameters which cannot be measured directly and whose physical significance may not be clear.

5.1.2 Intraparticle Diffusion Models

In the case of adsorption onto granular or beaded adsorbents mass transfer between the bulk liquid and the solid is partially or totally controlled by the resistances within the particle. The only exception is at very early times when the solid has not yet seen the molecules diffusing across the external film. Evidently, a more detailed description of intraparticle transport must rely on a distributed parameter model which allows for concentration profiles in the solid.
A variety of such diffusional models have been proposed and are discussed below.

5.1.2a Solid Diffusion Model

The simplest intraparticle diffusion model was developed by Rosen (1952,1954) and its use, particularly for single component systems, has continued to the present [Kondis and Dranoff 1971, Crittenden and Weber 1978, Liaw et al 1979]. The model is based on Fickian diffusion into a "solid" sphere as represented by the following equation:

\[
\frac{\partial q_1}{\partial t} = D_{c1} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_1}{\partial r} \right)
\]

where the diffusion coefficient \( D_{c1} \) is assumed independent of concentration. If the diffusion coefficient is a function of concentration, then an integral mean value may be calculated from:

\[
D_{c1} = \frac{1}{q_1} \int_{0}^{q_1} D_{c1}(q_1) \, dq_1
\]

One of the boundary conditions required to complete the above model is determined from symmetry at the centre of the particle

\[
\text{at } r = 0 \quad \frac{\partial q_1}{\partial r} = 0
\]

The other boundary condition must be obtained by coupling the bulk and adsorbate concentration at the particle surface \( r=R_p \). This is usually
obtained by assuming a lumped model for transport across the external film:

$$\rho_s D \frac{\partial q_1^i}{\partial r} = K_f (c_i - c_1^i)$$

(9)

The relationship between the interfacial concentration $c_1^i$ and $q_1^i$ is in turn obtained by assuming instantaneous equilibrium at the particle/liquid interface:

$$q_1^i = q_1(t,R_p) = q_i(c_1,c_2,\ldots,c_n)$$

(10)

However, it should be noted that establishment of equilibrium at the interface is not an essential feature of this model and instead we can assume a kinetic relationship at the particle surface. For example, adopting a Langmuir type expression \cite{Kondis and Dranoff 1971} the boundary condition at the particle surface becomes

$$\rho_s D \frac{\partial q_1^i}{\partial t} = k_{e_i} c_i^i (Q_i - q_1^i) - k_{d_i} q_1^i$$

(11)

where $Q_i$ is the ultimate loading capacity and $k_{e_i}$ and $k_{d_i}$ are the forward and backward rate constants for adsorption.

The continued use of the solid diffusion model owes a great deal to its simplicity. A major advantage of this model is that intraparticle diffusion is modeled on the basis of a diffusion equation. Its main drawback is that the mechanism of transport through the porous solid is expressed in terms of a model which fails to recognise the internal
structure of the particle. Hence, several structure dependent parameters are described by a single structure independent diffusivity. It is therefore not surprising that this model is often incapable of giving a good description of experimental batch uptake data for a single component [Chakravorti and Weber 1975]. In such cases, we have to resort to a more complicated model which recognises the internal structure of the solid particles.

5.1.2b Surface Diffusion Model

The surface diffusion model, unlike the solid diffusion model, recognises both the porous structure of the solid particles and the presence of the adsorbate in the free fluid in the (macro) pores. The model equations take the form

\[
\varepsilon_p \frac{\partial c_{p1}}{\partial t} + \rho_s \frac{\partial q_1}{\partial t} = \rho_s D_{s1} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_1}{\partial r} \right) \quad (12)
\]

where \( \varepsilon_p \) is the particle porosity and \( D_{s1} \) is the surface diffusion coefficient. The boundary conditions for this model are usually expressed as:

\[
\text{at } r = 0 \quad \frac{\partial q_1}{\partial r} = 0 \quad (13)
\]

\[
\text{at } r = R_p \quad \rho_s D_{s1} \frac{\partial q_1}{\partial r} = K_{r1} (c_1 - c_{11}) \quad (14)
\]

which are analogous to Eqs.(8) and (9). Similar arguments regarding the
achievement of instantaneous equilibrium (or not) at the pore walls may
be used here.

As for the solid diffusion model, the surface diffusion model only
allows for the transfer of adsorbate into the particle through the
(surface) adsorbed phase. The physical interpretation for the presence
of the adsorbate within the pore fluid must therefore be taken as a
consequence of either local equilibration or some kinetic transfer
mechanism between the (surface) adsorbed and pore fluid phases.
Assuming point-wise local equilibrium to exist everywhere within the
pores, the adsorbed phase concentration $q_i$ can be expressed in terms of
$c_i$ and Eq.(12) may be written in terms of the pore fluid concentration
$p_i$. However if local equilibrium is not assumed, the first term in Eq.(12)
must be replaced by a kinetic term representing the transfer of material
between the pore fluid and the adsorbed film [Mansour et al 1982].

The surface diffusion model only accounts for diffusion through the
adsorbed layer. The physical justification for the model is that mass
transfer by pore diffusion is so minor compared to that through the
concentrated surface layer that it may be ignored. This may indeed be
the case for strongly adsorbed species where it has been shown [Hand et
al 1983] that surface diffusion flux can be many times greater than the
pore diffusion flux. It should also be pointed out that the solid
diffusion model may be considered as a limiting case of the surface
diffusion model when the concentration of the adsorbate in the pore
fluid is sufficiently small. In such instances, the accumulation of the
adsorbate in the free pore fluid can be ignored and Eq.(12) effectively
is reduced to the solid diffusion model. Irrespective of the model used many investigations have been based on the use of Eq.(6) [Hand et al 1979, Tien 1982, Aguwa et al 1984] and this has led to some confusion in terminology. Thus, both solid and surface diffusion models as described here have been variously described as "solid", "surface", "homogeneous solid" or "homogeneous surface" or just "homogeneous" diffusion models. Despite the arguments which could be raised against both surface and solid diffusion models on physical grounds, they have been considerably successful in describing isothermal liquid phase adsorption, particularly for single component systems [Larsen and Tien 1984, Crittenden and Weber 1978].

5.1.2c Pore Diffusion Model

This model describes the intraparticle mass transfer in terms of diffusion through the fluid filled pores of the porous solid particles. The relative size of the pore diameter and the mean free path of the molecules under the conditions present within the pores would then determine the diffusional mechanism, e.g molecular, Knudsen or the intermediate type [Satterfield 1970].

The equations describing the pore diffusion model take the general form shown below [Schneider and Smith 1968, Ferrel et al 1976, Balzi et al 1978, Morbidelli et al 1982]:

\[
\epsilon_p \frac{\partial c_p}{\partial t} + \rho_s \frac{\partial q}{\partial t} = \epsilon_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_p}{\partial r} \right)
\]  

(15)
where $D_{p1}$ denotes the effective pore diffusivity and the boundary conditions take the form:

$$\begin{align*}
\text{at } r = 0 & \quad \frac{\partial c_{p1}}{\partial r} = 0 \\
\text{at } r = R_p & \quad \varepsilon_p D_{p1} \frac{\partial c_{p1}}{\partial r} = K_{r1} (c_{p1} - c_{p1}(R_p, t))
\end{align*}$$

If the external film resistance is assumed negligible, the concentration at the mouth of the pores $c_{p1}(R_p, t)$ is the same as in the bulk fluid.

The physical interpretation of Eq. (15) is the transfer of the adsorbate through the pore fluid accompanied by localised adsorption and immobilisation of the adsorbate onto the active sites. If the adsorption step is very rapid and the adsorbate is immobile, then the pore fluid and the adsorbed layer will be in point-wise equilibrium within the pore and Eq.(15) can be written as [Liapis and Rippin 1977],

$$\varepsilon_p \frac{\partial c_{p1}}{\partial t} + \rho \sum \frac{\partial g_i}{\partial t} = \varepsilon_p D_{p1} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c_{p1}}{\partial r})$$

where $q_i = g_i(c_1, c_2, ..., c_n)$ is the adsorption isotherm. Alternatively, as with the surface adsorption model, the rate of exchange of material between the pore fluid and adsorbed layer could be governed by some finite rate mechanism; the $\partial q_i/\partial t$ term in Eq.(15) must then be replaced by a suitable kinetic expression (eg. Masamune and Smith 1965, Ramuson 1982, Mansour et al 1982, Morbidelli et al 1982). Under suitable conditions, the pore diffusion model may be further simplified by...
ignoring the accumulation of the adsorbate in the pore fluid [Chakravorti and Weber 1975, Hashimoto et al 1975] so that

\[
\rho_s \frac{\partial q_1}{\partial t} = \varepsilon_p \frac{D_p}{r^2} \frac{1}{\partial} \left( r^2 \frac{\partial \rho_1}{\partial r} \right)
\]  (19)

In physical terms, Eq.(19) assumes that the differential flux into and out of the differential shell in the particle equals the change in the mass of the adsorbate. Hence, this approximation is more likely to be valid for gaseous rather than liquid systems. This is because the density of gas in the pores is much smaller than that in adsorbed phase, whereas for liquids the free pore fluid and adsorbed phases have similar density. Clearly, unless the bulk liquid is very dilute and the isotherm is favourable, this approximation could have significant error.

The validity of the pore diffusion model depends on the mobility of the adsorbed molecules which determines the relative contribution of pore diffusion and surface diffusion through the adsorbed layer. For instance, in one study Furusawa and Smith (1973,1974) have shown by superimposing the predictions of the pore diffusion model onto experimental uptake data that the intraparticle mass transfer rates were too rapid to be accounted for by pore diffusion alone. At this point it is worth noting that there are no a priori criteria available to decide which diffusion model suits a particular system best. Based on several investigations [Furusawa and Smith 1973, Neretnieks 1976, Crittenden 1976] it has been suggested that the surface diffusion model should provide a better description of intraparticle transport for
strongly adsorbed solutes (Peels et al. 1981). However, the pore
diffusion model has been shown to be equally if not more successful
than the surface diffusion model in a detailed study of multicomponent
isothermal fixed bed adsorption [Balzi et al. 1978], in a batch kinetic
study [Chakravorti and Weber 1975] and in another study involving fixed
bed column trials [Muira et al. 1977].

5.1.3d Simultaneous Pore and Surface Diffusion Model

In order to describe the intraparticle diffusion in more detail it may
be assumed that both pore and surface diffusion occur simultaneously
within the solid particles. Although such a dual diffusion mechanism
model is in theory capable of a better description of intraparticle
mass transfer, its practical application is complicated by two factors.
First, considerable extra numerical effort is required for solving the
ensuing model equations. Second, and more significantly, there are
considerable practical difficulties associated with the independent
experimental measurement of two intraparticle diffusivities. It is
therefore not surprising that comparisons between the predictions of
this dual mechanism model and experimental data are scarce [Furusawa
and Smith 1973, Mansour et al. 1982].

The model equations are obtained by adding the individual contributions
from surface and pore diffusion, Eq. (12) and (15) respectively [Fleck
et al. 1973],
and the boundary conditions take the form

\[ \frac{\partial c_{p1}}{\partial r} = 0 \quad \text{and} \quad \frac{\partial q_1}{\partial r} = 0 \]  

(21)

\[ \frac{\partial c_{p1}}{\partial r} \mid_{r = R_p} = K_{r1} (c_{1} - c_{p1}(R_p, t)) \]  

(22)

For spherical particles, the total (volume) average intraparticle concentration is given by:

\[ Q_1 = \frac{3}{R_p^3} \int_0^{R_p} \left[ \frac{\varepsilon_p}{\rho_s} c_{p1} + q_1 \right] r^2 \, dr \]  

(23)

To complete the model a relationship must be assumed between the pore fluid and the adsorbed layer. There are three possible mechanisms for this relationship. It may be assumed that: (1) point-wise equilibrium exists every where in the pores [Liapis and Rippin 1977], or (2) local equilibrium exists only at the particle surface [Aguwa et al 1984] or (3) the phases are related by some kinetics exchange mechanism. In the latter case, Eq.(20) can be decoupled into the following form...
\[
\frac{\partial q_i}{\partial t} = D_{s_i} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_i}{\partial r} \right) + S_i
\]  
(24)

\[
\varepsilon \frac{\partial c_p^1}{\partial t} = \varepsilon D_{p_1} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_p^1}{\partial r} \right) - \rho_s S_i
\]  
(25)

where \( S_i \) denotes the specific rate of transfer of component \( i \) from the pore fluid to the adsorbed layer [Mansour 1982].

The complexity of the simultaneous pore and surface diffusion model can be reduced for the special case of a linear adsorption isotherm and point-wise equilibrium within the pore. Under such conditions, a single effective diffusivity can be derived as a simple algebraic combination of the pore and surface diffusion coefficients [Carter 1966, Schneider and Smith 1968, Thomas et al 1971, Neretnieks 1976]. In general, however, the practical utility of this model is limited by the extra computational effort and the difficulties associated with the experimental determination of independent values for the pore and surface diffusion coefficients. The use of this model can therefore only be justified when intraparticle transport by pore and surface diffusion mechanism are within the same order of magnitude and considerable experimental data exists to enable a reliable estimation of \( D_{s_i} \) and \( D_{p_1} \).

5.1.2e Macro-Micro Pore Diffusion Models

In a number of batch kinetic studies of adsorption from both liquids and vapours, a high initial uptake rate has been observed followed by a much slower approach to equilibrium [Chakavorti and Weber 1975, Sircar
The failure of the single resistance intraparticle diffusion models to describe such behaviour, has in some cases, been attributed to their inability to account for the polydisperse pore structure of the solid. The presence of micropores where steric hindrance can affect the diffusion process is then used as an explanation for the slow final uptake. A simple lumped parameter approach to this problem was presented by Famularo et al (1980) as described in Section 5.1.1.

In an alternative approach Peel and Benedek (1981) modeled the adsorbent (activated carbon) as a randomly distributed network of macropores. The micropores were then assumed to branch off from each macropore. Transport in the macro pores was modeled as (Fickian) surface diffusion and transport through the micropores was described in terms of a linear driving force lumped parameter model:

\[
\frac{\partial q_{im}}{\partial t} = f D_{s1} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_{im}}{\partial r} \right) - R_{bi} \tag{26}
\]

where \( q_{im}(r,t) \) (mol i/cm\(^3\)) is the adsorbate concentration in the macropore, \( f \) is the fraction of the overall adsorption capacity contained in the macropores and \( R_{bi} \) is the rate of uptake by the micropores which is described by a linear driving force model:

\[
R_{bi} = (1-f) \frac{\partial \bar{q}_{ib}}{\partial r} = K_{rb} (q_{im} - \bar{q}_{ib}) \tag{27}
\]

with \( \bar{q}_{ib}(r,t) \) (mol i/cm\(^3\)) denoting the average concentration of the adsorbate in the micropores. The model was completed by assuming the usual equilibrium boundary conditions at the external surface of the
article and at the macropore-micropore interfaces. This model has been shown to be capable of describing the slow final uptake of batch experiments [Peel and Benedek 1981] and can also describe the tailing effect observed on many column breakthrough curves. A major drawback to the model is again the more or less arbitrary division of the adsorption capacity into macro and micro pore regions. There is also some ambiguity in the actual cause of the tailing in the breakthrough curves. For instance, Cooney et al (1983) have demonstrated that similar tailing effects can arise as a result of particle size distribution in fixed bed absorbers. Despite the drawbacks of this model, it is a useful tool for fitting of experimental data for activated carbon and silica gel adsorbents. However, its predictive nature is somewhat limited by the arbitrary nature of the parameters involved.

