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MULTICOMPONENT TRANSPORT ACROSS NONPOROUS POLYMERIC MEMBRANES

By

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**A thesis submitted for the degree of
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ABSTRACT

The theoretical description of multicomponent transport across nonporous polymeric membranes was investigated using two alternative frameworks: the phenomenological approach of irreversible thermodynamics and the mechanistic Stefan-Maxwell formulation. The transport models developed account for potential equilibrium and/or kinetic coupling of fluxes and the contribution of diffusion induced non-selective flow within the polymer.

Transient measurements coupled with transient models enable a more detailed evaluation of the complex multicomponent transport phenomena occurring within the nonporous polymer. The models developed in this study were validated against transient dialysis and pervaporation data for {ethanol-water}/silicone rubber system. A critical assessment was obtained by recovering the model parameters from the dialysis data and using the same parameters to *predict* the transient pervaporation performance.

Separate evaluation of the equilibrium and kinetic contributions requires a thermodynamic model to describe the non-ideality of the polymer solution. The uptake of small polar solutes by hydrophobic polymers is not well described by the classical Flory-Huggins model. An empirical modification was developed which retains the basic form of the Flory-Huggins model but allows the interaction parameters to be a simple function of activity. This modification provided a physically realistic description of the sorption equilibria for the {ethanol-water}/silicone rubber system over conditions ranging from a low pressure vapour to a saturated liquid.

The phenomenological approach of irreversible thermodynamics was used to develop transient models of dialysis and pervaporation. The numerical solution of the model equations, which constitute a set of coupled partial differential equations, was accomplished by the application of the method of lines. Average phenomenological diffusion coefficients recovered from dialysis data can give a good qualitative *prediction* of pervaporation performance provided the diffusion coefficients satisfy the Onsager reciprocal relationships. However, a quantitative prediction requires the explicit inclusion of the concentration dependence of the diffusivities, which is best achieved within the mechanistic Stefan-Maxwell formulation.

A generic model of membrane transport was formulated using the mechanistic Stefan-Maxwell approach and generalised driving forces, which included the contribution from the various internal and external driving forces. Transient models of dialysis and pervaporation were developed which used exactly the same generic model to describe the transport through the membrane. A notable advantage of the generic model lies in the fact that the Stefan-Maxwell diffusivities retain their physical significance irrespective of the number of components present. This offers the opportunity of recovering many of the model parameters from relatively simple binary experiments. The results obtained indicate that the generic model is capable of describing the transient dialysis and pervaporation of the {ethanol-water}/silicone rubber system with an identical set of concentration dependent equilibrium and diffusive parameters. The generic model provides a solid framework for the theoretical description of diverse processes employing a nonporous polymer as the selective separation barrier.

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NOMENCLATURE

a_i	Activity of component i (-)
$[B]$	Stefan-Maxwell matrix with elements B_{ij} (s/m^2) defined in Eq.(5.5)
C_i	Molar concentration of component i ($kmol/m^3$)
C_t	Total molar concentration ($kmol/m^3$)
$[D^T]_p$	Matrix of thermodynamically corrected diffusivity in the polymer fixed frame with elements $(D_{ij}^T)_p$ (m^2/s)
D_v	Binary Fick diffusion coefficient in the volume fixed frame (m^2/s)
$[D]_v$	Matrix of multicomponent Fick diffusion coefficients in the volume fixed frame with elements $(D_{ij})_v$ (m^2/s)
$\mathfrak{D}_{ij}$	Stefan-Maxwell diffusion coefficients (m^2/s)
d_i	Generalised driving force for component i defined in Eq. (5.19) (m^{-1})
$\tilde{F}_i$	External body force acting on component i (kN/kg i)
f	spacing between successive interference fringes (-)
ΔG_m	Molar Gibbs free energy change of mixing ($kJ/kmol$)
ΔG_m^{ex}	Molar excess Gibbs free energy change of mixing ($kJ/kmol$)
ΔH_m	Molar enthalpy change of mixing ($kJ/kmol$)
$(J_i)_R$	Molar diffusive flux of component i in reference frame R ($kmol/ m^2 s$)
$(j_i)_R$	Mass diffusive flux of component i in reference frame R ($kg/ m^2 s$)
L	width of the optical diffusion cell (m)
L_{Bot}	Height of the liquid in the bottom half of the dialysis cell (m)
L_{mem}	Thickness of the membrane (m)
L_{Top}	Height of the liquid in the top half of the dialysis and pervaporation cells (m)
L_v	Length of the vapour path in the pervaporation cell (m)
M	Mass of the dry polymer (kg)
M_i	Molecular weight of component i ($kg/kmol$)
m_i	mass of a molecule of species i ($kg/molecule$)
n	Refractive index(-)

N_i	Molar flux of component i relative to stationary coordinates (kmol/m ² s)
N^s	Total sorption in polymer (kmol/kg dry mem)
N_i^s	Individual sorption of component i in polymer (kmol i /kg dry mem)
P	Absolute pressure (kPa)
p_i	Partial pressure of component i (kPa)
p_i^0	Saturation vapour pressure of component i (kPa)
$P(Y)$	Optical path length (m) only in chapter 3
R	Universal gas constant (kJ/kmol K)
ΔS_m	Molar entropy change of mixing (kJ/kmol K)
ΔS_{cf}	Molar configurational entropy change of mixing (kJ/kmol K)
t	Time (s)
T	Absolute temperature (K)
T_g	Glass transition temperature of polymer (K)
u^R	Mixture velocity corresponding to reference frame R (m/s)
u_i	Velocity of component i relative to stationary coordinates (m/s)
$\bar{v}_i$	Partial molar volume of component i in a mixture (m ³ /kmol)
V_t	Total molar volume of a mixture (m ³ /kmol)
x_i	Mole fraction of component i (-)
z	Distance (m)

Greek symbols

$[\Gamma]$	Matrix of equilibrium interaction in polymer with elements Γ_{ij} defined in Eq.5.28 (-)
γ_i	activity coefficient of component i (-)
η_i	Relative sorption of component i in polymer (kmol/kg dry mem)
λ	Wave length of the He/Ne laser light source (m)
μ_i	Chemical potential of component i (kJ/kmol)
ρ_i	Mass concentration of component i (kg i/ m ³)
ρ_i	Mass density of mixture (kg / m ³)