Another more complex model involves picturing the adsorbent as a collection of micro spheres contained within a macro sphere with the voids between the micro spheres serving as macropore [Mingle and Smith 1961, Weber and Liang 1983]. Transport in each region is then described by an appropriate diffusion equation. A typical model accounting for (1) external mass transfer by a linear driving force mechanism, (2) macropore transport by pore diffusion and (3) micropore transport by solid diffusion takes the form:

\[
\varepsilon_p \frac{\partial c_{pl}}{\partial t} + (1-\varepsilon_p) \frac{\partial q_{li}}{\partial t} = \varepsilon_p \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 D_p \frac{\partial c_{pl}}{\partial R} \right)
\]  

(28)
In the above equations \( r \) and \( R \) refer to radial positions within the micro and macro spheres respectively, \( D_{p_1} \) is the macropore diffusion coefficient and \( D_{c_1} \) is the micropore diffusion coefficient. The average concentration within a micro sphere is given by:

\[
\bar{q}_1(R,t) = \frac{3}{r_c^3} \int_0^{r_c} \frac{r^2 \bar{q}_1(R,r,t)}{r^2} \, dr
\]  

(30)

where \( r_c \) is the diameter of the micro sphere. The total amount of the adsorbate within the macrosphere is given by:

\[
Q_1(t) = (1-c_p) \frac{3}{R_p^3} \int_0^{R_p} R^2 \bar{q}_1(R,t) \, dR + c_p \frac{3}{R_p^3} \int_0^{R_p} R^2 c_{p_1}(R,t) \, dR
\]

(31)

where \( R_p \) is the particle radius. The model is completed by applying the symmetry boundary conditions at the centre of each microsphere and at the centre of the macrosphere.

\[
\frac{\partial q_1}{\partial r} = 0 \quad \text{at } r = 0
\]  

(32)

\[
\frac{\partial c_{p_1}}{\partial r} = 0 \quad \text{at } R_p = 0
\]  

(33)
A linear driving force boundary condition is assumed at the external surface of the macrosphere:

$$\frac{\partial q_{1}}{\partial t} = K_{f} ( c_{p_{1}}(R_{p},t) - c_{\text{bulk}})$$  \hspace{1cm} (34)$$

and local equilibrium is also assumed to exist between the macropore fluid and the external surface of the microspheres,

$$q_{i}(R,r_{c},t) = g_{i}[c_{p_{1}}(R,t),...,c_{p_{n}}(R,t)]$$  \hspace{1cm} (35)$$

where $g_{i}(c_{p_{1}},...,c_{p_{n}})$ denotes the adsorption isotherm.

The above macropore-micropore diffusion model has been used successfully by Weber and Liang (1983) to predict the single component adsorption of various phenolic compounds onto activated carbon. The major area of application of this model however appears to be for zeolitic pellets which are actually formed by compacting micrometer sized molecular sieves crystals. This model has been successfully applied by Raghavan and Ruthven (1985) to investigate the single component isothermal chromatographic breakthrough curves for zeolitic pellets. Based on the physical characterisation discussed in Chapter 2, the macro-micropore model is the most realistic for describing mass transport mechanism within the bi-dispersed silicalite pellets.

5.2 DIFFUSION WITHIN SILICALITE ADSORBENT

Based on the above review of intraparticle mass transport models and the structural characteristics of the silicalite adsorbent, mass
transfer within the silicalite pellets can be assumed to involve the following idealized steps:

1. external film transfer
2. macropore diffusion
3. micropore diffusion

Schematic of intraparticle diffusion in silicalite pellets

The particles are assumed to consist of identical microporous crystals bound together to form a pellet. Diffusion through the external fluid film can be adequately described in terms of a linear driving force and the external film mass transfer coefficient can be determined with reasonable accuracy from available correlations - [Wakao and Funazkri 1978, Wilson and Geankopolis 1966]. Intraparticle diffusion may be partly or wholly controlled by either micro or macropore diffusion. The unambiguous determination of the contribution from macro and micro pore resistances is in general a very difficult task. Ideally, the intracrystalline micropore diffusion and the macropore diffusivity must be measured by independent experiments. A suitable technique for micropore diffusion is described in the next section. The independent
measurement of macropore diffusivity, however, presents practical difficulties which will be described subsequently. Fortunately, for the case at hand, the controlling mechanism can be established by considering the relation between the various models as described in section 5.2.3.

5.2.1 Intracrystalline Diffusion in Silicalite

Diffusion within the silicalite crystals involves the movement of molecules in micropores of molecular dimension. For instance, water (d=2.65 Å) and ethanol (d=3.8 Å) molecules must diffuse through pores of 5-6 Å diameter. The diffusion process is therefore strongly influenced by complex intermolecular interactions between the atoms forming the pore wall and the diffusing molecules. Such complex interactions are not open to theoretical prediction and this type of diffusion, which has been called configurational diffusion by Weisz (1973), must therefore be measured experimentally. Furthermore, configurational diffusivities can differ by several orders of magnitude for systems which appear to be relatively similar. The influence of pore size on diffusivity has been elegantly summarised by Weisz (1973) in the following diagram. For sufficiently large pores, the diffusive mechanism is either by molecular or Knudsen diffusion which are open to prediction. For pores of molecular dimensions, however, the diffusivity can vary between $10^{-6}$ cm$^2$/s to $10^{-14}$ cm$^2$/s depending on the system at hand.
The measurement of configurational diffusion within the 2 μm silicalite crystals presents considerable difficulty. Standard steady state procedures such as the Wicke-Kallenbach method can only be applied to crystals greater than about 200 μm [Paravar and Hayhurst 1983]. Standard chromatographic techniques are also not possible because of the large pressure drop associated with crystals as small as 2 μm. To overcome the above problems the pycnometer technique developed in Chapter 3 for the measurement of total uptake was modified to enable the determination of the rate of uptake. A similar approach was first proposed by Alexandrov et al (1967) and subsequently used by Satterfield and Cheng [1972] to measure the diffusivity of aromatic hydrocarbons in NaY zeolite.
The procedure developed is particularly suited to the measurement of unidirectional uptake of the pure components. This is because with a pure component there is no external film surrounding the crystals and the boundary conditions at the external surface of the crystals are well defined. The results presented below show that the uptake of pure water by silicalite is radically different from that observed with pure ethanol. The same technique can also be applied to binary co-diffusion of mixed adsorbates. In this case, however, the analysis is substantially complicated by factors which are described below. Even so, a qualitative rationalization of the binary uptake curves is possible with the aid of the equilibrium behaviour of the mixed adsorbates and the more or less one-dimensional nature of diffusion within the silicalite micropores.

5.2.1a Experimental Apparatus and Procedures

A schematic of the apparatus developed is shown in Figure 1 and consists of a jacketed auto-burette which serves as a liquid reservoir and a thermostated 10 cm³ adsorption vessel which can be connected via a valve arrangement to a vacuum line, the liquid reservoir or a jacketed graduated precision bore 1.0 mm capillary column. The change in the liquid level in the capillary was the desired measurement and was recorded via a camera and video system. The adsorption vessel was also fitted with an internal magnetic stirring device and the temperature of the entire apparatus was controlled to better than ± 0.05 °C using a recirculating thermostat (HETOFRIG).
To prepare for a run, the liquid reservoir and the precision bore capillary were filled with a *degassed* liquid of desired composition. A batch of silicalite crystals, typically 1-2 g, was placed in the adsorption flask which was then connected to vacuum. The crystals were activated in-situ at a temperature of 400 °C and a vacuum of $10^{-6}$ Torr for a period of 4 hours. The flask was then isolated, allowed to cool under vacuum and a thermostated vessel controlled at 25 °C was raised into position to surround the flask. To initiate a run, the evacuated flask was first connected to the liquid reservoir and allowed to fill completely, this process typically took about 3 seconds. As soon as the flask was full, the two-way valve was diverted to the precision bore capillary to follow the fall in the meniscus as a result of adsorption. Each step of this operation was video recorded.
continuously at a speed of 25 frames/second. The time at which the liquid first contacted the crystals and the time at which the capillary was connected were determined from the analysis of the recorded image. In all the runs, the adsorption process was allowed to proceed for at least 18 hours. Extensive tests were carried out with both inert (ballotini) particles and silicalite crystals to establish the reproducibility of the above procedure. In all cases where the liquid was properly degassed, the apparatus showed good reproducibility.

The most significant source of error in the above experiment is the failure to degas the liquid adequately. This is because the measurement is volumetric and any gas issued from the liquid during the filling period will gradually redissolve and will thus affect the measurement significantly. Mild degassing procedures such as boiling under relatively low vacuum were found to be totally inadequate. To achieve a thorough degassing of the liquid the method suggested by Van Ness and Abbott (1978) was tested and found adequate. The simple but highly effective apparatus suggested by Van Ness and Abbott (1978) is shown in Figure 2 and is essentially a packed distillation column operated at practically total reflux conditions. The liquid to be degassed was placed in a 1 litre flask connected to a packed column fitted with an overhead chilled condenser. The entire apparatus was first evacuated with a rotary pump through the large bore valves to remove the bulk of the residual air. These valves were then closed and vacuum was applied on one side of a 5 mm long and 0.1 mm bore capillary which is at the heart of this technique. The liquid was then heated to a temperature slightly above room temperature, the ensuing
vapours reaching the overhead condenser were refluxed back over the packing leaving the non-condensables to be removed through the fine capillary. This operation was continued for at least 24 hours after which the flask containing the degassed liquid was isolated. A simple test for the quality of the degassed liquid [Van Ness and Abbott 1978] then involved inverting the flask. For a thoroughly degassed liquid, the collapse of the non-condensable free vapour under the weight of the liquid should produce a sharp metallic "click". The absence of this sound was indicative of the presence of unacceptable amounts of dissolved gases in the liquid which could adversely affect the result of the diffusion experiments.
To establish the entire uptake curve it is necessary to measure the level in the capillary from the time the liquid first contacts the solid. With the above technique, however, no measurements can be taken until the capillary is connected to the flask. In cases where the uptake rate is sufficiently slow, it may be possible to establish the initial portion of the uptake curve by back extrapolation of the data recorded at sufficiently low loadings. This is because irrespective of the mechanism involved at uptake levels below about 30%, the uptake rate is effectively a linear function of $\sqrt{t}$ [Barrer 1980]. This was the procedure used by Satterfield and Cheng [1972] in their study of diffusion of aromatic hydrocarbons in NaY zeolite. The applicability of this extrapolation procedure depends on the diffusional time constant ($r^2/D$) which in Satterfield’s study was about 2000 s. For the system (ethanol-water)/silicalite however, the extrapolation technique was not feasible due to the very small crystal size and the relatively high diffusion rates. In fact more than 70% of the total uptake actually took place during the first 3 seconds where no direct measurements were possible. Consequently, the end point of the uptake curve was established from the independently measured equilibrium uptake of the solution by silicalite crystals (see Chapter 3).

Figure 3 shows typical total uptake curves determined for pure ethanol, pure water and their binary mixtures at 25 °C. The same data is reproduced in Figure 4 as normalized curves $m_t/m_\infty$, where $m_\infty$ denotes the equilibrium uptake. Several qualitative comments can be made on the basis of the data presented in Figure 4. First, in all cases,
Fig. 3 Uptake of ethanol, water and their mixtures by silicalite crystals at 25 °C.

Fig. 4 Fractional uptake of ethanol, water and their mixtures by silicalite crystals at 25 °C. ○ ethanol, ● water and ● 4.6 wt% ethanol-water solution.
substantial uptake takes place during the filling period of the flask, where measurements were not possible. Second, pure water appears to exhibit a different behaviour from pure ethanol. In particular, the rate of approach to equilibrium of water appears to be initially faster than that of ethanol but slows down more as saturation is approached. Third, the total uptake of a 4.6 wt% ethanol-water solution also appears to be initially faster than that of pure ethanol but slows down appreciably as saturation is approached. Whilst we are not in a position to comment quantitatively on such differences, a plausible explanation can be given on the basis of the independently measured equilibrium behaviour reported in detail in Chapters 3 and 4. We shall present this explanation after considering the uptake of the pure components.

(a) Uptake of pure ethanol and pure water

On the simplest level, the transient uptake of the pure components by silicalite crystals can be described on the basis of a simple solid diffusion model. Here we note that in the case of a pure component there is no external film surrounding the particles. Moreover, in the case of liquid phase adsorption the heat released is easily accommodated by the liquid and the suspension can be treated as isothermal. To a good approximation, therefore, the external surface of the crystals can be taken to be in equilibrium with a pure isothermal fluid. The scanning electron micrograph of silicalite crystals (see Figure 2.2) show that the crystals are approximately cubic. Diffusion within the crystals can therefore be described by the following expression,
The solution to the above equation for a cube with a side of length \( l \), constant diffusivity \( D_c \) and constant surface boundary condition is given by [Crank 1956, Carslaw and Jaeger 1959]:

\[
\frac{\partial q_i}{\partial t} = D_c \left( \frac{\partial^2 q_i}{\partial x^2} + \frac{\partial^2 q_i}{\partial y^2} + \frac{\partial^2 q_i}{\partial z^2} \right)
\]  

Figure 5 compares the experimental uptake rates for pure ethanol and pure water with the predictions based on the above equations for uniform 4.85 \( \mu m \) cubes for values of \( D_c \) = 1.0x10\(^{-10}\), 5.0x10\(^{-10}\) and 1.0x10\(^{-9}\) cm\(^2\)/s. It is clear that the above equation is incapable of representing the data adequately for either pure component. This discrepancy could be due to two factors. First, the intracrystalline diffusivity \( D_c \) may vary with the level of uptake. Second, the predictions in Figure 5 are based on uniform size cubes, where as the crystals show a definite and fairly broad size distribution. The influence of size distribution on the uptake of the pure components by silicalite crystals is easily accommodated:

\[
m_t = \int_{m_{\text{min}}}^{m_{\text{max}}} f(m) \, dm
\]

where \( f(m) \) is the volumetric size distribution and \( (m_t)_l \) is calculated through Eq.(37). The size distribution of the silicalite crystals was reported in chapter 2 and was reasonably well approximated with a log-normal distribution.
Fig. 5 Comparison of the uptake of (a) pure ethanol and (b) pure water with predictions based on Fickian diffusion within uniform 4.85 μm cubic silicalite crystals. (1). $D_c = 1.0 \times 10^{-9}$, (2). $D_c = 5.0 \times 10^{-10}$ and (3). $D_c = 1.0 \times 10^{-10}$ cm$^2$/s. 
\[ f(l) = \frac{1}{\sqrt{(2\pi)\sigma_{\ln(l)}}} \exp \left[ - \left( \frac{\ln(l) - \ln(l_{\text{median}})}{\sqrt{2} \sigma_{\ln(l)}} \right)^2 \right] \]  

with a median of \( \ln(l)_{\text{median}} = -7.88 \) and a standard deviation \( \sigma_{\ln(l)} = 0.44 \), see Figure 2.9. The uptake rates calculated on the basis of the above size distribution are compared with the experimental data in Figure 6. It is clear that with the size distribution accounted for, the uptake of pure ethanol is substantially better approximated with a constant diffusivity Fickian equation. The uptake of pure water, however, cannot be described by such a mechanism. We are therefore led to the conclusion that intracrystalline diffusivity of ethanol is less dependent on the level of loading than that of water. The diffusivity of water, shows a marked decrease with increasing loading and is reduced by several orders of magnitude as saturation is approached.

The above behaviour can be rationalized by considering the picture of molecular interactions suggested by our equilibrium studies. In the case of pure ethanol, the interaction of the ethanol molecules with the solid dominate over those between the ethanol molecules themselves. The ethanol molecules are, therefore, fairly localized and exhibit a near Fickian diffusion. In the case of water, however, there is little interaction between the water molecules and the "hydrophobic" solid and there is also a strong repulsion between the water molecules. At low loadings, the water intermolecular repulsion is small and the molecules are very mobile, hence the very high initial diffusivity of water. As more water molecules are loaded within the pores, however, the molecular repulsions become more and more significant and thus reduce the mobility of water.
Fig. 6 Comparison of the uptake of (a) pure ethanol and (b) pure water with Fickian diffusion in cubic crystals with a log-normal size distribution with median 3.78 μm. (1). $D_c = 1.0 \times 10^{-9}$, (2). $D_c = 5.0 \times 10^{-10}$, and (3). $D_c = 1.0 \times 10^{-10}$ cm$^2$/s.
The theoretical analysis of the uptake of (ethanol-water) mixtures by silicalite crystals is complicated for two basic reasons. First, to establish the boundary conditions we need to know the mass transfer coefficient through the external film surrounding the crystals. Reliable data on these coefficients are difficult to establish because the crystals are very small and (with our experimental set-up) the hydrodynamics of the suspension are ill defined. Second, a proper analysis of the binary uptake requires information on the uptake of each individual component. This in turn requires a knowledge of the transient concentration histories within the adsorption vessel which were not available to us. As a result of these major practical obstacles, a detailed quantitative analysis of binary uptake was not attempted. Nevertheless, we can make some tentative qualitative observations for the behaviour of the binary uptake curves.

The most significant observation is that for a mixture the rate of approach to equilibrium is initially faster than that of pure ethanol but slows down as saturation is approached. This may be explained as follows: on initial contact with the empty solid, water molecules enter the matrix and their diffusivity at low uptake is very high. This could explain why the initial stage of the total uptake of the mixture is faster than the pure ethanol uptake. In the later stages, the more strongly adsorbed ethanol diffuses into the solid replacing the water molecules. This could explain the lowering of the total uptake rate at higher loadings. This type of behaviour has also been observed experimentally by Karger and Bulow (1975) for the
co-adsorption of a mixture n-heptane and benzene within 13X zeolite. The experimental data for this system is reproduced in Figure 7 which shows an overshoot in the uptake of n-heptane (faster diffusing, less strongly adsorbed component) followed by a displacement of n-heptane with benzene (slower diffusing, more strongly adsorbed component).

Had we been able to measure the transient co-adsorption of water and ethanol within silicalite individually, we would have expected to see a similar behaviour.

It is also perhaps worth noting that the latter stages of the 4.6 wt% ethanol uptake curve are closer to that of pure ethanol, see Figure 4.
This could be at least partially rationalized by the one dimensional nature of diffusion within silicalite micropores. The micropores are sufficiently narrow to prevent the molecules from overtaking each other. Thus once an ethanol molecule has entered a channel it determines the diffusion rate of all other molecules behind it. However, the silicalite micropore network is three dimensional and the water molecules could find their way around this bottleneck via a much longer route. This may explain the small difference between uptake of pure ethanol and the uptake of a 4.6 wt% mixture.

5.2.2 Diffusion into Silicalite Pellets

We can now turn to a description of diffusion through the macro-pores of silicalite pellets. The (macro) pore size distribution of the pellets was reported in Chapter 2 and showed a mean pore radius of 0.3 μm, see Figure 2.10. The mechanism of macro pore diffusion is therefore by molecular diffusion. The determination of the effective macropore diffusivity, however, requires a knowledge of the tortuosity which is not open to direct measurement. Given the micro-pore diffusivity, macro pore diffusivity can be estimated by a suitable analysis of fixed-bed breakthrough curves which will be explored in the next chapter. For the present time, we note that the application of the technique used for the silicalite crystals to silicalite pellets is not straightforward.

In the case of the crystals, the pores are of molecular dimension and the concept of convective flow through such pores is irrelevant. In the case of the pellets, however, the evacuated macro pores are much
larger and can be filled by convective flow under a pressure gradient.
The applicability of the technique described above therefore depends on
the time scale for this bulk filling of the pores relative to the time
scale of diffusion within the micropores. Put another way, the method
described can be safely applied only when the macro pores can be filled
with a liquid at a sufficiently fast rate.

An estimate of the time required to fill the evacuated macro pores can
be obtained by a simple analysis. Consider an empty capillary exposed
to a liquid. At equilibrium the capillary will be penetrated to a depth
$L_\infty$ given by [Slatery 1972];

$$L_\infty = \frac{2\sigma}{R} \left( \frac{P_o + \rho g \sin \alpha}{R} \right)$$

where $P_o$ is the ambient pressure, $g$ is the acceleration due to gravity,
$\alpha$ is the tilt angle of the capillary, $R$ the radius of the capillary,
and $\sigma$ and $\nu$ the surface tension and viscosity of the liquid
respectively. It has also been assumed that the liquid wets the
capillary perfectly and the contact angle is zero. The time required
to fill the capillary to a given depth $L < L_\infty$ is then given by the
Poiseuille equation [Slatery 1972]:

$$t = \frac{8\nu}{R^2 \rho g \sin \alpha} \left[ L_\infty \ln \left( \frac{L_\infty}{L_\infty - L} \right) - L \right]$$

Thus, given the liquid properties and the dimensions of the capillary,
the time required to fill a capillary of a given length can be
Figure 8 shows the result of such a calculation for a range of capillary diameters between 0.1 to 0.5 μm all with a length of 2.25 mm, this length corresponds to the assumption of a tortuosity of 3 for the 0.75 mm silicalite particles used in our studies. From Figure 8 it is evident the time required to fill the macro pores is substantially longer than 3 seconds during which much of the adsorption within the micropores has already taken place. A direct determination of the macro pore diffusivity by the volumetric method described above is not therefore feasible. The

![Graph showing time required to penetrate micron sized capillaries to a depth of 2.25 mm.](image)

**Fig. 8** Estimate of the time required to penetrate micron sized capillaries to a depth of 2.25 mm.

macropore diffusivity must therefore be estimated from the analysis of fixed bed breakthrough curves which will be described in the next chapter. Although the macropore diffusion cannot be measured directly,
its contribution to the overall resistance can be obtained by a
simplified sensitivity analysis which is presented next.

5.2.3 The Controlling Intraparticle Diffusion Mechanism

The relative contribution of external film mass transfer, macro pore
diffusion and micropore diffusion can be obtained by analysing the
moments of the macro-micro pore diffusion model under the assumption of
a linear isotherm. This assumption is reasonable for the
(ethanol-water)/silicalite system at sufficiently low concentrations.
The first and second moments of the macro-micro pore model for
spherical particles packed in an isothermal fixed bed adsorber with
axially dispersed plug flow have been reported by Haynes and Sarma
[1973]. The material balance for the interstitial fluid takes the
form,

\[ -D_L \frac{\partial^2 c_i}{\partial z^2} + v \frac{\partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + \left( \frac{1 - \varepsilon}{\varepsilon} \right) \frac{\partial Q_i}{\partial t} = 0 \]  (43)

where \( c_i(z,t) \) is the interstitial fluid concentration, \( v \) is the
interstitial linear fluid velocity, \( \varepsilon \) is the packed bed voidage, \( D_L \)
the axial dispersion coefficient and \( Q_i(z,t) \) is the total holdup of the
adsorbate in the macro and micro pores of the particle. The
intraparticle macro and micro pore diffusion equations were taken as
those given by Eqs.(28) through to (35) presented in section 5.1.2e.

For a linear isotherm, the first and second moments of the impulse
response of this complex model can be obtained through the van der
Laan's theorem [1958]:

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first moment \[ \mu = \frac{\int_0^\infty c_i(t,r)dt}{\int_0^\infty c_i(t,r)dt} = -\lim_{s \to 0} \left[ \frac{\partial \tilde{c}_i}{\partial s} \frac{1}{c_0} \right] \] (41)

second moment \[ \sigma = \frac{\int_0^\infty [c_i(t-\mu_1,r)]^2dt}{\int_0^\infty c_i(t,r)dt} = -\lim_{s \to 0} \left[ \frac{\partial^2 \tilde{c}_i}{\partial s^2} \frac{1}{c_0} \right] - \mu^2 \] (42)

where \( \tilde{c}_i \) denotes, the two dimensional Laplace transform of \( c_i(r,t) \).

The application of the above formulae leads to the following expression for the first moment [Haynes and Sarma 1973],

\[ \mu_1 = \frac{L}{v} \left[ 1 + \left( \frac{1-\varepsilon}{\varepsilon} \right) K_1 \right] \] (44)

where \( L \) is the length of the column and \( K_1 = \varepsilon_p + (1-\varepsilon_p)K_{\text{cl}} \). The second moment takes the form [Haynes and Sarma 1973]:

\[ \sigma_1^2 = \left( \frac{2L}{v} \right) \left( \frac{D_L}{v^2} \right) \left[ 1 + \left( \frac{1-\varepsilon}{\varepsilon} \right) K_1 \right]^2 \] "dispersion"

\[ + \frac{2}{3} \left( \frac{L}{v} \right) \left( \frac{R_p}{K_{r1}} \right) \left( \frac{1-\varepsilon}{\varepsilon} \right) K_1^2 \] "external mass transfer"

\[ + \frac{2}{15} \left( \frac{L}{v} \right) \left( \frac{R_p^2}{\varepsilon_p D_{p1}} \right) \left( \frac{1-\varepsilon}{\varepsilon} \right) K_1^2 \] "macropore diffusion"

\[ + \frac{2}{15} \left( \frac{L}{v} \right) \left( \frac{r_c^2}{D_{c1}} \right) \left( \frac{1-\varepsilon}{\varepsilon} \right) K_{\text{cl}} \] "micropore diffusion" (45)
Eqs.(44) and (45) can be combined to the following form

\begin{equation}
\frac{\sigma_1^2}{2\mu_1} = \frac{D_L}{vL} + \frac{\nu}{(1-\varepsilon)} \left[ \frac{R_p}{3K_{fL}} + \frac{R_p^2}{15\varepsilon D_p} + \frac{r_c^2}{15K_{Dc1}} \right] \left[ 1 + \left( \frac{1-\varepsilon}{\varepsilon} \right) K_1 \right]^{-2}
\end{equation}

It is evident that for systems with linear (decoupled) isotherms the various mass transfer resistances are linearly additive. We can therefore conduct a sensitivity analysis to establish the relative contribution of the various mass transfer resistances for the silicalite pellets.

The linear slope of the isotherm can be estimated from the initial slope of the isotherms presented in Chapter 3 (eq. 3.16) and takes on the value \(K_{c1} = 9.8\). The radius of the silicalite pellets used in this study was 0.0375 cm and the radius of the silicalite crystals was taken as 2.4 \(\mu\)m. The packed bed voidage was taken as 0.4 and the pellet macro pore voidage was taken from the data in Chapter 2 as \(\varepsilon_p = 0.26\). The interstitial velocity was taken as 0.41 cm/s which corresponds to a particle Reynolds number 1.2. The external film mass transfer coefficient \(K_{fL}\) at this Reynolds number was estimated at \(4.6 \times 10^{-3}\) cm/s from the correlation of Wilson and Geankoplis (1966). The micro pore diffusion coefficients in the silicalite crystals were measured independently and reported above, a value of \(D_{c1} = 5 \times 10^{-8}\) cm\(^2\)/s was taken as a reasonable estimate. The only parameter remaining is then the macro pore diffusivity \(D_{p1}\). Macro pore mass transfer occurs by molecular diffusion and the molecular diffusivity of ethanol in water.
is $1.28 \times 10^{-5} \text{ cm}^2/\text{s}$ [Perry et al. 1973, Hammond and Stokes 1953]. The effective macro pore diffusivity was therefore taken as $4.3 \times 10^{-6} \text{ cm}^2/\text{s}$ which corresponds to an assumed tortuosity of 3. With the above estimated parameters, the various extra and intraparticle mass transfer time constants take on the following values:

- External film transfer: $R_{p}/3K_{f1} = 2.72 \text{ s}$
- Macropore diffusion: $R_{p}^{2}/15 e_{p} D_{p1} = 82.32 \text{ s}$
- Micropore diffusion: $r_{c}^{2}/15 K_{c1} D_{c1} = 0.07 \text{ s}$

It is clear therefore that the dominating resistance is diffusion through the macro pores followed by the external film mass transfer resistance. Diffusion through the micro pores of the silicalite crystals offers an insignificant contribution to the overall resistance. This is a direct consequence of the small size of the crystals and the relatively high intracrystalline diffusivity in silicalite. For all practical purposes therefore, we may assume that the silicalite crystals are in point-wise local equilibrium with the macro pore fluid. The appropriate theoretical model to be used for intraparticle diffusion in fixed bed adsorption of (ethanol-water) mixtures is therefore the pore diffusion model described in Section 5.1.2c which will be considered in the next chapter.

5.4 CONCLUSION

Several mathematical models for describing the intraparticle mass transfer were reviewed. Based on this review and the physical
characteristics of silicalite, a macro-micro pore diffusion model is the most appropriate to describe the intraparticle transport mechanism within the silicalite pellets. An attempt was made to establish the various parameters of the macro-micro pore model to determine the controlling intraparticle mass transfer mechanism. The intracrystalline diffusivity of pure ethanol, pure water and their mixtures were measured by a volumetric technique. The results obtained for pure ethanol were reasonably well fitted with a solid diffusion model taking the size distribution of the crystals into account. The diffusion of pure water, however, was found to be radically different and could not be described with a constant diffusivity. In particular, the diffusivity of water in silicalite was found to decreases strongly with the level of loading. This behaviour was rationalised on the basis of the equilibrium behaviour described in Chapter 3 and 4. Furthermore, the uptake of dilute ethanol-water mixtures was found to be substantially closer to that of pure ethanol. An explanation for this observation was given on the basis of the one-dimensional nature of diffusion within the silicalite crystals. A sensitivity analysis based on realistic model parameters, however, showed that for the \(\text{ethanol-water}/\text{silicalite}\) pellet system, diffusion within the micropores of silicalite exerts an insignificant role and the controlling resistance is that through the macro pores. The dynamics of intraparticle diffusion in silicalite pellets can therefore be adequately described by the much simpler pore diffusion model which is considered next.
CHAPTER 6

DYNAMICS OF FIXED-BED ADSORPTION
6.1 INTRODUCTION

The dynamics of a fixed-bed adsorber are characterised by the development and transient propagation of one or more concentration and temperature fronts through the bed of solid. A quantitative understanding of the behaviour of such fronts can only be obtained by the formulation and the numerical solution of a sufficiently detailed and fundamentally correct differential model. In particular, such a model must allow for the combined influence of the hydrodynamics, the adsorption equilibria and the interphase heat and mass transfer limitations; all of which are more or less affected by the shape, size and internal structure of the solid adsorbent. Chapters 2 through 5 were concerned with a detailed examination of the parameters influencing the adsorption of ethanol-water mixtures onto silicalite and culminated in the identification of a macropore diffusion model for the description of intraparticle diffusion. This chapter is devoted to the application of this model to the analysis of the experimental fixed-bed breakthrough curves.

The model used makes proper allowance for axial dispersion and external film mass transfer resistance as well as intraparticle diffusion. The projection of the model predictions onto the experimental breakthrough curve enables the estimation of the effective macropore diffusivity. This is the only model parameter which was not measured independently or predicted through appropriate correlations. Considerable effort is also put into the experimental work to allow for the distortions caused
by entrance and exit effects which can influence the breakthrough curve of small scale laboratory columns significantly, a point which is all too frequently ignored.

6.2 EXPERIMENTAL APPARATUS AND PROCEDURES

An automated small scale pilot unit shown in Figure 1 was designed and constructed to examine fixed-bed adsorption, a schematic of this unit is shown in Figure 2 and consists of the following. Two stainless steel reservoirs for water and ethanol solutions, the temperature in these tanks was controlled to better than 0.1 °C by means of two independent 3 term digital controllers (WEST 2070, Gluton). Two positive displacement pumps (MPL) with micrometer adjustment provided independent "constant" flow of pure distilled water and ethanol solutions. All flows were monitored with appropriately sized and calibrated rotameters preceded by pressure pulsation dampers. Several solenoid valves were included to enable the automatic selection of adsorption, elution and recirculation operations.

The stainless steel adsorption column had an internal diameter of 2.54 cm and was equipped with an integral heating/cooling jacket. The coolant through the jacket was provided by an independent recirculating thermostat which could be controlled to better than 0.05 °C (HETOFRIG). The bottom of the column was equipped with a specially designed valve arrangement and a differential pressure transducer to enable the introduction of a sharp concentration step without excessive disturbance of the volumetric flow rate. The need for this valve arrangement is described in the experimental procedure below.
Fig. 1 Photograph of the pilot adsorption unit used for breakthrough studies.
The breakthrough curve was monitored continuously with an on-line differential refractometer (Waters R403 series) through a specially designed sample system shown in Figure 3. The refractometer cell was only 7 µl in volume and it was therefore imperative to prevent any solid particles entering the cell. This was achieved with a 0.8 µm in-line filter placed in a low-dead volume stainless steel housing supplied by Amicon. The presence of this filter can cause a distortion of the breakthrough curve which is considered in the next section. A 16 bit high quality data-logger (ORION) was used to digitize the refractometer output at a rate of 10 samples/s.