σ_{dif}	Rate of entropy production due to diffusion per unit volume ($\text{kJ}/\text{m}^3\text{s K}$)
τ_v	Vapour residence time in bottom half of pervaporation cell (s)
ϕ_i	Volume fraction of component i (-)
ω_i	Weight fraction of component i (-)
$[\Omega]_M$	Matrix of phenomenological coefficient in mass fixed frame with elements $(\Omega_{ij})_M (\text{kmol}^2/\text{m s kJ})$
$[\Omega]_P$	Matrix of phenomenological coefficient in polymer fixed frame with elements $(\Omega_{ij})_P (\text{kmol}^2/\text{m s kJ})$
χ_{ij}	Flory-Huggins interaction parameter between component i and j (-)

Special symbols

$[m]$	Matrix of properties with components m_{ij}
$(m)_M$	Property m measured relative to the mass fixed frame of reference
$(m)_P$	Property m measured relative to the polymer fixed frame of reference
$(m)_R$	Property m measured relative to frame of reference R
$(m)_V$	Property m measured relative to the volume fixed frame of reference
$\bar{m}$	Partial molar property m
$\hat{m}$	Average value of property m
$\tilde{m}$	Specific value of property m

CHAPTER 1

INTRODUCTON

1. Introduction

Membrane separation processes have assumed an increasing importance in diverse areas ranging from gas separation in the process industries to the separation of macromolecules in the pharmaceutical industries. Table 1.1 lists the major membrane separation processes in current use. In this study we are concerned with processes which employ a nonporous polymeric membrane as the selective separation barrier, examples of such processes include reverse osmosis, dialysis, electrodialysis, gas permeation and pervaporation. Nonporous membranes employed in practice are often asymmetric and are manufactured with a thin nonporous skin layer superimposed on a more open support layer. In most cases, the major resistance to mass transfer is almost exclusively in the dense nonporous skin layer with the support layer only providing mechanical support. Selective transport through an asymmetric polymeric membrane is therefore primarily governed by the passage through the dense nonporous skin layer.

Table 1.1 Membrane Separation Processes

Process	Driving force for mass transport	Type of membrane employed	Separation mechanism	Application
Micro-filtration	Hydrostatic pressure (50-100 Kpa)	Symmetrical porous (with a pore radius of 0.1-20 μ m)	Sieving effect	Separation of suspended material
Ultra-filtration	Hydrostatic pressure (100-1000 Kpa)	Symmetrical porous (with a pore radius of 1-20 nm)	Sieving effect	Concentration, fractionation and cleaning of macromolecular solutions
Reverse osmosis	Hydrostatic pressure (1000-10000 Kpa)	Asymmetrical nonporous membrane	Solution-diffusion	Concentration of components with low molecular weight
Dialysis	Concentration difference	Symmetrical nonporous membrane	Solution-diffusion	Separation of low molecular weight components from macromolecular solutions and suspensions
Electrodialysis	Difference in electrical potential	Ion-exchange membrane	Difference in charge of components	Desalting and deacidifying
Gas Permeation	Partial pressure difference (1000-5000 Kpa)	Asymmetric nonporous membrane	Solution-diffusion	Separation of gases and vapours
Pervaporation	Partial pressure difference	Asymmetric nonporous membrane	Solution-diffusion	Separation of solvents and azeotropic mixtures

A molecule diffusing within a homogenous nonporous polymer moves in response to the sum of the forces exerted on it. Such forces may arise as a result of local chemical potential gradients caused by departure from equilibrium or may be due to an external potential imposed across the polymeric matrix. A molecule within the polymeric membrane moves in response to the *local* gradients and has no memory of how it entered the membrane or how the local gradients were generated. In principle, therefore, a properly formulated transport model accounting for the various driving forces should be equally applicable to any separation process employing a homogenous nonporous polymer as the selective separation barrier. The major difference between such processes lies in the manner in which the driving force for separation is generated. In dialysis the membrane is maintained between liquids of differing composition. In pervaporation the upper membrane interface is in contact with a liquid while the activities at the lower interface are maintained at a low value by pulling a vacuum or using a sweep gas. In vapour permeation the driving force is generated by contacting the membrane with vapours maintained at different pressures. The basic transport processes occurring within the nonporous polymeric matrix are, however, the same in all cases. The ultimate aim of this theoretical study is to develop a "generic" model of multicomponent transport across nonporous polymeric membranes with physically well defined equilibrium and diffusive parameters. Such a model offers great practical utility in as far as the parameters recovered under one set of processing conditions can be used for the design, scale-up and optimisation of other processes employing the same membrane.

Multicomponent mass transfer exhibits a number of characteristics which are absent in a binary system. In general, the flux of a component is not only driven by its own concentration gradient but also by the concentration gradient of all other components present in the system. Therefore, the concentration gradient of a component may strongly increase or decrease the flux of another component. A clear understanding of such multicomponent coupling is essential for formulation of reliable transport models. Theoretical description of the transport phenomena occurring within nonporous polymers is severely complicated by intricate permeant-permeant and polymer-permeant molecular interactions. As a result of such interactions, sorption and diffusion in multicomponent membrane systems often exhibit extreme concentration dependence. An accurate description of such

multicomponent interactions and their influence on the diffusivity and solubility of the various species within the polymer matrix is a prerequisite for accurate design, scale up and optimisation of membrane separation processes.

1.1 A Brief Review of Theoretical Description of Membrane Transport

Theoretical modelling of multicomponent mass transport across nonporous membranes can be undertaken under various levels of detail. The following brief review is used to place the theoretical approach adopted in this study in the context of previous work. The majority of previous theoretical studies of membrane transport suffer from one or more common deficiencies. In many cases, the thermodynamic and kinetic coupling of multicomponent fluxes is ignored completely. In other cases, equilibrium coupling is accounted for but only under idealised assumptions that are difficult to justify. Another common difficulty is the arbitrary use of 'binary' results for multicomponent systems through the introduction of *effective* diffusivities. Such parameters are inherently ill defined and show very complex concentration dependence, which severely limits their range of application. Concentration dependence of multicomponent solubility and diffusivity within polymeric matrices has also received relatively little attention.

The total flux within a polymeric matrix may have a selective diffusive contribution and a non-selective contribution due to hydrodynamic flow. The hydrodynamic flow may arise as a result of external forces, for example a pressure difference, imposed across the membrane or may be induced by the diffusion process itself. The non-selective contribution to the flux is usually considered for transport through porous polymers but is often ignored in the case of nonporous polymers. The flux within the nonporous polymer is then assumed to be totally diffusive, which can cause significant error in certain cases for the following reason. Non-selective bulk flow within a nonporous polymer may arise as a result of volume changes of mixing and unequal volumetric flux of the various species through the membrane. This contribution can become important for systems with a high level of sorption and can only be ignored under fairly restrictive conditions, a point that is often ignored. Allowing for the diffusion induced bulk flow demands a careful definition of the frame of reference used to describe the multicomponent diffusion coefficients. Unfortunately, many reported theoretical models of membrane transport pay scant

regard to this fundamental point and do not even mention the frame of reference employed.