The silicalite extrudates supplied by Union Carbide were crushed and sieved and a fraction with a narrow size distribution 0.75 ± 0.25 mm was activated at 400°C for 12 hours and used as the packing.
entrance to the column was packed to a depth of 6 cm with 0.75 mm ballotini, the silicalite particles were then packed to a height of 13 cm and the remainder of the column was also packed with 0.75 mm ballotini. Thin coarse gauzes were used to demark the active bed from the inert entrance and exit sections. With this arrangement, the interface between the various sections can be reasonably approximated by the open boundary conditions [Levenspiel 1972]. The effluent through the column was partly withdrawn through a large bore by-pass and partly through a fixed length capillary sample line (1/16 in) which could be extended to any position within the column, see Figure 3. This arrangement was used to minimise the disturbance of the flow due to sample withdrawal.

Fig. 3 Schematic of the packed column and sampling device.
A series of three separate stages, wash, pressure equalisation and adsorption steps, shown schematically in Figure 4. During the wash stage distilled water at a controlled temperature and flow rate was passed through the column for at least 12 hours. This was necessary to elute the column from any residual ethanol, to release any entrapped air bubbles which interfered with the operation of the refractometer and also to ensure thermal equilibrium at the desired temperature. The pressure equalization step was made necessary because the ethanol reciprocating pump showed a delay of about 30 seconds to build up to its set flow rate. To ensure minimal flow disturbance, the ethanol pump was switched on and the pressure in the stagnant ethanol line was compared with that in the flowing

Fig. 4 Schematic diagram of the wash, pressure equalisation and adsorption steps. A. ethanol pump, B. DP cell, C. 3-way valve, D. water pump, E. packed bed, F. needle valve, G. sample line and H. by pass.
water line using a DP cell. Once the pressures were equalised, which typically took about 30 s, the three way valve was switched to start the adsorption step. The adsorption step was continued until no change was detectable with the refractometer, which typically took about 2 hours.

6.3 ANALYSIS OF EXPERIMENTAL RESULTS

The interpretation of the experimental results with small scale columns requires careful consideration, a point which is frequently ignored. This is because the theoretical model relates the input and output concentration profiles from the active section of the fixed bed. The experimental arrangement, however, introduces delays and dispersion of these signals which cannot be recorded directly. In a large column, such effects are usually minor and can be ignored. In a small scale column, however, this distortion may become significant and must be accounted for. This was achieved by means of fast Fourier analysis which allows the accurate characterization of the entrance and exit effects without the need for an assumed physical model of these sections.

6.3.1 Characterization of the Sampling System

The presence of the sample line and filter can distort the concentration profile exiting the active bed section. An allowance for this distortion can be made in two ways. The first approach requires the physical modeling of flow through the capillary line and the filter in terms of suitable models, eg. *tanks in series, dispersed plug flow*
etc. This approach is unsatisfactory because of the complicated
geometry of the filter. A better alternative is to use fast Fourier
techniques (see Appendix 1) to determine the impulse response
(Transfer Function) of the entire sampling system in digital form. This
has the major advantage of circumventing the need for a physical model
but requires independent experimentation with the sample arrangement.
Once the (digitized) impulse response is established, the response for
any other given input can be easily determined. Similarly, given the
recorded output of the refractometer, the true input to the sampling
system can be found by de-convolution.

The impulse response of the sampling system was obtained using the
experimental arrangement shown in Figure 5. Water was passed through
the sampling arrangement at a controlled flow rate. A small pulse
(≈ 10 μl) of ethanol was then injected through the specially
constructed injector and the response of the refractometer was logged
at a frequency of 10 samples/s. The injector was designed as a 0.63 cm
diameter and 6 cm long packed bed filled with fine ballotini.

![Diagram of the arrangement used to characterise the sampling device](image-url)

**Fig. 5** The arrangement used to characterise the sampling device
approximating the flow through the packed injector by the axially dispersed plug flow model and treating the input pulse as a square wave of 0.5 s duration. The impulse response of the sampling system was then determined from the calculated input to the capillary line (point A) and the measured output from the detector (point B) both of which are shown in Figure 6.

![Figure 6](image)

**Fig. 6** The input and output signals to the sampling device.

Initially the above analysis proved totally unsatisfactory, the impulse response obtained was very noisy and bore no resemblance to the form expected. This was traced to the fact that in the initial calculations the flow rate was assumed constant; whereas, despite the pulsation damper used, the positive displacement pump actually
produced a variable flow rate. The amplitude and frequency of the flow variations were estimated at 17 and 0.66 cycles/s by the direct observation of the rotameter. The calculations were then repeated on the basis of a sinusoidal flow variation and the impulse response obtained is shown in Figure 7.

![Impulse response of the sampling device.](image)

It is clear that the assumption of constant flow rate introduces an oscillatory error in the impulse response recovered. This error is largely removed by allowing for the flow variations. The high frequency noise in the impulse response could possibly be reduced by a more refined description of the flow. However, for present purposes the impulse response presented in Figure 7 is more than adequate. This impulse response will be used subsequently to determine the true input to the sampling system from a given recorded output of the refractometer.
6.3.2 Determination of True Inlet/Outlet Curves

The input to the adsorption column must first pass through the entrance flow smoothing section packed with ballotini. To determine the true input to the active section it is necessary to allow for any distortion caused by this process. This was achieved by the experimental arrangement shown in Figure 3. The procedure used was identical to that used in an actual adsorption run but with the entire bed packed with ballotini and the sample line extended to the entrance section. The response of the detector to a step change from pure water to a 0.81 wt% ethanol solution was recorded at a frequency of 10 samples/s. The true input to the active section was obtained by de-convoluting this response with the impulse response of the sampling system and is shown in Figure 8. This figure shows the delay and the small

![Graph showing step response of the entrance section](image)

Fig. 8 Step response of the entrance section: (a) after the sample line and filter and (b) the true inlet curve to the active section determined by de-convolution.
in-line filter of the sampling system. With the precautions taken, it is likely that the switching of the rapid acting solenoid valve produces a fairly sharp step change. This step change is, however, substantially distorted on passing through the entrance section. The true outlet from the active section was determined by a similar procedure except the middle section was packed with silicalite adsorbent and the capillary line was now placed at the end of the active section. The deconvolution of the recorded refractometer response with the sampling system impulse response gave the true outlet curve, a typical result is shown in Figure 9. It is clear that failure to recognise the influence of the various delays and the dispersion caused by the experimental set-up can lead to error. The true inlet/outlet curves were used in the comparison of the theoretical predictions with the experimental results.

Fig. 9 Typical breakthrough curve. (a) signal measured after the sample line and filter (b) the true outlet curve from the active section determined by de-convolution.
The relative importance of the various mass transport resistances were discussed in Chapter 5, where it was shown that intraparticle mass transport in the silicalite pellets is mainly controlled by macropore diffusion. Accordingly, the mathematical model presented below accounts for axial dispersion, external film mass transfer and describes the intraparticle resistances with a macropore diffusion model. The microporous silicalite crystals are therefore assumed to be in point-wise local equilibrium with the macropore fluid. For the purpose of repetitive column calculations it is also necessary to represent the adsorption equilibria with a simple expression. A Freundlich isotherm was chosen for this purpose and its suitability will be discussed subsequently.

6.4.1 Differential Material Balances

The differential material balances constituting the model were derived under the following assumptions. The adsorbent was treated as identical spheres packed uniformly with a bed/particle diameter ratio large enough (> 30) for any wall effects to be negligible. The hydrodynamics can then be adequately described by the axially dispersed plug flow model. The column was assumed to operate isothermally and the interstitial fluid velocity was assumed to vary in a prescribed manner (eg. constant, sinusoidal etc.). External film mass transfer was described by a linear driving force mechanism and this film was assumed to be established instantaneously. The adsorption isotherm was expressed by a single component Freundlich expression.
The notation and the units used in the derivation and the simulations are summarised below for ease of reference:

### Fluid:
- Bulk concentration: $c'(z,t)$, mmol/l
- Interstitial velocity: $v$, cm/s
- Packed bed voidage: $\varepsilon$

### Solid:
- Particle density: $\rho_p$, g/l
- Particle porosity: $\varepsilon_p$
- Particle radius: $R_p$, cm
- Pore fluid concentration: $c'(x,r,t)$, mmol/l
- Solid concentration: $q'(x,r,t)$, mmol/g
- Average solid concentration: $\bar{Q}(x,t)$, mmol/l

### Equilibria:
- Freundlich constant: $\alpha$
- Freundlich exponent: $\beta$

### Transport:
- Axial dispersion coefficient: $D_L$, $\text{cm}^2$/s
- External film mass transfer coefficient: $K_f$, cm/s
- Effective intraparticle diffusivity: $D_p$, $\text{cm}^2$/s
Consider a differential element of the column:

\[ c'(x+\Delta x, t) - c'(x, t) = Q(x, t) \]

A material balance for the interstitial fluid over this element assuming a dilute solution yields:

\[
\frac{\partial c'}{\partial t} = D_L \frac{\partial^2 c'}{\partial x^2} - v \frac{\partial c'}{\partial x} - \frac{\partial Q}{\partial t} (1 - \varepsilon) \frac{\partial Q}{\partial x} \] (1)

The above equation is subject to the usual open boundary conditions

[Danckwerts 1953],

at \( x = 0 \) \quad \frac{\partial c'}{\partial x} = 0 \quad (2)

Here we note that the inlet concentration to the active bed \( c'(t) \) is not constrained to a constant value but can vary with time in a prescribed fashion.
Next consider a differential shell within the particle

A material balance over this differential shell yields:

$$
\varepsilon_p \frac{\partial c'}{\partial t} + \rho_p \frac{\partial q'}{\partial t} = \varepsilon_p D_p \frac{1}{r^2} \frac{\partial}{\partial r'} \left( r'^2 \frac{\partial c'}{\partial r'} \right)
$$

(4)

One boundary condition for the above equation is determined from symmetry at the centre of the particle

$$
\text{at } r' = 0 \quad \frac{\partial c'}{\partial r'} = 0
$$

(5)

The other boundary condition is obtained by assuming there is no accumulation at the external surface of the particle,

$$
\text{at } r' = R_p \quad \varepsilon_p D_p \frac{\partial c'}{\partial r'} \bigg|_{R_p} = K_r (c' - c'_p|_{R_p})
$$

(6)
The model is completed by assuming the crystals are in point-wise local equilibrium with the pore fluid according to a Freundlich isotherm,

\[ q'(x,r,t) = \alpha [c'_p(x,r,t)]^\beta \]  

The average concentration of the adsorbate in the particle is given by

\[ \bar{Q}(x,t) = \frac{3}{R_p^3} \int_0^{R_p} r^2 (c'_{p,p} + \rho_p q') \, dr \]  

so that the rate of (total) accumulation in the adsorbent may be written as;

\[ \frac{\partial \bar{Q}(x,t)}{\partial t} = \frac{3}{R_p^3} \int_0^{R_p} r^2 \frac{\partial}{\partial t} (c'_{p,p} + \rho_p q') \, dr \]  

Combining this equation with Eq. (4) we have

\[ \frac{\partial \bar{Q}(x,t)}{\partial t} = \frac{3K_f}{R_p^3} (c' - c'_p |_{R_p}) \]  

Using the boundary condition Eq.(6) we may therefore write

\[ \frac{\partial c'}{\partial t} = D \left( \frac{\partial^2 c'}{\partial x^2} - v \frac{\partial c'}{\partial x} - \frac{(1 - \varepsilon)}{\varepsilon} \frac{3K_f}{R_p} (c' - c'_p |_{R_p}) \right) \]
The above equations also apply to a situation where the linear velocity through the column varies sinusoidally. All that is required is to treat the velocity $v$ as:

$$ v = v_R [1 + A \sin(\omega t)] $$

where $v_R$ is a constant (mean) reference velocity, and $A$ and $\omega$ the amplitude and frequency of the variations.

The model equations are made dimensionless using the following variables,

$$ c = \frac{c^'}{c_R}, \quad c_p = \frac{c_p^'}{c_R}, \quad q = \frac{q^'}{q_R}, \quad r = \frac{r^'}{R_p}, \quad z = \frac{x}{L} \quad \text{and} \quad \tau = \frac{tv_R}{L} $$

(14)

This in turn leads to the following dimensionless variables:

$$ D = \frac{\rho_p q_R}{c_R c_p}, \quad \text{Pe}_L = \frac{v_R L}{D_L} $$

$$ (Sh)_m = \frac{K_f}{\varepsilon D_p}, \quad N_d = \frac{D_p L}{v_R R_p^2}, \quad \text{St} = 3 \left( \frac{1-\varepsilon}{\varepsilon} \right) \frac{K_f L}{R_p v_R} $$

(15)

The dimensionless equations for the interstitial fluid then take the form:

$$ \frac{\partial c}{\partial \tau} = \left( \frac{1}{\text{Pe}_L \delta z^2} - \frac{\partial c}{\partial z} \right) \delta c - \text{St} \left( c - c_p |_R \right) $$

(16)
and its associated boundary conditions can be written in the following dimensionless form:

$$c(0,t) = c_0(t) + \frac{1}{\text{Pe}_L} \frac{\partial c}{\partial z} \bigg|_{z=0}$$  \hspace{1cm} (17)

$$\frac{\partial c}{\partial z} \bigg|_{z=1} = 0$$  \hspace{1cm} (18)

The model equations for intraparticle mass transfer (cf Eqs.4 to 6) take the form,

$$\left[ 1 + D \frac{\partial q}{\partial c} \right] \frac{\partial c}{\partial \tau} = N_d \left[ -\frac{\partial}{\partial r} \left( \frac{\partial c}{\partial r} \right) + \frac{2}{r} \frac{\partial c}{\partial r} \right]$$  \hspace{1cm} (19)

where $\partial q/\partial c_p$ denotes the slope of the isotherm and the boundary conditions may be written as:

at $r = 0$ \hspace{1cm} $\frac{\partial c}{\partial r} = 0$  \hspace{1cm} (20)

at $r = R_p$ \hspace{1cm} $\frac{\partial c}{\partial r} = (\text{Sh})_m \left( c - c_p \right)_{R_p}$  \hspace{1cm} (21)

Finally, the dimensionless equilibrium relationship (cf Eq. 7) can be stated as,

$$q = (c_p)^\beta$$  \hspace{1cm} (22)
The dimensionless equations (16) to (19) constitute a complex set of coupled partial differential equations which must be solved numerically. This was achieved through the method of orthogonal collocation. The details of this method can be found in the text by Villadsen and Michelsen (1978). The basic concept is, however, readily demonstrated.

First the dependent variable $Y(z, \tau)$ is approximated in space by an $n$th order polynomial:

$$Y_{N-1}(z, \tau) = \sum_{i=1}^{N} L_i(z) Y_i(z, \tau) \quad (23)$$

where the $z_i$ are the roots of the Lagrangian polynomial $L_i(z)$ defined by:

$$L_i(z) = \prod_{j=1}^{N} \frac{z - z_j}{z_i - z_j} \quad (24)$$

With the above approximation, the (partial) derivatives of the dependent variable with respect to space can be approximated by the following algebraic functions [Villadsen and Michelsen 1978]:

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\[
\frac{\partial Y}{\partial z} \bigg|_{z_i} = \sum_{j=1}^{N} \frac{dL_j(z)}{dz} \bigg|_{z_i} Y(z_j, \tau) = \sum_{j=1}^{N} A_{ij} Y(z_j, \tau)
\] (25)

\[
\frac{\partial^2 Y}{\partial z^2} \bigg|_{z_i} = \sum_{j=1}^{n} \frac{d^2L_j(z)}{dz^2} \bigg|_{z_i} Y(z_j, \tau) = \sum_{j=1}^{n} B_{ij} Y(z_j, \tau)
\] (26)

Similarly, integrals of the dependent variable with respect to space can also be transformed into an algebraic equation based on a quadrature formula with predetermined weight parameters \( W_i \):

\[
\int Y(z, \tau) \, dz = \sum_{i=1}^{n} W_i Y(z_i, \tau)
\] (27)

All the discretisation constants \( A_{ij}, B_{ij} \) and the weight parameters \( W_i \) for various quadrature formulae may be determined as suggested by Finlayson (1972) and Villadsen and Michelsen (1978) and appropriate subroutines are given in the text of Villadsen and Michelsen (1978). With the above spatial approximation, a partial differential equation and its boundary conditions may be transformed into a set of ordinary differential equations. However, it must be recognised that the resultant ordinary differential equations tend to be stiff. This is because the concentration at all spatial points are considered simultaneously. Evidently, the point concentrations near the surface of the particle, vary on a much faster time scale than those near its centre. Thus, the set of ordinary differential equations contains elements which vary on radically different time scales and are stiff. The solution of stiff equations by standard explicit techniques such as
Euler or Runga-Kutta methods is doomed to failure and special implicit methods are required [Villadsen and Michelsen 1978, Gear 1971]. For our simulations we used a powerful variable step, variable order method suggested by Gear (1971) and available in the NAG library as subroutine D02EAF (the computer program is included in Appendix 2).

6.4.3 Discretised Model Equations

The model equations (16) to (19) were spatially discretised using the collocation scheme below:

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<td>M+2</td>
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<td>M-1</td>
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Collocation scheme for column and particles

The fluid material balance (16) and its boundary conditions, (17) and (18) are then reduced to;
\[
\frac{dc}{dt} = \frac{1}{Pe} \sum_{j=1}^{M+2} AB_{ij} C_j - \sum_{j=1}^{M+2} AB_{ij} C_j - St \left( C_1 - C_{p, N+1, 1} \right)
\]  
\[l = 1, \ldots, M+1\]

\[C_1 = C_0 + \frac{1}{Pe} \sum_{j=1}^{M+2} AB_{1,j} C_j\]

\[\sum_{j=1}^{M+2} AB_{M+2,j} C_j = 0\]

The pore diffusion model leads to a symmetrical concentration profile within the spherical particles. It is customary to employ the transformation \(u = r^2\) for these equations prior to discretisation. This has the advantage of satisfying the symmetry condition at the centre of the particle inherently. Equation (19) can then be re-stated as

\[
\frac{\partial c_p}{\partial t} = N_d \left[ 6 \frac{\partial c_p}{\partial u} + 4u \frac{\partial^2 c_p}{\partial u^2} \right]
\]

and its discretised form becomes

\[
\begin{align*}
\frac{dC_{p,k}}{d\tau} \bigg|_1 &= N_d \left[ 4 \sum_{k=1}^{N+1} \frac{BB_{k1} c_{p, l1}}{k} + 6 \sum_{l=1}^{N+1} AB_{k1} C_{p, l1} \right] / S \\
k &= 1, \ldots, N \text{ and } i = 2, \ldots, M+1
\end{align*}
\]
where

\[ S = \left[ 1 + D_\varepsilon \left( \frac{dg}{dc_p} \right)_{kl} \right] \]  

The boundary conditions, Eqs.(20) and (21) can be discretised as;

\[ \sum_{l=1}^{N+1} AB_{N+1l,1} C_{p,1l} = \frac{(Sh)^m}{2} \left[ C_1 - C_{p,N+1,1} \right] \]  

\[ \sum_{l=1}^{N+1} AB_{k1,1} C_{p,1l} = 0 \]  

The set of differential and algebraic equations (28) to (35) were solved by a stiff integrator from the NAG library routines (Subroutine D02EAF). Preliminary tests indicated that an accuracy of 1x10^{-6} in the computed variables could be achieved with M=8 interior collocation points along the bed and N=6 interior collocation points in the particles.

6.5 SENSITIVITY ANALYSES

Before comparing the model predictions with the experimental breakthrough curves, it is advantageous to conduct a sensitivity analysis to establish the relative importance of the various model parameters. For the purpose of this analysis the flow rate \( v_r \) was set at 0.41 cm/s which corresponds to the value used for the experimental runs presented in the next section. The base value for the axial
dispersion coefficient was estimated from the correlation of Wakao and Funazkri (1978):

$$D_L = 2 \left[ \frac{20}{\text{ReSc}} + \frac{1}{2} \right] v R_p$$

at $D_L = 0.026$ cm$^2$/s which corresponds to an axial Peclet number of over 205.

The base value of the external film mass transfer coefficient was estimated from the correlation of Wakao and Funazkri (1978)

$$\frac{2K_f R}{D_m} = 2.0 + 1.1 \text{Re}^{1/3} \text{Sc}^{0.6} \quad 3 < \text{Re} < 10^4$$

at $K_f = 1.8 \times 10^{-3}$ cm/s. Similar results were also estimated from the correlation of Wilson and Geankoplis (1966)

$$\frac{1.09}{\varepsilon} \text{Sc}^{0.33} \text{Re}^{0.33} \quad 0.0055 < \text{Re} < 55$$

$$\frac{0.25}{\varepsilon} \text{Sc}^{0.33} \text{Re}^{0.69} \quad 55 < \text{Re} < 1050$$

The base value of the effective pore diffusivity was chosen as $4.0 \times 10^{-6}$ cm$^2$/s from a knowledge of the bulk liquid ethanol diffusivity $D_m = 1.28 \times 10^{-5}$ cm$^2$/s [Hamond and Stokes 1953] and an assumed tortuosity of 3. Finally, the exponent for the Freundlich isotherm was taken as $\beta = 0.816$ which corresponds to that measured experimentally as described in section 6.6.1. With this choice of parameters the sensitivity results obtained are close to the behaviour expected from the actual
As mentioned previously, the positive displacement pump used produced an oscillatory flow which was well approximated by \( v = v_R [1 + 0.1 \sin(4.15t)] \). Figure 10 shows the comparison of the calculated breakthrough curve in response to a step change in inlet concentration for this variable velocity with that for a constant velocity set at \( v = v_R \). The difference observed was minute and the 

\[ \text{Fig. 10 Influence of flow variations on the calculated breakthrough curve for (a) } v = 0.41 \text{ cm/s and (b) } v = 0.41 [1.0 + 0.1 \sin(4.15t)] \text{ cm/s} \] 

\( R = 0.0325 \text{ cm}, K_f = 4.6 \times 10^{-3} \text{ cm/s}, D_L = 0.016 \text{ cm}^2/\text{s}, D_p = 4.0 \times 10^{-6} \text{ cm}^2/\text{s} \).
breakthrough curves were practically indistinguishable. It is evident therefore that the flow variations are effectively damped out by the packed bed and the subsequent analyses were performed under the assumption of a constant velocity $v_R$.

(b) Influence of the Input Concentration Profile

The concentration step change produced at the bottom of the apparatus is substantially distorted as it passes through the inert entrance section packed with glass ballotini, see Figure 8. Figure 11 compares the breakthrough curve for an idealised step change with that

![Figure 11](image-url)

Fig. 11 Influence of input concentration profile on the breakthrough curve. (a) idealised step (b) the true input after passage through the entrance section. ($R = 0.0325$ cm, $K_f = 4.6 \times 10^{-3}$ cm/s, $D_L = 0.016$ cm²/s, $D_p = 4.0 \times 10^{-6}$ cm²/s).
It is clear that there are substantial differences and failure to account for the entrance effect can lead to significant error in model parameter estimation. This simple fact is all too frequently ignored in reported investigations of small scale fixed bed column dynamics. Consequently, all the subsequent results were based on the actual concentration input profile to the active section rather than an idealized step change.

\( (c) \) Influence of Axial Dispersion

Figure 12 compares the influence of axial dispersion on the breakthrough curve for various values of \( D_L \). It is clear that 50\% variation in the axial dispersion coefficient has little influence on the breakthrough curve. This is to be expected since the axial Peclet

\[
\frac{D_L \times \text{Time}}{\text{Height of Column}}
\]

\[
D_L = 0.010 \text{ cm}^2/\text{s}
\]

\[
D_L = 0.026 \text{ cm}^2/\text{s}
\]

\[
D_L = 0.035 \text{ cm}^2/\text{s}
\]

\( \theta \) Influence of axial dispersion on the breakthrough curve. (\( R_p =0.0625 \text{ cm}, K_f=3.3\times10^{-3} \text{ cm/s}, D_p=1.0\times10^{-5} \text{ cm}^2/\text{s}, L=13 \text{ cm} \)).
number is 315 and the column length to the particle diameter ratio is \( L/d_p = 173 \). This result also confirms that the estimation of the axial dispersion coefficient by the available correlations is satisfactory for the laboratory column used in this study.

(d) Influence of External Film Mass Transfer

The independent analysis presented in section 5.2.3 indicated that external film mass transfer may make a contribution to the behaviour of a fixed-bed for the (ethanol-water)/silicalite system. This influence is reflected in Figure 13 which compares the breakthrough curve for various values of the film mass transfer coefficient. It is clear that with the parameter values used, this influence is more substantial at low values of \( K_f \). The influence of a 60\% reduction from the base value of \( K_f = 1.8 \times 10^{-3} \) cm/s is much more pronounced than that for a five fold increase in \( K_f \). This is also to be expected since at sufficiently high

![Figure 13](image-url)

Fig. 13: Influence of external film mass transfer coefficient on the breakthrough curve (\( R_p = 0.0625 \) cm, \( D_L = 0.026 \) cm\(^2\)/s, \( D_p = 4.0 \times 10^{-6} \) cm\(^2\)/s).
values of $K_f$, the concentration at the external surface of the particles is effectively equal to that in the bulk liquid. It should be recognized, however, that the influence of external film mass transfer depends also on the intraparticle diffusivity and can become much more substantial for faster intraparticle diffusion rates.

The above discussion indicates that the value of the external film mass transfer coefficient must be estimated with some care. The correlation of Wakao and Funakiri (1978) which makes due allowance for the porous nature of the particles is probably the best available. In any event, the accuracy of the various correlations for $K_f$ presented in the literature is generally believed to be ±20%. The results presented in Figure 13 therefore indicate that, for the system at hand, this level of uncertainty in the value of $K_f$ can only produce a small error in the breakthrough time and the dynamic capacity of the column.

(e) Influence of Effective Intraparticle Pore Diffusivity

Finally, the sensitivity of the breakthrough curve to variations in the effective macropore diffusivity $D_p$ was tested and the results are presented in Figure 14. It is clear that for the parameter values used, the value of $D_p$ has the most significant influence on the breakthrough curve. This is evident in particular in the breakthrough time and the initial gradient of the breakthrough curve. This is fortunate since it enables the confident recovery of the effective pore diffusivity $D_p$ from the experimentally measured breakthrough curve.
6.6 MEASUREMENT AND INTERPRETATION OF THE BREAKTHROUGH CURVE

We are now in a position to consider the theoretical interpretation of the experimentally measured breakthrough curves for the system (ethanol-water)/silicalite. The pore diffusion model proposed contains two equilibrium parameters, i.e., the $\alpha$ and $\beta$ parameters of the Freundlich isotherm, and three kinetic parameters, i.e., the axial dispersion coefficient $D_L$, the external film mass transfer coefficient $K_f$ and the effective macro pore diffusivity $D_p$. The equilibrium parameters were determined independently for the silicalite crystals in Chapter 3. The pellets, however, contain about 20 wt% dealuminised clay binder which could affect the equilibria. It is therefore important to measure the isotherm for the pellets directly and compare the results with those based on the crystal isotherms.
According to the manufacturer (Union Carbide) the bidispersed silicalite pellets were formed by extrusion of a paste consisting approximately 80 wt% crystals and 20 wt% de-aluminised clay as a binder. The presence of this binder is clearly seen in the scanning electron micrograph of the pellets shown in Figure 2.10. Unfortunately, Union Carbide was unable to provide a more accurate estimate of the amount and the composition of the binder in silicalite pellets. The prediction of the pellet isotherm from that determined for the crystals would therefore at best be an approximation. In particular, the binder used could show a different adsorption characteristic from that of the crystals. To avoid such approximations, the excess isotherm for the silicalite pellets was measured directly by a conventional technique and fitted with a Freundlich isotherm expression. The experimental results are compared in Figure 15 with the curves predicted on the basis of pure crystal isotherms at various levels of binder content. It is clear that the binder level lies somewhere between 10–30 wt% and that the binder exhibits a different adsorption characteristic from the crystals.

To avoid substantial errors in the adsorption isotherm, the experimental data was fitted with a Freundlich expression as shown in Figure 15. A sensitivity test was then carried out to establish the influence of the exponent of this isotherm on the calculated column breakthrough curve. The results shown in Figure 16 show that the adsorption isotherm has a significant influence on the breakthrough
with $q=0.012 (c_p)^{0.816}$ is sufficiently accurate.

Fig. 15 Comparison of the experimentally measured silicalite pellet isotherms with those predicted from the pure crystal isotherms. (o experimental data, --- Freundlich isotherm, ----- pure crystal).

Fig. 16 The influence of the isotherm on the breakthrough curve ($R = 0.0625 \text{ cm}, D_p = 0.026 \text{ cm/s}, K_f = 3.3 \times 10^{-3} \text{ cm/s}, D = 4.0 \times 10^{-5} \text{ cm}^2/\text{s}$).
6.6.2 Experimental Measurement of the Breakthrough Curve

The experimental breakthrough curve of the silicalite column was determined using the apparatus shown in Figures 1 to 4. The true inlet concentration profile and the true exit concentration profiles were obtained by the fast Fourier analysis technique. Typical results obtained for duplicate runs using the following set of parameters are shown in Figures 17 and 18 and show good reproducibility.

Column and Particle Dimensions Used for Experimental Determination of The Breakthrough Curves

<table>
<thead>
<tr>
<th></th>
<th>run 1</th>
<th>run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet concentration</td>
<td>173 mmol/l</td>
<td>173 mmol/l</td>
</tr>
<tr>
<td>Column length</td>
<td>13 cm</td>
<td>13 cm</td>
</tr>
<tr>
<td>Column diameter</td>
<td>2.54 cm</td>
<td>2.54 cm</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.3791</td>
<td>0.3791</td>
</tr>
<tr>
<td>Bed density</td>
<td>0.7979 g/cm³</td>
<td>0.7979 g/cm³</td>
</tr>
<tr>
<td>Particle porosity</td>
<td>0.263</td>
<td>0.263</td>
</tr>
<tr>
<td>Particle size (dia.)</td>
<td>0.075 cm</td>
<td>0.075 cm</td>
</tr>
<tr>
<td>Particle density</td>
<td>1.285 g/cm³</td>
<td>1.285 g/cm³</td>
</tr>
</tbody>
</table>

6.6.3 Estimation of the Effective Macropore Diffusivity

We can now turn to the problem of obtaining the model parameters describing adsorption of ethanol by silicalite pellets. The equilibria were measured independently and approximated by:
The sensitivity analyses above confirmed that both both $D_L$ and $k_f$ can be estimated from available correlations with an acceptable accuracy. The external film mass transfer was estimated at $4.6 \times 10^{-3}$ cm/s from the correlation of Wilson and Geankoplis (1966) and the axial dispersion coefficient was estimated $D_L = 0.016$ cm$^2$/s from the correlation of Wakao and Funazkri (1978). The only remaining parameter is the effective macropore diffusivity which was obtained by matching the model predictions with the experimental breakthrough curve. Figs. 17 and 18 show the best fit obtained with a value of $D_p = 4.0 \times 10^{-6}$ cm$^2$/s. It is also worth pointing out that the fit is adequate over the entire range of the breakthrough curve, which taken with the independent analysis given in Chapter 5, confirms the validity of the pore diffusion model.

Finally, the effective macropore diffusion coefficient may be related to the molecular diffusivity of ethanol in water by the definition of a tortuosity factor:

$$D_p = \frac{D_m}{\tau_p} \quad (40)$$

The above result indicates that the tortuosity of the silicalite pellet is $\tau_p = 3.2$. The value of the tortuosity cannot be measured directly but the result obtained is within the range of typical values, i.e. $2 < \tau_p < 10$, quoted by Satterfield (1970).
Fig. 17 Comparison of the measured (-----) and calculated (--------) breakthrough curve for run 1. \( R = 0.0325 \text{ cm}, \ K_f = 4.6 \times 10^{-3} \text{ cm/s}, \ D_L = 0.016 \text{ cm}^2/\text{s}, \ D_p = 4.0 \times 10^{-6} \text{ cm}^2/\text{s} \).