Early attempts in theoretical modelling of membrane transport were aimed at the development of simple permeation equations for industrial design applications. As a starting point for the analysis, the steady state flux of each species was related to its own chemical potential gradient [eg Lee 1975] and the contribution from the gradient in chemical potential of other species (i.e. kinetic coupling) was ignored. Further simplifications are introduced by assuming ideal equilibrium behaviour, for example a Henry's law description, and constant concentration independent diffusivities. Integrated transport equations developed specifically for binary systems were then employed to describe the flux for multicomponent systems in terms of permeability coefficients. It is interesting to note that the binary equation employed by Lee [1975] accounts for non-selective bulk flow but its extension to a multicomponent system is largely arbitrary. Such simplifications result in easy to use descriptions of multicomponent membrane transport which ensures their continued usage. Similar models have been used more recently by other authors [e.g. Kataoka *et al*, 1990; Wijmans and Baker 1995]. However, the permeability coefficients are often a very strong function of composition and of little help for separate evaluation of the equilibrium and kinetic contributions to the overall transport process.

Steady state selective transport of liquid mixtures through a nonporous membrane inevitably results in the development of a boundary layer in the liquid adjacent to the membrane (concentration polarisation). In some cases, especially the selective transport of dilute organic mixtures by pervaporation, the resistance in the concentration polarisation layer becomes important. Several studies have been aimed at allowing for this extra resistance to transport under pervaporation conditions [e.g. Raghunath and Hwang 1991, Ji, Sikdar and Hwang 1994 and Wijmas *et al*, 1995]. However, in all of these models the transport through the polymer was described in terms of overall permeability factors that are difficult to interpret.

Selective transport across a nonporous membrane can arise as a result of differences in the solubility and/or diffusivity of the permeating components in the polymer matrix. Huang and Lin [1968] attribute the observed enhancement in the permeation rate of {benzene-hexane} mixtures across polyethylene to an increase in

diffusion rate of the slower moving species due to the presence of the other component. Similar conclusions are reached for other systems by Rauthenbach and Albericht [1985], Rhim and Huang [1989], Huang and Rhim [1991] and Yeom and Huang [1992]. On the other hand, Mulder and Smolders [1985] consider preferential sorption, rather than enhanced diffusivity, to be responsible for the selective transport of {ethanol-water} mixtures across a variety of nonporous membranes. A separate evaluation of sorption (solubility) and diffusion in multicomponent transport across polymeric membranes will certainly provide valuable information concerning the mechanism responsible for selective transport.

In the absence of external forces, the driving force for mass transport across a nonporous membrane is the local gradient in the chemical potentials. The extent of equilibrium coupling can, therefore, be directly evaluated by considering the concentration dependence of the chemical potential of the permeating species within the membrane. This would of course require a thermodynamic model to describe the thermodynamic non-ideality of the polymer solution. A variety of simplified models have been employed to relate the activity (chemical potential) and composition within the membrane phase. In some cases, it is suggested that the activity of each permeating species is related to its composition within the polymer by simple linear Henry's law type expressions [e.g. Brun *et al* 1985, Wijmans and Baker 1995]. It must be clearly understood that such linear expressions preclude the possibility of equilibrium coupling of fluxes altogether. Sorption of small molecules within polymeric membranes is often highly non-ideal. Thermodynamic non-ideality in a polymeric membrane may arise simply as a result of the size difference between the permeating and polymer molecules. Specific molecular interactions only serve to make the thermodynamics more complex. Separate evaluation of equilibrium coupling demands a fairly comprehensive thermodynamic model, which recognises the size differences and also makes proper allowance for any specific polymer-permeant and permeant-permeant interactions.

A number of studies pioneered by the work of Mulder and Smolders [1985] have attempted to assess the extent of equilibrium coupling using the Flory-Huggins model [1953] to describe the thermodynamic non-ideality of the membrane system. This model, which allows for the large size difference between the penetrant and

polymer molecules, provides a suitable starting point for the description of multicomponent sorption in polymeric systems, in particular elastomers. Mulder and Smolders [1985] related the flux of each species to its own chemical potential gradient. The Flory-Huggins model was then used to relate the chemical potential (activity) to concentration of permeating species within the polymer. The model was used to assess the extent of equilibrium coupling for the {ethanol-water}/cellulose acetate system. A similar approach was used by Bansal [1988] for the {ethanol-water}/silicon rubber system. It was suggested that equilibrium coupling could affect the flux of the less preferentially sorbed component significantly. This approach has also been used by some authors using assumptions that are hard to justify. For example, Chen and Chen [1998] and Yang *et al* [1998] use the Flory-Huggins model to relate the activity in a ternary system to the volume fraction of the two permeating species. The flux equations used by these authors are, however, incomplete and ignore the equilibrium coupling of fluxes. On the other hand, Jonquieres *et al* [1996] use the correct flux equations but employ a thermodynamic model in which the activity of each species is related to its own composition alone. The result is that the cross terms in the flux equations vanish and the equilibrium coupling of fluxes is ignored.

A major drawback to all of the models reviewed so far is that the potential for the kinetic coupling of fluxes is ignored. There is in fact some confusion in the literature concerning kinetic coupling. For example, in some theoretical models the flux of a particular species is related to its own chemical potential gradient through single (effective) diffusivity. This (effective) diffusivity is then assumed to be a function of composition of all permeating species and such concentration dependence is often taken to represent 'kinetic coupling' [Mulder and Smolders 1985, Karlson *et al* 1992, Doong *et al* 1995, Janquieres *et al* 1996, Kammaruddin and Koros 1997, Shieh and Huang, 1998]. This approach is unsatisfactory since the effective diffusivities employed do not have the same physical significance as a binary diffusion coefficient. The use of effective diffusivities in multicomponent systems has been heavily and correctly criticised by Taylor and Krishna [1993]. It has been clearly demonstrated by Toor and Sebelsky [1961] that from a theoretical view point an effective diffusivity in a multicomponent system can take on values ranging from minus to plus infinity. The kinetic coupling of fluxes in a multicomponent system

cannot therefore be properly handled by a concentration dependent effective diffusivity.