Fig. 18 Comparison of the measured (-----) and calculated (--------) breakthrough curve for run 2. \( R = 0.0325 \text{ cm}, \ K_f = 4.6 \times 10^{-3} \text{ cm/s}, \ D_L = 0.016 \text{ cm}^2/\text{s}, \ D_p = 4.0 \times 10^{-6} \text{ cm}^2/\text{s} \).
In this chapter the various factors contributing to the adsorption breakthrough curve of ethanol on a packed bed of bi-dispersed silicalite pellets were examined. The adsorption process was described in terms of a mathematical model which took into account axial dispersion and both extra and intra-particle mass transfer resistances. In keeping with the results obtained in chapter 5, intraparticle mass transfer resistance was described in terms of a macropore diffusion model. The silicalite crystals were therefore assumed to be in point wise local equilibrium with the macropore fluid. This is justified because of the small size of the crystals ($\approx 2 \mu$m) and the relatively fast intracrystalline diffusion of water and ethanol within silicalite. In chapter 5, the time constant for diffusion in the crystals was estimated at $0.07 \text{ s}$ while that through the macropores was estimated at over $80 \text{ s}$. The model equations constitute a complex set of nonlinear parabolic partial differential equations which were solved by the orthogonal collocation technique.

In addition to the adsorption isotherm parameters, which were determined by independent experimentation, the model contains three mass transfer related parameters: the axial dispersion coefficient, the external film mass transfer coefficient and the effective macropore diffusion coefficient. The axial dispersion coefficient and the external film mass transfer coefficient were estimated from literature correlations. This leaves only the effective macropore diffusivity to be determined from a match with the experimental breakthrough curve. A detailed sensitivity analysis was conducted to estimate the influence of all the model parameters on the predicted breakthrough curves. This
analysis demonstrated the crucial importance of the accurate determination of the adsorption isotherm. We should also point out that the literature correlations for external film mass transfer and axial dispersion coefficient are subject to about 20% uncertainty. A detailed sensitivity analysis confirmed that for the system examined here such uncertainty is not sufficient to affect the predicted breakthrough curves significantly.

The mathematical model was verified against breakthrough curves measured on a carefully designed small scale pilot adsorption unit. Considerable effort was put into the determination of the true inlet and outlet concentration curves to the active section of the packed bed. The entrance and exit effects from the small scale column used were shown to be significant and were included in the theoretical analysis, a point which is frequently ignored. The model was fitted to the experimental breakthrough curves to obtain a value for the effective macropore diffusion coefficient of ethanol in silicalite pellets. The experimental breakthrough curve was well fitted across its full range with an effective macropore diffusivity of 4.0x10^{-6} \text{ cm}^2/\text{s}. The slight difference observed is most probably due to the small error in the isotherm and the size distribution of the silicalite pellets which was not accounted for. It is also comforting that the tortuosity value recovered is 3.2 which is within the range of values reported for commercial catalysts [Satterfield 1970]. To conclude, the separation of ethanol-water mixtures by silicalite pellets was accurately described by a macropore diffusion model with all the model parameters determined independently. Such a model provides a valuable tool for future scale-up and design studies.
CHAPTER 7

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK
7. CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

The recovery of low molecular weight water soluble organics, such as alcohols, ketones, aldehydes, carboxylic acids etc., presents considerable practical difficulty. This is primarily because such simple molecules lack specific exploitable functional groups. In addition, such products are of low value and are usually produced on a large scale. The desired organics are also present in low concentration and are frequently intended for internal consumption. Amongst the various alternative separation techniques, eg distillation, vacuum distillation, solvent extraction, membrane processes and sorptive separations, the latter offers several inherent advantages. In addition, hydrophobic adsorbents offering good selectivity and a reasonable capacity for such simple organics are available commercially.

The primary objective of this work was to investigate the sorptive separation of ethanol–water mixtures by a crystalline hydrophobic adsorbent, silicalite. The system ethanol–water was chosen because of its direct practical relevance to the breakage of chemical azeotropes, the production of alternative fuels and the rapidly growing area of dealcoholised beverages. This is also a good model system in as far as the thermodynamic and diffusive behaviour of the bulk liquid is well documented. The silicalite adsorbent was chosen for its superior thermal and chemical stability and its reported organophilic surface properties. This crystalline adsorbent offers a regular 6 Å pore network structure which will admit small organics but excludes larger
organics such as sugars or proteins which may be present in the feedstock.

The design and analysis of the sorptive process is complicated by the transient mode of operation and complex interaction between

1. hydrodynamics and mode of contacting
2. solid/liquid sorption equilibria and
3. interphase mass transfer limitations

which together determine the overall performance. In addition, all of the above factors are more or less strongly influenced by the shape, structural characteristics and the surface properties of the adsorbent. The aims of this work were to (a) identify the important parameters affecting the sorptive process, (b) to measure such parameters independently and (c) to incorporate the measured parameters into a mathematical model capable of accurately describing the complex column dynamics involved.

The structural characteristics of silicalite were examined in some detail. The crystal size distribution was measured with good agreement by several techniques including electronic image analysis (Quantimet), electrical sensing zone method (Coulter Counter) and forward lobe light scattering (Malvern). The crystals were found to lie in the micrometer size range with a mean size (number basis) of 2.4 μm. Such small crystals cannot be liquid fluidised and also offer excessive pressure drop in packed bed operation. Unfortunately the silicalite crystals cannot be easily grown to larger sizes and for
practical purposes, therefore, it is necessary to bind the crystals to form larger pellets in the mm size range. This was achieved by using a de-aluminised clay binder which leaves a bi-dispersed pellet with large non-selective macropores giving access to the selective micropores of the embedded crystals. The volume and size distribution of the macropores was measured by mercury porosimetry which indicated an average macropore diameter of 0.6 μm. This is in keeping with the void size expected between the 2.4 μm crystals forming the pellets. The information obtained on the structural characteristics of the silicalite crystals and pellets was used in subsequent investigation of interphase mass transfer limitations.

The accurate measurement and correlation of the phase equilibria are by far the most important steps in the analysis of the sorptive process. This is because errors in the adsorption isotherm can affect both the calculated breakthrough time and the dynamic capacity of the column. Chapters 3 and 4 of this thesis were devoted to a comprehensive and in parts novel examination of liquid phase adsorption equilibria for the system (ethanol-water)/silicalite. The basic difficulty in liquid phase adsorption equilibria arises because the adsorbed phase is not open to direct measurement. Consequently, the prediction of the selectivity and the capacity of the solid towards the individual components is normally based on theoretical assumptions whose validity had not been previously verified.

A significant contribution of this investigation was the development of a novel pycnometer technique which enables the direct measurement of the total adsorption without the need to remove the finely divided
solid from the bulk solution. This measurement coupled with the normally measured excess adsorption allows the determination of the individual amounts adsorbed and the selectivity of the solid on the basis of material balances alone. This has two important implications. First, for the purpose of kinetic studies we are able to use the true individual adsorption and selectivity of the solid. Second, we are also able to conduct a fairly detailed examination of the thermodynamic behaviour of the adsorbed phase.

With the technique developed here, the individual adsorption can be determined without any \textit{a priori} theoretical assumptions other than the existence of a distinct adsorbed phase. This in turn enabled, for the first time, a direct test of the validity of the assumptions inherent in the proposed theories of adsorption from solution. Comparison of the directly measured data with the predictions based on pseudo-ideal adsorption theory and volume filling mechanism revealed considerable discrepancy. Such discrepancies can be traced directly to the assumptions inherent in the theoretical development. For pseudo-ideal adsorption the total amount adsorbed (on a molar basis) is assumed to be constant and independent of the adsorbed phase composition. For the volume filling mechanism the total amount adsorbed is assumed to vary linearly between the respective amounts adsorbed from the pure components. Our direct measurements, however, indicated that the total amount adsorbed exhibits a pronounced maximum. This is indicative of substantial volume changes of mixing taking place within the adsorbed phase. To the best of our knowledge, however, all the proposed theories of adsorption from solution contain, in analogy with bulk liquids, the \textit{inherent} assumption of no volume change of mixing.
Clearly, the development of suitable predictive thermodynamic theories of adsorption from solution making an allowance for the volume change of mixing provides a fertile ground for future work.

The direct measurement of total adsorption also revealed very interesting information about the nature of the adsorbed phase within the "hydrophobic" silicalite micropores. For pure water, the density of the adsorbed phase was found to be lower than that of water vapour. This indicates that within the silicalite micropores, the water molecules are in a highly mobile state with little or no affinity for the surface. The density of the pure adsorbed ethanol was however close to that of liquid ethanol. Thus confirming that adsorbed ethanol is localised onto the surface at its hydrophobic end. The density of the mixed adsorbate on the other hand showed considerable variation with composition. Thus indicating that the packing density and the total number of molecules adsorbed is a strong function of the adsorbed phase composition. In particular, for the system \{(ethanol–water)/silicalite\}, the directly measured data points to as much as 30\% volume change of mixing in the adsorbed phase whereas in bulk liquids the volume change of mixing is never greater than 5\%. It is likely that such behaviour will also be observed with the adsorption of other water soluble organics within hydrophobic micropores.

The above observations suggest that, within the silicalite micropores, the ethanol molecules are localised onto the surface leaving their hydroxyl end free. The adsorbed water is then attached to the free hydroxyl end of the ethanol molecule. Put another way, the adsorbed water is largely associated with the adsorbed ethanol and the
selectivity of the crystals is limited by this association. This has a very important implication: namely, the selectivity of the crystals cannot be substantially improved by surface modifications. A better alternative is the addition of a third large molecular weight component to the bulk liquid to structure the water and therefore retain it in the bulk solution. This is in some way similar to extractive distillation and offers an exciting opportunity for tailoring the adsorption process and is clearly worthy of future work.

To conclude the work on the sorption equilibria, a comprehensive thermodynamic analysis of the adsorption from solution was also undertaken. The significant contribution of this analysis lies in the fact that it was based on directly measured rather than predicted adsorbed phase composition. The results obtained showed quite clearly that the behaviour of the adsorbed phase is radically different from that of the bulk liquid. In the bulk liquid, molecular interactions between ethanol-ethanol and water-water molecules dominate over those between the unlike molecules. This produces sufficiently strong positive deviations from Raoult’s law to lead to the formation of an azeotrope. In the adsorbed phase, however, the interactions between ethanol-water molecules overshadow those between the like molecules. The adsorbed phase therefore shows negative deviations from Raoult’s law and no azeotrope is formed. Finally, we should also point out the direct measurement of both the total and excess adsorption also enabled for the first time a rigorous thermodynamic consistency test of the measured data for adsorption from solution.

We now turn to the determination of the important kinetic parameters.
affecting the recovery of ethanol with silicalite. Mass transfer to or from the silicalite pellets could be affected by the resistance in the external film surrounding the particles and intraparticle diffusional resistances. The silicalite adsorbent used in this work was bi-dispersed with non-selective 0.6 μm macropores giving access to the selective 6 Å micropores of the embedded crystals. The intraparticle mass transfer could therefore be significantly affected either by macropore diffusion or by micropore diffusion, or by both mechanisms.

The relative contribution of extra and intra particle mass transfer resistances was analysed by considering the first and second moments of a complex macro-micro pore diffusion model under the assumption of a linear isotherm. The external film mass transfer coefficient was estimated from empirical literature correlations available for packed beds. An estimate of the effective macropore diffusivity was obtained from the molecular diffusivity in ethanol-water solutions and an assumed value of 3 for the tortuosity of the pellets. The slope of the linear isotherm was obtained from an approximation of the directly measured adsorption data for the crystals. This leaves only the micropore diffusivity which is not open to prediction or approximation and must be measured experimentally.

The pycnometer technique developed for the equilibrium investigations was modified to enable the direct measurement of the uptake rate. The data obtained was analysed in terms of Fickian (solid) diffusion into cubic particles taking the measured size distribution of the crystals into account. The results obtained indicated that, for the purpose of
estimating the mass transfer contributions, the micropore diffusivity of ethanol within silicalite crystals could (conservatively) be taken as $5.0 \times 10^{-8}$ cm$^2$/s. Based on this value, the time constants for external film mass transfer, macropore diffusion and micropore diffusion were estimated to be 2.72 s, 82.32 s and 0.07 s respectively. It is clear therefore that for the system at hand micropore diffusion makes virtually no contribution to intraparticle mass transfer resistances. This is a direct consequence of the small size of the embedded silicalite crystals and the relatively fast intracrystalline diffusion. The dominating intraparticle resistance is therefore macropore diffusion and for all practical purposes the crystals may be assumed to be in point wise equilibrium with the macropore fluid. The column dynamics can therefore be adequately described in terms of a macropore diffusion model making due allowance for axial dispersion and external film mass transfer. Before discussing the predictions based on such a model, however, it is worthwhile to point out several interesting observations regarding intracrystalline diffusion in silicalite.

The experimental intracrystalline uptake rates showed an interesting anomaly between the diffusion of pure ethanol and pure water within silicalite. The uptake of the more strongly adsorbed ethanol was reasonably well approximated by a Fickian mechanism. The uptake of pure water, however, appeared to be initially faster than that of ethanol but slowed down by several orders of magnitude as saturation was approached. Evidently, such behaviour cannot be described in terms of Fickian diffusion with a constant diffusivity. This observation is in qualitative keeping with the equilibrium behaviour...
already described. In the case of pure ethanol, the molecule is localised and its interaction with the solid surface dominates over the interaction between the individual ethanol molecules diffusing within the crystal. The intracrystalline diffusivity of ethanol therefore appears to be less dependent on the level of uptake. Water on the other hand has little affinity for the silicalite surface and is highly mobile. At low uptakes, therefore, the water molecules are free to move and diffuse faster than the strongly adsorbed ethanol. As the level of loading and hence the number of water molecules within the micropores is increased, a repulsive force is set up between the water molecules which slows down the uptake rate considerably. With the time and the experimental equipment available to us we were only able to measure the total uptake of the mixed adsorbate; the concurrent measurement of the mixed adsorbate concentration with time was not unfortunately possible. We are not therefore in a position to comment quantitatively on the co-adsorption of ethanol-water mixtures in silicalite crystals. Qualitatively, however, the total uptake of 4.6 wt% and 10.3 wt% ethanol solutions were considerably closer to that of pure ethanol than pure water. A tentative explanation of this behaviour is the essentially one-dimensional nature of diffusion in silicalite micropores. The ethanol and water molecules are unable to overtake each other due to the steric hindrances in the 6 Å micropores of silicalite. Thus once a slow moving ethanol molecule has entered a micropore, it will essentially determine the diffusion rate of all other molecules behind it. The one dimensional nature of diffusion in the micropores of silicalite has important implications, particularly for desorption, which is left for future work.
The dynamics of fixed adsorption of ethanol-water mixtures by a fixed-bed of bi-dispersed hydrophobic adsorbents were analysed in terms of a macropore diffusion model taking into account axial dispersion and external film mass transfer. In addition to the isotherm parameters, which were measured independently and approximated by a Freundlich isotherm, this model contains three mass transfer related parameters: the axial dispersion coefficient, the external film mass transfer coefficient and the effective macropore diffusivity. Both the axial dispersion coefficient and external film mass transfer coefficient can be predicted from literature correlations. This leaves only the effective macropore diffusivity to be determined from a match with experimental breakthrough curves.

A comprehensive sensitivity analysis was conducted to determine the influence of all the model parameters on the predicted breakthrough curves for the system (ethanol-water)/silicalite. The results obtained highlighted the crucial importance of the accurate measurement of the adsorption isotherm. The empirical literature correlations for the prediction the axial dispersion and external film mass transfer are subject to about 20% error. The sensitivity analysis confirmed that this level of uncertainty does not have a significant influence on the predicted breakthrough curve. The experimental breakthrough curve for the system (ethanol-water)/silicalite was measured on a carefully designed small scale fixed-bed adsorption unit. Considerable effort was put into accounting for the distortions caused by entrance and exit effects and the sampling device; a point which can be quite significant for small columns and which is frequently neglected. The only remaining unknown model parameter, i.e. the effective macropore
The value recovered was $4.0 \times 10^{-6}$ cm$^2$/s which when compared to the liquid phase diffusivity of ethanol-water, ie. $1.28 \times 10^{-5}$ cm$^2$/s, indicates a tortuosity of 3.2 for the silicalite pellet which is well within the range of values reported for similar solids.

The present investigation was confined to a systematic examination of the major factors affecting sorptive separation of ethanol from aqueous solutions with hydrophobic adsorbents. Many of the experimental techniques developed and the conclusions reached have a wider implication on the recovery of other simple water soluble organics. It is hoped that the techniques presented here will find future applications for other systems, in particular multicomponent fluids such as those encountered in practice. The present work has also raised a number of fundamental questions regarding sorption and diffusion in micropores of molecular dimension. This is an area highly recommended for future study and should lead to a better understanding of the intricacies of one-dimensional diffusion. On a more practical side, the desorption of the desired product was not addressed in this thesis and presents another challenging area for future study.
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Additional reference

APPENDIX I

Characterization of the sampling device
Characterization of the sampling device

In most experiments, the measuring device is usually at some distance from the desired measurement point and separated by a transfer line as shown below:

![Diagram of transfer line](image)

In many cases, the distortion of the measured signal resulting from passage through the transfer line can become significant and must be accounted for. This is the case for many small scale adsorption columns, particularly when the transfer line has a complicated geometry and the delay involved is not insignificant compared to the time scale of the process.

Two approaches can be used to correct for the distortion caused by the transfer line. The first and more obvious approach requires the physical modeling of the hydrodynamic flow conditions through the transfer line. This approach is, however, unsatisfactory when the geometry is complex and can prove subjective. A better approach is to allow for any distortion without resorting to a specific physical model of the transfer line. This is made possible through convolution and de-convolution procedures utilising Fast Fourier Transform (FFT) techniques. This basic idea is therefore to conduct independent
experiments with the transfer line/sampling device so that its impulse response (or transfer function) can be obtained in discrete digital form. Once the impulse response has been obtained, the response to any other input signal can be obtained by the application of the superposition principle. This procedure is particularly attractive when used in combination with the discrete Fourier transform for which many efficient algorithms exist.

The continuous and discrete Fourier transforms of a function \( g(t) \) are defined by:

\[
\begin{array}{|c|c|c|}
\hline
\text{Time Domain} & \text{Continuous Domain} & \text{Discrete Domain} \\
\hline
\text{g}(t) & \int_{-\infty}^{\infty} g(t)e^{2\pi ift} \, dt & \sum_{k=0}^{N-1} g_k e^{2\pi ik\omega/N} \\
\hline
\end{array}
\]

In the above equations \( f \) is the frequency, which when time \( t \) is measured in seconds has the units of cycles/s or Hertz. To determine the discrete Fourier transform from a finite number \( N \) of sample points available at equal interval \( \Delta \),

\[
g_k = g(t_k); \quad t_k = k \Delta \quad k = 0,1,2,\ldots,N-1
\]

we may proceed as follows. Evidently, with \( N \) independent number of discrete input samples we can only produce \( N \) independent number of
outputs. So instead of trying to calculate the Fourier transform at all frequencies (as in the continuous case) we seek to evaluate the discrete transform at N frequencies defined by:

\[ f_n = \frac{n}{N \Delta}, \quad n = -\frac{N}{2}, \ldots, +\frac{N}{2} \]  \hspace{1cm} A2

The continuous integral can then be approximated with a discrete summation:

\[ G(f_n) = \int_{-\infty}^{\infty} g(t)(e^{2\pi i f_n t}) dt \approx \sum_{k=0}^{N-1} g_k (e^{2\pi i f_n k}) \Delta \]

\[ \approx \Delta \sum_{k=0}^{N-1} g_k (e^{2\pi i k n/N}) \]  \hspace{1cm} A3

The last summation above is called the discrete Fourier transform of the N points \( g_k \) and denoted by \( G_n \):

\[ G_n = \sum_{k=0}^{N-1} g_k (e^{2\pi i k n/N}) \]  \hspace{1cm} A4

The relationship between the continuous and discrete Fourier transform is therefore,

\[ G(f_n) \approx \Delta G_n \]  \hspace{1cm} A5

and the discrete Fourier transform has the same properties as the
The formula for inverting the discrete Fourier transform is given by [Brigham 1974, Press et al 1988]:

\[
g_k = \frac{1}{N} \sum_{k=0}^{N-1} G_n (e^{-2\pi i kn/N})
\]

This formula enables the exact recovery of the N values \(g_k\) from the N discrete values of its transform \(G_n\). The evaluation of equations A4 and A6 can be carried out using Fast Fourier algorithms with great computational efficiency [Brigham 1974, Borland 1986, Press et al 1988].

The application of this technique is shown schematically below:

A known input variation \(x(t)\) is applied to the transfer line and its response \(y(t)\) is measured experimentally at a suitable sampling rate. The discrete Fourier transform of the input and output signals, \(X_n\) and \(Y_n\) respectively, are then determined numerically. The discrete impulse response of the transfer line is then simply obtained from:

\[
F_n = \frac{Y_n}{X_n}
\]

where \(Y_n\), \(X_n\), and \(F_n\) represent complex numbers.
Next, consider a situation where an experimental response has been recorded and it is desired to find the true input to the sampling system.

The recorded output is first transformed using (A4) to obtain $Y_n$. The transform of the unknown input is then determined from:

$$X_n = \frac{Y_n}{F_n} \quad A7$$

The inversion formula (A6) is then applied to obtain the input $x(t)$ in the time domain. The following self-explanatory programme enables the above calculations through Fast Fourier Transform techniques.

References:


CHARACTERISATION OF THE SAMPLING DEVICE

IMPLICIT REAL*4(A-H,O-Z)
CHARACTER DFILE*16, OFILE*16
COMMON XI(2050),Y1(2050),FD(2050),X2(2050),Y2(2050),T(2050),
1 XX1(2050),YY1(2050),FDD(2050),XX2(2050),YY2(2050),
2 ZZ1(2050)
DIMENSION A1(2050),AA1(2050),B1(2050),BB1(2050),
1 CI(2050),CC1(2050)

C INPUT DATA

C X1  INPUT SIGNAL TO SAMPLING DEVICE
C Y1  OUTPUT SIGNAL FROM SAMPLING DEVICE (RECORDED BY REFRACTOMETER)
C Y2  OUTPUT SIGNAL FROM THE PROCESS (RECORDED BY REFRACTOMETER)
C T   TIME

C OUTPUT DATA

C X2  OUTPUT SIGNAL FROM THE PROCESS RECOVERED BY FOURIER TRANSFORM
C FD  TRANSFER FUNCTION OF THE SAMPLING DEVICE

PRINT *, 'INPUT DATAFILE:'
READ *, DFILE
PRINT *, 'OUTPUT FILE:'
READ *, OFILE
OPEN(5,FILE=DFILE,STATUS='OLD')
OPEN(6,FILE=OFILE,STATUS='NEW')
READ(5,*)N,FACT
N=2048
DELT=0.1
DO 10 I=1,N
READ(5,*) T(I),XI(I),Y1(I),Y2(I)
XX1(I)=0.0
YY1(I)=0.0
ZZ1(I)=Y2(I)
10 CONTINUE

C DISCRETIZE X1

DO 15 I=1,N
A1(I)=XI(I)/N
AA1(I)=XX1(I)/N
15 CONTINUE

CALL FFT(A1,AA1,N,NU)
DO 18 I=1,N
XX1(I)=A1(I)
18 CONTINUE

A1.7
A1(I) = Y1(I)/N
AA1(I) = YY1(I)/N

20 CONTINUE
CALL FFT(A1, AA1, N, NU)
DO 23 I = 1, N
   Y1(I) = A1(I)
   YY1(I) = AA1(I)

23 CONTINUE

C CALCULATE THE TRANSFER FUNCTION
C FD(S) = Y1(S)/X1(S)

DO 25 I = 1, N
   A1(I) = X1(I)
   AA1(I) = XX1(I)
   B1(I) = Y1(I)
   BB1(I) = YY1(I)

25 CONTINUE
CALL DIVID(A1, AA1, B1, BB1, C1, CCl, N)
DO 27 I = 1, N
   FD(I) = C1(I)
   FDD(I) = CCl(I)

27 CONTINUE

C DISCRETIZE Y2

DO 29 I = 1, N
   A1(I) = Y2(I)/N
   AA1(I) = YY2(I)/N

29 CONTINUE
CALL FFT(A1, AA1, N, NU)
DO 32 I = 1, N
   Y2(I) = A1(I)
   YY2(I) = AA1(I)

32 CONTINUE

C CALCULATE X2

C X2(S) = Y2(S)/FD(S)

DO 35 I = 1, N
   A1(I) = FD(I)
   AA1(I) = FDD(I)
   B1(I) = Y2(I)
   BB1(I) = YY2(I)

35 CONTINUE
CALL DIVID(A1, AA1, B1, BB1, C1, CCl, N)
DO 37 I = 1, N
   X2(I) = C1(I)
   XX2(I) = CCl(I)

37 CONTINUE

C INVERSE X2

DO 40 I = 1, N

A1.8
40 CONTINUE
   CALL FFT(A1,AA1,N,NU)
   SUM1=0.0
   SUM2=0.0
   DO 45 I=1,N
   X2(I)=A1(I)
   XX2(I)=-AA1(I)
   SUM1=SUM1+X2(I)*0.1
   SUM2=SUM2+ZZ1(I)*0.1
   WRITE(6,100) T(I),SUM1,SUM2
45 CONTINUE
100 FORMAT(IX,3(F10.5,3X))
   CLOSE(5)
   CLOSE(6)
   STOP
   END

C FAST FOURIER TRANSFORM ROUTINE
C REF:
C   BRIGHAM, E. O.,
C   THE FAST FOURIER TRANSFORM

SUBROUTINE FFT(XREAL,XIMAG,N,NU)
IMPLICIT REAL*4(A-H,O-Z)
DIMENSION XREAL(N),XIMAG(N)

C XREAL REAL PART OF THE FUNCTION
C XIMAG IMAGINARY PART
C N NUMBER OF POINTS
C NU FROM N=2**NU

N2=N/2
NU1=NU-1
K=0
DO 100 L=1,NU
100 DO 101 I=1,N2
   P=IBITR(K/2**NU1,NU)
   ARG=6.283185D0*P/N
   C=COS(ARG)
   S=SIN(ARG)
   K1=K+1
   KIN2=K1+N2
   TREAL=XREAL(KIN2)*C+XIMAG(KIN2)*S
   TIMAG=XIMAG(KIN2)*C-XREAL(KIN2)*S
   XREAL(KIN2)=XREAL(K1)-TREAL
   XIMAG(KIN2)=XIMAG(K1)-TIMAG
   XREAL(K1)=XREAL(K1)+TREAL
   XIMAG(K1)=XIMAG(K1)+TIMAG
   K=K+N2
   IF(K.LT.N) GO TO 102
   K=0

A1.9
N2=N2/2
100 N2=INT(N2/2)
    DO 103 K=1,N
    I=IBITR(K-1,NU)+1
    IF(I.LE.K) GO TO 103
    TREAL=XREAL(K)
    TIMAG=XIMAG(K)
    XREAL(K)=XREAL(I)
    XIMAG(K)=XIMAG(I)
    XREAL(I)=TREAL
    XIMAG(I)=TIMAG
103 CONTINUE
RETURN
END

FUNCTION IBITR(J,NU)
    J1=J
    IBITR=0
    DO 200 J=1,NU
    J2=J1/2
    IBITR=IBITR*2+(J1-2*J2)
200 J1=J2
RETURN
END

SUBROUTINE DIVID(TA1,TA2,TB1,TB2,TC1,TC2,N)
IMPLICIT REAL *4 (A-H,O-Z)
C GIVEN DISCRETE FOURIER TRANSFORMS OF A=A1+IA2
C AND B=B1+IB2 FIND THE DISCRETE TRANSFER FUNCTION
C C=(B/A)=C1+IC2
DIMENSION TA1(N),TA2(N),TB1(N),TB2(N),TC1(N),TC2(N)
C FIND SYSTEM TRANSFER FUNCTION
A=FLOAT(N)
AA=1.0
    DO 435 K=1,N
    TC1(K)=AA*(TA1(K)*TB1(K)+TA2(K)*TB2(K))/(TA1(K)**2+TA2(K)**2)
    TC2(K)=AA*(TB2(K)*TA1(K)-TB1(K)*TA2(K))/(TA1(K)**2+TA2(K)**2)
435 CONTINUE
RETURN
END
APPENDIX II

Numerical Solution of the Column Partial Differential Equation by Orthogonal Collocation.
The following programme solves the partial differential equations describing an adsorption column allowing for axially dispersed plug flow, external film mass transfer and intraparticle transport by a pore diffusion mechanism. The flow chart for the programme is listed below:

**Inputs:**
- Particles properties
- Bed properties
- Flow conditions
- Isotherm parameters
- Axial dispersion coefficient
- External mass transfer coefficient
- Pore diffusion coefficient

**Routine JACOBI** - evaluate roots of polynomial
**DFOPR** - evaluate discretisation matrices
**RADAU** - evaluate integration weights

\[ t = t + \Delta t \]

**Routine: NAG D02EAF**
Solve a system of stiff ordinary differential equations with the Gear-Hindmarsh integrator

\[ t = t_{\text{end}} \]

**Function FCN**
evaluate the time derivatives

**Output**
- Stop

A2.2
SUBROUTINE TO EVALUATE COLUMN BREAKTHROUGH CURVES FOR A
PORE DIFFUSION MODEL USING ORTHOGONAL COLLOCATION.

IMPLICIT REAL*8 (A-H,O-Z)

INPUT PARAMETERS

FIXED BED PROPERTIES
   RAD: PARTICLE RADIUS, CM
   VOID: COLUMN VOIDAGE
   XL: COLUMN LENGTH, CM

FIXED BED OPERATIONAL PARAMETERS
   SVEL: SUPERFICIAL VELOCITY, CM
   CC: INFLUENT CONCENTRATION
   DP: COLUMN DISPERSION COEFFICIENT

EQUILIBRIA AND DIFFUSIVITY PARAMETERS
   B: COEFFICIENT FOR FRUENDLICH ISOTHERM
   BEXP: EXPONENT FOR FRUENDLICH ISOTHERM
   DS: EFFECTIVE DIFFUSIVITY, CM2/S
   XXF: EXTERNAL FILM TRANSFER RESISTANCE, CM/S

LEGENDER POLYNOMIAL PARAMETERS
   N: DEGREE OF POLYNOMIAL IN THE PARTICLE
   NO: 1 IF BOUNDARY CONDIITION INCLUDED
        AS AN INNER COLLOCATION POINT, OR 0
   N1: 1 IF BOUNDARY CONDITION INCLUDED
        AS AN OUTER COLLOCATION POINT, OR 0
   MD: MAXIMUM LIMIT OF N+NO+N1
   PALFA: PARAMETER FOR SOLID PHASE POLYNOMIAL
   PBETA: AS PALFA
   M: DEGREE OF POLYNOMIAL IN THE FLUID PHASE
   MO: 1 IF BOUNDARY CONDITION INCLUDED
        AS AN INNER COLLOCATION POINT, OR 0
   M1: 1 IF BOUNDARY CONDITION INCLUDED
        AS AN OUTER COLLOCATION POINT, OR 0
   MD: MAXIMUM LIMIT OF M+MO+M1
   BALFA: PARAMETER FOR FLUID PHASE POLYNOMIAL
   BBETA: AS BALFA

PARAMETERS FOR SEMI-IMPLICIT RUNGE-KUTTA ROUTINE
   XO: INITIAL TIME
   HO: INITIAL STEP SIZE, USUALLY 1.D-04
   EPS: TOLERANCE
   W: WEIGHT FUNCTIONS
   XTAB: TIME VECTOR FOR PRINTING
   NTAB: NUMBER OF XTAB'S
   IPRNT: PRINTING INDEX, MAXIMUM ALLOWABLE STEPS BETWEEN
          EACH XTAB

EXTERNAL FCN
DIMENSION AB(22,22), AP(22,22), BB(22,22), BP(22,22), C(22), CS(22),

A2.3
DIMENSION WORK(72,90)
COMM /XXX/ AP,BP,AB,BB,U,V
COMM /YYY/ DG,PC,SH,ST,XNS
COMM /ZZZ/ APR,BPR,BEXP
COMM /CY/ CS,YN
COMM /SYM/ SYM1,SYM2,SYM3
COMM /MN/ M,N,MP1,MP1,MP2,NDIF
COMM /CON/ C0,CC1,CC2,CC3,CC4,WRAD
DATA XTAB/156*0.DO/