Theoretical consideration of kinetic coupling of fluxes must recognise the fact that the diffusive flux of each species is driven by the chemical potential gradient of all permeating species. For example, the steady state diffusive fluxes in a ternary system (composed of component 1 and 2 and the polymer p) is given by:

$$\begin{aligned}(J_1)_R &= (D_{11})_R \frac{d\mu_1}{dz} + (D_{12})_R \frac{d\mu_2}{dz} \\ (J_2)_R &= (D_{21})_R \frac{d\mu_1}{dz} + (D_{22})_R \frac{d\mu_2}{dz}\end{aligned}$$

The origin of this equation will be explored in detail in Chapter 2. For the moment we note that this is a phenomenological relationship which describes the diffusive fluxes as a linear combination of the independent driving forces. The definition of the fluxes and the phenomenological diffusion coefficients must be completed by adopting a particular reference velocity for the whole mixture. Four multicomponent diffusion coefficients are required to describe the diffusive fluxes in a ternary system and each of these coefficients may be a function of composition of the mixture. Setting the cross terms, $D_{12}d\mu_2/dz$ and $D_{21}d\mu_1/dz$, simplifies the flux equations substantially but is equivalent to ignoring the potential for kinetic coupling of fluxes.

The separate evaluation of the extent of kinetic coupling of fluxes in a multicomponent system requires the determination of the concentration dependent multicomponent phenomenological diffusion coefficients, which is not a trivial task and is rarely attempted. The basic theoretical difficulty arises because the multicomponent phenomenological diffusivities are not based on a mechanistic model of the diffusion process. Such phenomenological coefficients do not have a simple relationship with the binary diffusivities and do not have the same physical significance. A better alternative for such studies is provided by the Stefan-Maxwell formulation of multicomponent diffusion, which originates from the kinetic theory of gases and is based on a mechanistic model of the diffusion process. This approach has been successfully applied to multicomponent transport in gaseous and liquid systems [Taylor and Krishna 1993], but its application to multicomponent membrane transport is scarce. Heintz and Stephan [1994] developed a model of pervaporation based on the

Stefan-Maxwell formulation and report that it can provide a much better description than alternative kinetically de-coupled models.

In most reported theoretical investigations of transport through nonporous membranes it is assumed the flux through the dense polymer is purely diffusive. Many multicomponent polymer mixtures are thermodynamically non-ideal and exhibit a volume change on mixing. For such systems, unequal volumetric fluxes of the various species may cause a diffusion induced non-selective flow. This extra non-selective contribution to the flux is often ignored but may have a significant effect in membrane transport. There are only a few articles in the literature which deal with diffusion induced non-selective bulk flow explicitly. Doong *et al* [1995] and Shieh and Huang [1998] consider the contribution of non-selective bulk flow in their transport model but do not comment on its influence for the systems investigated. An elegant and clear study of the contribution of non-selective bulk flow in multicomponent membrane transport was reported by Kamaruddin and Koros [1997]. It was clearly demonstrated that the contribution of non-selective bulk motion to the total flux through the membrane depends on the ratio of the fluxes of the permeating species and the level of sorption. For polymeric systems with high sorption levels, the non-selective contribution to the total flux may be significant and can dominate the diffusive contribution. Ignoring this contribution, particularly for the component with the smaller total flux, can cause substantial error.

Irrespective of the approach used for the description of the fluxes, the diffusion coefficients used can be a very strong function of composition. The concentration dependence of membrane diffusivity has been described by a variety of empirical relationships. A linear relationship was proposed by Long [1965] and used by Greenlaw *et al* [1977]. For many membrane systems the concentration dependence of diffusivity is highly nonlinear. Mulder and Smolders [1985] used an exponential form in which the diffusion coefficient of each species was considered to be a function of its own concentration. Nguyen [1987] used the same form but considered the diffusivity of either permeating species as a function of the concentration of the preferentially sorbed material. An exponential form with the diffusivity taken as a function of the concentration of all permeating species was considered by Brun *et al* [1985]. A less empirical approach for the concentration dependence of diffusivity in

polymeric membranes was developed by Fujita [1961] and extended by Vrentas and Duda [1977]. The free volume theory of Fujita was used by Fels and Hunag [1971] and Yeom and Huang [1992] to describe the concentration dependence of diffusivity.

1.2 Scope and Objectives

From the above review it is clear that there are many ways for modelling of multicomponent transport across a nonporous membrane, ranging from simple expressions based on permeability to very detailed solution-diffusion models accounting for equilibrium and kinetic coupling under various levels of simplifying assumptions. A serious attempt for theoretical modelling must enable a clear separation between kinetic and equilibrium coupling effects, consider the potential for diffusion induced non-selective bulk flow and the concentration dependence of multicomponent sorption and diffusion parameters. Such a model will inevitably contain a large number of parameters, which must be determined from suitable experimental measurements. For practical utility, the complexity of the model and the effort required for determining its parameters must remain commensurate. This is best achieved by ensuring that the model parameters are (as far as possible) physically well defined and can be obtained from simple experiments.

The ultimate objective of this study is to develop a generic model, with well defined equilibrium and diffusive parameters, for the multicomponent transport of low molecular weight components across nonporous polymeric membranes. The generic model should be capable of handling any kind of internal or external driving force, so that it may be applied to any separation process employing a nonporous polymer as the selective separation barrier. Such a generic model contains a large number of equilibrium and diffusive parameters, which may be concentration dependent. An important objective of this study is to establish a solid foundation for estimating the model parameters from a limited amount of experimental data and identify the type of experimentation required.

The particular system considered in this study is the transport of {ethanol-water} mixtures across a nonporous silicone rubber membrane. This is a difficult system in as far as the bulk liquid is highly non-ideal and the transport of polar water and ethanol molecules through the hydrophobic silicone rubber matrix leads to

complex coupling of the fluxes of the permeating species. However, the diffusive and equilibrium behaviour of the bulk liquid is well studied and we are also fortunate in having available transient dialysis data [Bansal, 1988] and transient pervaporation data [Abdel-Ghani, 1992] measured for the same silicon rubber membrane by previous workers in our research group. The validity and reliability of the generic model can therefore be critically tested by recovering the parameters from data measured under dialysis (pervaporation) conditions and *predicting* the performance for unseen experimental data measured under pervaporation (dialysis) conditions.

In Chapter 2 we give a general description of multicomponent transport and consider some aspects of the transport of small molecules through nonporous polymers. Three alternative approaches, empirical generalisation of Fick's law, the phenomenological approach of irreversible thermodynamics and the mechanistic Stefan-Maxwell formulation can be used to describe multicomponent diffusion. Each approach defines a particular set of "multicomponent diffusion coefficients" and a clear understanding of the basis for each approach and the inter-relationship between the various diffusion coefficients is an essential initial task. We shall also provide a clear definition of the various frames of reference used to describe the diffusion process and give a theoretical treatment of diffusion induced bulk flow. The empirical and theoretical procedures for handling the concentration dependence of polymer phase diffusivities are highlighted using a number of practical examples. Separate evaluation of equilibrium and kinetic contributions to the transport process within nonporous polymers demands an independent determination of sorption equilibria. The practical difficulties inherent in the measurement of sorption equilibria for systems with small uptake are discussed in chapter 2. The Flory-Huggins model is identified as a suitable thermodynamic model for sorption of small molecules in nonporous elastomers. A description of the classical Flory-Huggins model and various modifications of this model are also presented.

Chapter 3 is devoted to a description of the data used in this study and the development of the various integration and optimisation procedures employed. The conventional techniques for the experimental investigation of multicomponent membrane transport are usually based on the measurement of steady state fluxes. Such measurements do not, in general, carry sufficient information to enable a

confident evaluation of the individual contributions to the overall transport process. The measurement of transient fluxes coupled with transient models of membrane transport enables a more critical evaluation [Bansal 1988, Watson 1991 and 1995, Yeom *et al* 1999]. The transient pervaporation apparatus used by Abdel-Ghani [1992] is described in chapter 3 and the data obtained for {ethanol-water}/silicon rubber system is presented. A brief description of the non-intrusive laser interferometer used by Bansal [1988] to measure the transient refractive index profile in the liquid boundary layer bathing the membrane is also provided in Chapter 3. The interpretation of the experimental fringe patterns requires careful attention to various points, in particular deflection of light in a medium of varying refractive index, and is considered in detail in chapter 3. Transient models of multicomponent membrane transport constitute a highly coupled set of nonlinear partial differential equations. A general method, the method of lines, capable of solving the transient models in their full complexity is presented in chapter 3. A robust constrained optimisation procedure for parameter extraction is also described in this chapter. The stability and accuracy of the numerical solution and the reliability of the parameter optimisation procedures are also critically tested with the aid of a hypothetical model system.

The data and the numerical techniques presented in chapter 3 are used in the remainder of the thesis to assess the reliability and predictive power of general models of membrane transport using two alternative approaches. In chapter 4 we develop a general transient model of membrane transport based on the phenomenological approach of irreversible thermodynamics. This model employs the classical Flory-Huggins model to describe the non-ideality of the polymer solution and average phenomenological diffusion coefficients. Considerable attention is paid to the correct formulation of the transport equations and boundary conditions. Application of this model to the {ethanol-water}/silicon rubber system confirms that it can provide a good qualitative *prediction* of pervaporation results using parameters recovered from data measured under dialysis conditions. However, the results obtained indicate that both the equilibrium parameters and the phenomenological diffusion coefficients are concentration dependent. Unfortunately, the phenomenological diffusion coefficients do not have a mechanistic basis, which complicates the explicit inclusion of concentration dependence of the diffusive parameters.

A generic model of membrane transport is developed in chapter 5 by resorting to the mechanistic Stefan-Maxwell formulation of multicomponent diffusion in nonporous polymers. An expression for a generalised driving force, which can accommodate both external and internal driving forces, is developed from postulates of irreversible thermodynamics. A significant advantage of this model over the phenomenological approach of chapter 4 is that the Stefan-Maxwell diffusivities are open to physical interpretation and retain their physical significance irrespective of the number of components present. Appropriate procedures for extraction of many of the model parameters from simple binary experiments are described in chapter 5. In particular, it is demonstrated that constrained optimisation, with appropriate physical constraints, enables the reliable estimation of the model parameters from limited data sets. Application of the generic model to the {ethanol-water}/silicon rubber system confirms that it can provide an excellent quantitative *prediction* of pervaporation performance using parameters recovered from data measured under dialysis conditions.

The generic model and the parameter estimation techniques developed provide a convenient framework for the description of multicomponent transport across nonporous polymers. The generic model can be applied to any separation process employing a nonporous membrane as the selective separation barrier. More significantly, the model parameters are physically well defined, retain their physical significance under different operating conditions and many of them can be obtained from relatively simple binary experiments. Potential improvements to measurement techniques and better procedures for model validation are highlighted in chapter 6.

CHAPTER 2

MULTICOMPONENT DIFFUSION AND SORPTION IN NONPOROUS POLYMERIC MEMBRANES

2. Multicomponent Diffusion and Sorption in Nonporous Polymeric Membranes

2.1 Introduction

The transfer of multicomponent mixtures across nonporous polymeric membranes arises in diverse processes such as dialysis, pervaporation and vapour permeation. Selective transport can arise as a result of differences in the solubility and/or diffusivity of the permeating species in the membrane matrix. Diffusion in multicomponent systems exhibits a number of characteristics that are absent for a binary system. In many cases the fluxes of the individual components are coupled due to complex polymer-permeant and permeant-permeant interactions [Mears, 1979]. In general, the flux of any component is not only driven by its own concentration gradient but is also affected by the concentration gradient of all other species present. Consequently, the concentration gradient of one component may strongly increase or decrease the flux of another component. An adequate understanding of such multicomponent interactions and their influence on the transport of the various species within the membrane is a prerequisite for accurate design and scale-up.

The purpose of this chapter is to give a general description of multicomponent diffusion and sorption and consider some aspects of the transport of small polar molecules in nonporous polymers. A number of alternative approaches can be used to describe multicomponent diffusion and each approach defines a particular set of “multicomponent diffusion coefficients”. A clear understanding of the basis for each approach and the inter-relationship between the various diffusion coefficients is an essential initial task. We start this chapter with a careful consideration of the various frames of reference used to describe the diffusion process. This is followed by a brief review of the empirical generalisation of Fick’s law, the phenomenological approach of irreversible thermodynamics and the mechanistic Stefan-Maxwell formulation of diffusion. In particular the relationship between the empirical multicomponent Fick diffusivities and the phenomenological coefficients of irreversible thermodynamics is highlighted. The latter approach enables a clear separation of the kinetic and equilibrium coupling of fluxes but still lacks a mechanistic model for the diffusion

process. Such a model is provided by the Stefan-Maxwell formulation that results in diffusion coefficients with a clear physical interpretation. The three approaches mentioned are all equivalent and a brief comparison is made to highlight their chief advantages and shortcomings in practical applications.