READ(5,*) RAD,RHO,VOID,XL
READ(5,*) SVEL,CC,CINIT,DP
READ(5,*) B,BEXP,DS,XKF,VOIDP
READ(5,*) NI,N,NO,N1,ND,PALFA,PBETA
READ(5,*) MI,M,MO,M1,MD,BALFA,BBETA
READ(5,*) XO,HO,EPS,NTAB,IPRINT
READ(5,*) (XTABCI),1=1,NTAB)

C MATHEMATICAL ECONOMISATION

DIA=RAD
QC=B*CC**BEXP
DG=QC*RHO/(VOIDP*CC)
XIVEL=SVEL/VOID
TAU=XL/XIVEL
XNS=DS*TAU*VOIDP/(DIA*DIA)
ST=XKF*TAU*(1.DO-VOID)/(DIA*VOID)
SH=XKF*DIA/(VOIDP*DS)
PC=XIVEL*XL/DP
WRITE(6,3000) DG,XIVEL,TAU,XNS,ST,SH,PC
WRITE(1,3000) DG,XIVEL,TAU,XNS,ST,SH,PC
3000 FORMAT(1H,'DG=',D15.6/1H,'XIVEL=',D15.6,'TAU=',D15.6/
1 1H,'XNS=',D15.6/1H,'ST=',D15.6/1H,'SH=',D15.6/
2 1H,'PC=',D15.6//)

C INICIALISATION OF ARRAYS

NP1=N+1
MP1=M+1
MP2=M+2
NDIF=M+NP1*M

A2.4
CALCULATION OF THE REQUIRED DISCRETISATION CONSTANTS
BY STANDARD ROUTINES

WRITE(6,7) N
WRITE(1,7) N
CALL JACOBI(ND,N,NO,N1,PALFA,PBETA,DIF1,DIF2,DIF3,U)

CALL RADAU(ND,N,NO,N1,1,PALFA-1.DO,PBETA,U,DIF1,WRAD)
WRITE(6,3345)
WRITE(1,3345)
3345 FORMAT(15X,'RADAU QUADRATURE WEIGHTS'/)
WRITE(6,9) (WRAD(I),I=1,NP1)
WRITE(1,9) (WRAD(I),I=1,NP1)

WRITE(6,8)
WRITE(6,9) (U(I),I=1,NP1)
WRITE(1,8)
WRITE(1,9) (U(I),I=1,NP1)
DO 21 ID=1,2
IF(ID.EQ.2) GO TO 4
WRITE(1,3)
DO 20 I=1,NP1
CALL DFOPR(ND,N,NO,N1,I,ID,DIF1,DIF2,DIF3,U,VECT)
WRITE(1,23) I
DO 20 K=1,NP1
AP(I,K)=VECT(K)
WRITE(1,22) K,AP(I,K)
20 CONTINUE
GO TO 21
4 CONTINUE
WRITE(1,5)
DO 21 I=1,NP1
CALL DFOPR(ND,N,NO,N1,I,ID,DIF1,DIF2,DIF3,U,VECT)
WRITE(1,23) I
DO 21 K=1,NP1
BP(I,K)=VECT(K)
WRITE(1,22) K,BP(I,K)
21 CONTINUE
WRITE(6,24) M
WRITE(1,24) M
CALL JACOBI(MD,M,MO,M1,BALFA,BBETA,DIF1,DIF2,DIF3,V)
WRITE(6,8)
WRITE(6,9) (V(I),I=1,MP2)
WRITE(1,8)
WRITE(1,9) (V(I),I=1,MP2)
DO 28 ID=1,2
IF(ID.EQ.2) GO TO 26
WRITE(1,3)
28 CONTINUE

A2.5
DO 27 J=1,MP2
CALL DFOPR(MD,M,MO,M1,ID,DIF1,DIF2,DIF3,V,VECT)
WRITE(1,23) I
DO 27 K=1,MP2
AB(I,K)=VECT(K)
WRITE(1,22) K,AB(I,K)
27 CONTINUE
GO TO 28

DO 28 I=1,MP2
CALL DFOPR(MD,M,MO,M1,I,ID,DIF1,DIF2,DIF3,V,VECT)
WRITE(1,23) I
DO 28 K=1,MP2
BB(I,K)=VECT(K)
WRITE(1,22) K,BB(I,K)
28 CONTINUE

TRANSFORMATION OF BOTH SOLID PHASE CONCENTRATION, Q(I,J), AND FLUID PHASE CONCENTRATION, C(I), INTO A SYSTEM OF ORDINARY DIFFERENTIAL EQUATIONS, Y(I)

DO 30 I=2,MP1
Y(I-1)=C(I)
DO 30 J=1,NP1
II=M+NP1*(I-2)+J
Y(II)=Q(I,J)
30 CONTINUE

MATHEMATICAL ECONOMISATION

SYM1=1.DO+AB(1,MP2)*AB(MP2,1)/AB(MP2,MP2)/(PC-AB(1,1))
SYM2=PC-AB(1,1)
SYM3=AB(1,MP2)/AB(MP2,MP2)
WRITE(6,3001) SYM1,SYM2,SYM3
WRITE(1,3001) SYM1,SYM2,SYM3

3001 FORMAT(1H , ' SYM1=' , D15.6 , '  SYM2=' , D15.6 , '  SYM3=' , D15.6/ /)

SOLUTION OF A SYSTEM OF ORDINARY DIFFERENTIAL EQUATIONS WITH GEAR-HINDMARSH STIFF INTEGRATOR

DO 77 I=1,NTAB
X1=XTAB(I)
CALL D02EAF(XO,X1,NDIF,Y, EPS,FCN, WORK, 90, 0)
CALL OUT(X1,Y,0,1.DO, NDIF)
77 XO=X1
3 FORMAT(//20X,'CONSTANTS OF FIRST DERIVATIVES')
5 FORMAT(//20X,'CONSTANTS OF SECOND DERIVATIVES')
SUBROUTINE FCN(T,Y,F)

THE PDES FOR SOLID PHASE, Q(I,J), AND LIQUID PHASE, C(I), WERE
TRANSFORMED INTO A SYSTEM OF ODES

IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Y(42),F(42)
DIMENSION AB(22,22),AP(22,22),BB(22,22),BP(22,22),
1       CQ(22,22),CC(22),Q(22,22),C(22),
2       U(22),V(22),CS(22),YN(22)
DIMENSION CCCO(22),CC1(22),CC2(22),CC3(22,22),CC4(22,22),WRAD(22)
COMMON /XXX/ AP,AB,BB,UC,V
COMMON /YYY/ DG,PC,SH,ST,XNS
COMMON /ZZZ/ APR,BPR,BEXP
COMMON /CY/ CS,YN
COMMON /SYM/ SYM1,SYM2,SYM3
COMMON /MN/ M,N,MP1,MP2,NDF
WRITE(1,3332)
3332 FORMAT(1H , 'ENTERED FUN' )

C SET ALL CONCENTRATIONS BELOW 1.D-20 TO 1.D-20
C
DO 7788 I=1,ND
   IF(Y(I).LT.1.D-20) Y(I)=1.D-20
7788 CONTINUE
C
C(I)=PC/SYM2
C(MP2)=0.DO
DO 31 I=1,M
   I1=I+1
   C(I1)=Y(I)
DO 31 J=1,NP1
   II=M+NP1*(I-1)+J
   Q(I,J)=Y(II)
31 CONTINUE
DO 61 J=2,MP1
   C(1)=C(1)+((AB(1,J)-SYM3*AB(MP2,J))*C(J)/SYM2
61 CONTINUE
C(1)=C(1)/SYM1
C(MP2) = C(MP2) + AB(MP2, J) * C(J)
611 CONTINUE
C(MP2) = -C(MP2) / AB(MP2, MP2)

C

DO 613 I = 2, MP1
    Q(I, N+1) = Q(I, N+1) - AP(N+1, L) * Q(I, L)
DO 612 L = 1, N

612 Q(I, N+1) = Q(I, N+1) / (AP(N+1, N+1) + SH/2. DO)

DO 105 I = 2, MP1
    F(I) = (BB(I, 1) / PC - AB(I, 1)) * C(1)
    F(I) = F(I) + (BB(I, MP2) / PC - AB(I, MP2)) * C(MP2)
    F(I) = F(I) - 3. DO * (C(I) - Q(I, N+1))
DO 100 J = 2, MP1
    F(I) = F(I) + (BB(I, J) / PC - AB(I, J)) * C(J)
100 CONTINUE

105 F(I) = F(I) * DG

DO 200 I = 2, MP1
    I1 = I - 1
    DO 205 K = 1, N
        IJ = M + N * (I - 2) + K
        DQSDQ = BEXP * Q(I, K) ** (BEXP - 1. DO)
        CONST = DG / (1. DO + DG * DQSDQ)
        F(IJ) = CONST * (6. DO * AP(K, N+1) + 4. DO * U(K) * BP(K, N+1)) * Q(I, N+1)
    DO 210 L = 1, N
        F(IJ) = F(IJ) + CONST * (6. DO * AP(K, L) + 4. DO * U(K) * BP(K, L)) * Q(I, L)
    210 CONTINUE

205 F(IJ) = F(IJ) * XNS
200 CONTINUE

WRITE(1, 3333)
3333 FORMAT(1H, 'LEFT FUN')
RETURN
END

SUBROUTINE OUT(X, Y, IHA, QA, ND)
IMPLICIT REAL*8 (A-H, O-Z)

PRINTING SUBROUTINE
CS(I), QS(I, NP1), C(I), Q(I, J)

DIMENSION AP(22, 22), BP(22, 22), AB(22, 22), BB(22, 22)
DIMENSION U(22), V(22), Q(22, 22), Y(ND), C(22), CS(22), YN(22)
COMMON /XXX/ AP, BP, AB, BB, U, V
COMMON /YYY/ DG, PC, SH, ST, XNS

A2.8
IF (Y(I).LT.1.D-20) Y(I)=1.D-20

C(1)=PC/SYM2
C(MP2)=0.DO
DO 31 I=1,M
   I1=I+1
   C(I1)=Y(I)
   DO 31 J=1,MP1
      II=M+MP1*(I-1)+J
      Q(I,J)=Y(II)
   31 CONTINUE

   DO 61 J=2,MP1
      C(J)=C(1)+(AB(1,J)-SYM3*AB(MP2,J))*C(J)/SYM2
   61 CONTINUE

   C(MP2)=C(MP2)/SYM2
   DO 3444 J=1,MP2
      GRAD=GRAD+AB(MP2,J)*C(J)
   3444 CONTINUE

   33 FORMAT(//15X,'BULK FLUID PHASE CONCENTRATION')
   34 FORMAT(//,20X,5(D15.6,5X))
   35 FORMAT(//15X,'PORE FLUID CONCENTRATION')
   37 FORMAT(//20X,'AT NODE POINT',I3)
   38 FORMAT(//,20X,5(D15.6,5X))
   41 FORMAT(//15X,'INTERFACIAL FLUID CONCENTRATION')
   42 FORMAT(//,20X,5(D15.6,5X))

RETURN
END
SUBROUTINE JACOBI (ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND)

AB=AL+BE
AD=BE-AL
AP=BE*AL

DIF1(1)=(AD/(AB+2)+1)/2
DIF2(1)=0.

IF (N.LT.2) GOTO 15
DO 10 I=2,N
Z1=I-1
Z=AB+2*Z1
DIF1(I)=(AB*AD/Z/(Z+2)+1)/2
IF (I.NE.2) GOTO 11
DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1)
GOTO 10

11 Z=Z*Z
Y=Z1*(AB+Z1)
Y=Y*(AP+Y)
DIF2(I)=Y/Z/(Z-1)
CONTINUE

15 X=0.
DO 20 I=1,N
25 XD=0.
XN=1.
XD1=0.
XN1=0.
DO 30 J=1,N
XP=(DIF1(J)-X)*XN-DIF2(J)*XD
XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
XD=XN
XD1=XN1
XN=XP
30 XN1=XP1
ZC=1.
Z=XN/XN1
IF (I.EQ.1) GOTO 21
DO 22 J=2,I
ZC=ZC-Z/(X-ROOT(J-1))
22 ZC=ZC-Z/(X-ROOT(J-1))
21 Z=Z/ZC
X=X-Z
IF (DABS(Z).GT.1.D-09) GOTO 25
ROOT(I)=X
X=X+.0001
30 CONTINUE

NT=N+NO+N1
IF (NO.EQ.0) GOTO 35
DO 31 I=1,N
J=N+1-I
31 ROOT(J+1)=ROOT(J)
ROOT(1)=0.
35 IF(N1.EQ.1) ROOT(NT)=1.
SUBROUTINE DFOPR(ND, N, NO, N1, I, ID, DIF1, DIF2, DIF3, ROOT, VECT)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION DIF1(ND), DIF2(ND), DIF3(ND), ROOT(ND), VECT(ND)
NT=N+NO+N1
IF (ID.EQ.3) GOTO 10
DO 20 J=1,NT
IF (J.NE.I) GOTO 21
IF (ID.NE.1) GOTO 5
VECT(I)=DIF2(I)/DIF1(I)/2
GOTO 20
5 VECT(I)=DIF3(I)/DIF1(I)/3
GOTO 20
21 Y=ROOT(I)-ROOT(J)
VECT(J)=DIF1(I)/DIF1(J)/Y
IF (ID.EQ.2) VECT(J)=VECT(J)*(DIF2(I)/DIF1(I)-2/Y)
20 CONTINUE
GOTO 50
10 Y=0
DO 25 J=1,NT
X=ROOT(J)
AX=X*(1-X)
IF (NO.EQ.0) AX=AX/X/X
IF (N1.EQ.0) AX=AX/(1-X)/(1-X)
VECT(J)=AX/DIF1(J)**2
25 Y=Y+VECT(J)
DO 60 J=1,NT
VECT(J)=VECT(J)/Y
60 RETURN
END

SUBROUTINE INTRP (ND, NT, X, ROOT, DIF1, XINTP)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION ROOT(ND), DIF1(ND) , XINTP(ND)
P0L=1.
DO 5 I=1,NT
Y=X-ROOT(I)
XINTP(I)=0.
IF (Y.EQ.0) XINTP(I)=1.
5 IF(POL.EQ.0.DO) GOTO 10
6 DO 6 I=1, NT
7 XINTP(I)=POL/DIF1(I)/(X-ROOT(I))
8 10 RETURN
9 END

C

SUBROUTINE RADAU(ND,N,NO,N1,ID,AL,BE,ROOT,DIF1,VECT)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION ROOT(ND), DIF1(ND), VECT(ND)
S=0.
NT=N+NO+N1
DO 40 I=1,NT
X=ROOT(I)
10 AX=X
IF(ID.EQ.0) AX=1/AX
GOTO 40
20 AX=1-X
IF(NO.EQ.0) AX=1/AX
GOTO 40
30 AX=1.
40 VECT(I)=AX/DIF1(I)**2
IF(ID.NE.2) VECT(NT)=VECT(NT)/(1+AL)
IF(ID.GT.1) VECT(1)=VECT(1)/(1+BE)
DO 50 I=1,NT
50 S=S+VECT(I)
DO 60 I=1,NT
60 VECT(I)=VECT(I)/S
RETURN
END

C

SUBROUTINE GAUSL(ND, NCOL, N, NS, A)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION A(ND, NCOL)
N1=N+1
NT=N+NS
IF(N.EQ.1) GOTO 50
DO10 I=2,N
IP=I-1
I1=IP
X=DABS(A(I1,I1))
DO 11 J=I,N
IF(DABS(A(J, I1)).LT.X) GOTO 11
X=DABS(A(J, I1))
11 CONTINUE
12 A(IP, J)=X
13 DO 10 J=I,N
DO 10 K=I,NT
10 A(J,K)=A(J,K)-X*A(I1,K)
50 DO 20 IP=1,N
   I=N1-IP
   DO 20 K=N1,NT
   A(I,K)=A(I,K)/A(I,I)
   IF(I.EQ.1) GOTO 20
   I1=I-1
   DO 25 J=1,I1
25 A(J,K)=A(J,K)-A(I,K)*A(J,I)
20 CONTINUE
RETURN
END