Many multicomponent mixtures are thermodynamically non-ideal and exhibit a volume change on mixing. For such systems, unequal diffusive fluxes of the various species may induce an extra contribution to any hydrodynamic flow present. This extra non-selective contribution to the transport process is often ignored but may have a significant effect in membrane transport [Kamaruddin and Koros, 1997]. Diffusion in flowing systems is considered in section 2.2.5 and an independent relationship for the calculation of the diffusion-induced contribution to non-selective bulk flow is presented. Diffusion coefficients in polymeric systems are usually a very strong function of concentration. The discussion on diffusion is closed by considering a number of specific examples involving the transport of small molecules through polymers and highlighting the empirical and theoretical approaches used to describe the concentration dependence of membrane phase diffusion coefficients.

Separate evaluation of the equilibrium and kinetic contributions to the transport process within a polymeric membrane demands an independent determination of the sorption equilibria. This requires the measurement of the relative and total sorption as well as the swelling of the polymer due to sorption. We start by considering the practical difficulties inherent in the measurement of the swelling and the total sorption for volatile solutes with low uptake. Faced with such difficulties, it is necessary to resort to a thermodynamic model in order to quantify the sorption equilibria using the easily measured relative sorption. This procedure inevitably involves inherent assumptions about the nature of the sorbed phase and the choice of the model is therefore critical. The Flory-Huggins model [1953] which allows for the large size difference between the penetrant and polymer molecules provides a suitable equilibrium model. The fundamental features of the classical Flory-Huggins model are discussed and its limitations are examined. A number of modifications of the classical model are also briefly introduced with reference to a number of practical examples involving the uptake of small molecules by nonporous membranes. Such modifications

prove inadequate in the case of polar molecules and non-polar polymers, for example the {ethanol-water}/silicone rubber system considered in this study. An alternative empirical modification of the classical Flory-Huggins model is suggested to describe the phase equilibria for such systems.

2.2 Multicomponent Diffusion

Diffusion in binary systems is often expressed in terms of the familiar Fick's law:

$$(J_1)_V = -(D)_V \frac{\partial C_1}{\partial z} \quad \text{binary system} \quad (2.1)$$

Here $(J_1)_V$ is the diffusive flux in the direction of flow, $(D)_V$ is the binary diffusion coefficient and $\partial C_1 / \partial z$ is the gradient in molar concentration. We have used the suffix $()_V$ to emphasise that measurement is with respect to a volume-fixed frame of reference. It is of course possible to use another frame of reference and this will be discussed shortly. A binary mixture diffusing through a polymer must be considered as a multicomponent system. Extension of Fick's law to a ternary system is often expressed as:

$$\begin{aligned} -(J_1)_V &= (D_{11})_V \frac{\partial C_1}{\partial z} + (D_{12})_V \frac{\partial C_2}{\partial z} \\ -(J_2)_V &= (D_{21})_V \frac{\partial C_1}{\partial z} + (D_{22})_V \frac{\partial C_2}{\partial z} \end{aligned} \quad \text{ternary system} \quad (2.2)$$

Equation (2.2) accounts for the fact that the gradient in concentration of one component may influence the flux of another component. The important practical implication of such multicomponent effects was recognised by Toor [1957] and is clearly depicted in the Figure 2.1, which is drawn under the assumption of constant $(D)_V$ and $(D_{ij})_V$. In a binary mixture, the flux $(J_1)_V$ is a linear function of $\partial C_1 / \partial z$ and passes through the origin, diffusion is "normal" and along the direction of decreasing concentration. In the ternary mixture, the line of $(J_1)_V$ versus $\partial C_1 / \partial z$ is shifted up (or down) by an amount equal to $(D_{12})_V \partial C_2 / \partial z$ and this leads to a number of phenomena which are absent for the binary system. For example it may so happen that

$(D_{11})_V \partial C_1 / \partial z = -(D_{12})_V \partial C_2 / \partial z$ in which case $(J_1)_V = 0$ and we have what Toor [1957] called a diffusion barrier. On the other hand if $\partial C_1 / \partial z = 0$ but $(D_{12})_V \partial C_2 / \partial z \neq 0$ we have a movement of component 1 even though its own concentration gradient is zero, Toor [1957] called this phenomena osmotic diffusion. If $\partial C_1 / \partial z > 0$ and $\partial C_2 / \partial z < 0$ but $(D_{11})_V \partial C_1 / \partial z + (D_{12})_V \partial C_2 / \partial z < 0$ component 1 may diffuse against its own concentration gradient leading to a region of reverse diffusion.

Figure 2.1 Multicomponent interaction effects [Toor, 1957]

In general, the diffusivities are often strong functions of composition, which makes the problem even more complex. It is the description of such multicomponent effects that makes the subject of mass transport a difficult but fascinating subject. Equation (2.2) as it stands is of little help in gaining an insight into multicomponent diffusion effects. For example there is no formal relationship between the binary diffusivity $(D)_V$ and the multicomponent diffusion coefficients $(D_{ij})_V$. Description of multicomponent diffusion requires a more detailed approach and the review below provides the necessary background.

2.2.1 Diffusive Fluxes and Frames of Reference

The diffusive flux is a measure of the movement of a particular species relative to the movement of the entire mixture. The diffusive flux equation is incomplete and the diffusion coefficients are not properly defined until a particular reference velocity is specified for the mixture. The most convenient frame of reference is dictated by the experimental conditions at hand. The diffusion coefficients defined relative to one frame of reference can always be related to those defined for another frame of reference [Kirkwood *etal*, 1959; Crank, 1975; Taylor and Krishna, 1993]. In this section we give a careful definition of various frames of reference following the procedure developed by Kirkwood *etal* [1959].

We consider isothermal diffusion in a homogeneous multicomponent system containing p components numbered 1 to p with the solvent arbitrarily denoted by p . The flux J_i and concentration C_i will be expressed in molar units. The flux $(J_i)_R$ of component i measured relative to some frame of reference R is related to the flux $(J_i)_S$ of this component relative to another frame S by:

$$(J_i)_R = (J_i)_S + C_i u^{SR} \quad (2.3)$$

where u^{SR} is the velocity of frame S relative to frame R . The most commonly used frames of reference are the mass-fixed, mole fixed, solvent-fixed and volume-fixed frames, which will be denoted by suffixes M , m , P and V respectively. These are defined as:

Mass-fixed frame of reference: This frame is defined such that no net mass flux occurs across a plane moving at the mass average velocity, u^M ,

$$u^M = \sum_{j=1}^p \omega_j u_j \quad (2.4)$$

Here ω_j is the mass fraction and u_j the velocity of species j in the mixture. The diffusive fluxes measured relative to the mass-fixed frame, $(J_i)_M = C_i(u_i - u^M)$, are subject to the constraint:

$$\sum_{j=1}^P M_i(J_j)_M = 0 \quad (2.5)$$

Mole-fixed frame of reference: This frame is defined such that no net molar flux occurs across a plane moving at the molar average velocity, u^m ,

$$u^m = \sum_{j=1}^P x_j u_j \quad (2.6)$$

Here x_j is the mole fraction and u_j the velocity of species j in the mixture. The diffusive fluxes measured relative to the mole-fixed frame, $(J_i)_m = C_i(u_i - u^m)$, are subject to:

$$\sum_{j=1}^P (J_j)_m = 0 \quad (2.7)$$

Solvent-fixed frame of reference: This frame is defined such that there is no net flux of solvent across a plane moving with the solvent velocity, u^P . The diffusive flux in this frame are defined by $(J_i)_P = C_i(u_i - u^P)$ and the diffusive flux of the solvent is zero by definition:

$$(J_P)_P = 0 \quad (2.8)$$

Volume-fixed frame of reference: This frame is defined such that there is no volumetric flux across a plane moving with the volume average velocity, u^V , defined as:

$$u^V = \sum_{j=1}^P c_j \bar{v}_j u_j = \sum_{j=1}^P \phi_j u_j \quad (2.9)$$

Here $\bar{v}_j$ and ϕ_j are the partial molar volume and volume fraction of species j , respectively. Fluxes $(J_i)_V = C_i(u_i - u^V)$ measured relative to this frame are subject to the constraint:

$$\sum_{j=1}^P \bar{v}_j (J_j)_V = 0 \quad (2.10)$$

The flux appearing in differential material balances is relative to stationary coordinates (i.e. the walls of the diffusion cell) and will be denoted by N_i to distinguish it from the diffusive flux, which is denoted by J_i . For any reference frame R, equation (2.3) may be stated as:

$$N_i = (J_i)_R + C_i u^R \quad (2.11)$$

where u^R represents the reference velocity of the mixture. In the case of the mass-fixed frame ($R=M$), writing (2.11) for all components, multiplying by M_j , summing the resultant equations and using (2.5) leads to:

$$u^M = \frac{\sum_{j=1}^p M_j N_j}{\sum_{j=1}^p M_j C_j} \quad \text{mass-fixed frame} \quad (2.12)$$

In the case of the mole-fixed frame ($R=m$), writing (2.11) for all components, summing the resultant equations and using (2.7) leads to:

$$u^m = \frac{\sum_{j=1}^p N_j}{\sum_{j=1}^p C_j} = \frac{\sum_{j=1}^p N_j}{C_t} \quad \text{mole-fixed frame} \quad (2.13)$$

Writing (2.11) for component p (the solvent) in the solvent-fixed frame of reference ($R=P$),

$$N_p = (J_p)_P + C_p u^P$$

and using (2.8) leads to:

$$u^P = \frac{N_p}{C_p} \quad \text{solvent-fixed frame} \quad (2.14)$$

For the volume-fixed frame of reference ($R=V$), multiplying (2.11) by the partial molar volume $\bar{v}_i$, summing over all components and noting that $\sum_{i=1}^p \bar{v}_i C_i = 1$ leads to:

$$u^V = \sum_{i=1}^p \bar{v}_i N_i \quad \text{volume-fixed frame} \quad (2.15)$$

In the absence of concentration gradients, all the frame velocities are identical $u^M = u^m = u^P = u^V$ and equal to the hydrodynamic (bulk) velocity. Within a mass transfer boundary layer, however, there are concentration gradients with different components moving relative to each other. The frame velocities relative to the cell will then be different $u^M \neq u^m \neq u^P \neq u^V$. A convention is therefore required to define the hydrodynamic velocity in a mass transfer boundary layer and it is customary to adopt u^V as the hydrodynamic velocity.

Diffusive transport in multicomponent systems can be described in different ways, among which the empirical generalisation of Fick's law, the phenomenological approach of irreversible thermodynamics and the Stefan-Maxwell formulation have found frequent applications. In the following sections, we present a brief description of the various approaches and their relationship.

2.2.2 The Empirical Generalisation of Fick's law

According to Fick's law, the diffusive flux for a binary system in the mole fixed-frame of reference is given by:

$$(J_1)_m = C_1(u_1 - u^m) = -C_t D_{12} \nabla x_1 \quad (2.16)$$

Here $(J_1)_m$ is the molar flux of component 1, u^m is the mole average velocity, C_t is the total molar concentration and D_{12} is the binary Fick diffusion coefficient. A similar relation may also be written for component 2:

$$(J_2)_m = C_2(u_2 - u^m) = -C_t D_{21} \nabla x_2 \quad (2.17)$$

Noting that in the mole-fixed frame $(J_1)_m + (J_2)_m = 0$, and $\nabla x_1 + \nabla x_2 = 0$, we may conclude that $D_{12} = D_{21} = (D)_m$ and a single diffusivity is sufficient for a binary system.

The generalisation of Fick's law to multicomponent diffusion is a subject with extensive literature [see Bird, 1960; Dunlop *et al* 1972 and Cussler, 1976]. For a ternary system there are only two independent fluxes (J_1 and J_2) and two independent driving forces (∇x_1 and ∇x_2) which must be related to each other using four multicomponent diffusivities:

$$\begin{aligned}(J_1)_m &= -C_t (D_{11})_m \nabla x_1 - C_t (D_{12})_m \nabla x_2 \\ (J_2)_m &= -C_t (D_{21})_m \nabla x_1 - C_t (D_{22})_m \nabla x_2\end{aligned}\tag{2.18}$$

The multicomponent $(D_{ij})_m$ do not have the physical significance of the binary Fick diffusivity and do not in any way reflect i-j interactions. The multicomponent diffusion coefficients required to characterise a ternary system should not be confused with the binary diffusion coefficients $(D)_m$. The cross coefficients may take on positive or negative values and they are not, in general, symmetric $(D_{12})_m \neq (D_{21})_m$. The diffusion coefficients appearing in (2.16) and (2.18) may be termed practical in the sense that they can be obtained from the direct measurement of the concentration profiles in a diffusion apparatus.

For a p-component mixture, the diffusive flux of each component depends on p-1 independent composition gradients:

$$(J_i)_m = -C_t \sum_{k=1}^{p-1} (D_{ik})_m \nabla x_k, \quad k=1,2,\dots,p-1\tag{2.19}$$

We shall find it more convenient to write (2.19) in the compact vector-matrix notation as:

$$-\underline{J}_m = [\underline{D}]_m \nabla \underline{x}\tag{2.20}$$

where $\underline{J}_m = [(J_1)_m, (J_2)_m, \dots, (J_{p-1})_m]^T$, $\nabla \underline{x} = [\nabla x_1, \nabla x_2, \dots, \nabla x_{p-1}]^T$ and $[\underline{D}]_m$ is a

(p-1) x (p-1) matrix of multicomponent diffusion coefficients,

$$[D]_m = \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1,p-1} \\ D_{21} & D_{22} & \dots & D_{2,p-1} \\ \dots & \dots & \dots & \dots \\ D_{p-1,1} & D_{p-1,2} & \dots & D_{p-1,p-1} \end{bmatrix}_m$$

Similar expressions can be developed in the other frames of reference. For example, the generalisation of Fick's law in the volume fixed frame of reference is given by:

$$-\underline{J}_v = [D]_v \nabla \underline{C} \quad (2.21)$$

The matrices $[D]_m$ and $[D]_v$ are in general different but can be related to each other using appropriate transformations [Taylor and Krishna, 1993]. In particular, it can be shown that the multicomponent Fick diffusivity matrices in the various frames have identical eigenvalues [Cullinan, 1965].

2.2.3 The Phenomenological Approach of Irreversible Thermodynamics

Theoretical support for the form of the generalised Fick's law, (2.19), is provided by the postulates of irreversible thermodynamics [Degroot and Mazur, 1962]. The purpose of irreversible thermodynamics is to extend classical thermodynamics to systems in which irreversible processes (e.g. diffusion or heat transfer) are taking place. Such an extension is made possible by assuming that '*local equilibrium*' can be applied for systems '*not too far from equilibrium*'. The first postulate of irreversible thermodynamics is that for systems with small deviation from equilibrium, the thermodynamic state quantities can be defined by the same relationships used for systems at equilibrium. Under isobaric and isothermal conditions, the driving force for diffusion can therefore be taken as the "local" gradient in the specific chemical potential $(\nabla \tilde{\mu}_i)_{T,p}$. The second postulate of irreversible thermodynamics is that a linear relationship exists between the diffusive mass fluxes measured relative to the mass average velocity and the independent driving forces:

$$-(j_i)_M = \sum_{j=1}^{p-1} (\hat{\Omega}_{ij})_M (\nabla \tilde{\mu}_j) \quad (2.22)$$

Here $(\hat{\Omega}_{ij})_M$ are a set of phenomenological transport coefficients and satisfy the Onsager reciprocal relationship:

$$(\hat{\Omega}_{ij})_M = (\hat{\Omega}_{ji})_M \quad (2.23)$$

In this thesis we prefer to work with diffusive fluxes measured in molar rather than mass units $(J_i)_M = (j_i)_M / M_i$ and molar rather than specific chemical potential $(\mu_i)_M = (\tilde{\mu}_i)_M / M_i$. Using the molar quantities we may express (2.22) as:

$$-(J_i)_M = \sum_{j=1}^{p-1} (\Omega_{ij})_M (\nabla \mu_j) \quad (2.24)$$

where $\Omega_{ij} = (\hat{\Omega}_{ij})_M M_i / M_j$ and the Onsager reciprocal relationships (2.23) take the form:

$$\frac{M_j \Omega_{ij}}{M_i} = \frac{M_i \Omega_{ji}}{M_j} \quad (2.25)$$

Equation (2.24) can be written in compact matrix notation as:

$$-\underline{J}_M = [\underline{\Omega}]_M (\nabla \underline{\mu}) \quad (2.26)$$

where $(\nabla \underline{\mu})$ and $\underline{J}_M$ are $(p-1)$ -vectors and $[\underline{\Omega}]_M$ is a $(p-1) \times (p-1)$ matrix. For a ternary system, equation (2.26) reduces to:

$$\begin{aligned} -(J_1)_M &= (\Omega_{11})_M (\nabla \mu_1) + (\Omega_{12})_M (\nabla \mu_2) \\ -(J_2)_M &= (\Omega_{21})_M (\nabla \mu_1) + (\Omega_{22})_M (\nabla \mu_2) \end{aligned} \quad (2.27)$$

The chemical potential μ_i is a function of the independent mole fractions x_1 and x_2 and $(J_i)_M$ may be related to the composition gradients by:

$$(J_1)_M = \left[(\Omega_{11})_M \left(\frac{\partial \mu_1}{\partial x_1} \right)_{x_2} + (\Omega_{12})_M \left(\frac{\partial \mu_2}{\partial x_1} \right)_{x_2} \right] \nabla x_1 + \left[(\Omega_{11})_M \left(\frac{\partial \mu_1}{\partial x_2} \right)_{x_1} + (\Omega_{12})_M \left(\frac{\partial \mu_2}{\partial x_2} \right)_{x_1} \right] \nabla x_2 \quad (2.28)$$

$$(J_2)_M = \left[(\Omega_{21})_M \left(\frac{\partial \mu_1}{\partial x_1} \right)_{x_2} + (\Omega_{22})_M \left(\frac{\partial \mu_2}{\partial x_1} \right)_{x_2} \right] \nabla x_1 + \left[(\Omega_{21})_M \left(\frac{\partial \mu_1}{\partial x_2} \right)_{x_1} + (\Omega_{22})_M \left(\frac{\partial \mu_2}{\partial x_2} \right)_{x_1} \right] \nabla x_2$$

Comparison of (2.28) with (2.18) lends theoretical support for the empirical form used for the generalisation of Fick's law. In particular, the multicomponent Fick diffusivity matrix is shown to be related to the phenomenological coefficients by:

$$C_t \begin{bmatrix} (D_{11})_M & (D_{12})_M \\ (D_{21})_M & (D_{22})_M \end{bmatrix} = \begin{bmatrix} (\Omega_{11})_M & (\Omega_{12})_M \\ (\Omega_{21})_M & (\Omega_{22})_M \end{bmatrix} \begin{bmatrix} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{x_2} & \left(\frac{\partial \mu_1}{\partial x_2} \right)_{x_1} \\ \left(\frac{\partial \mu_2}{\partial x_1} \right)_{x_2} & \left(\frac{\partial \mu_2}{\partial x_2} \right)_{x_1} \end{bmatrix} \quad (2.29)$$

Kinetic coupling Equilibrium coupling

The irreversible thermodynamics approach enables us to separate the kinetic coupling measured by the magnitude of the off-diagonal elements of the matrix $[\Omega]_M$ and the equilibrium coupling measured by the magnitude of the off-diagonal elements of the matrix $[\partial \mu / \partial x]$. The multicomponent Fick diffusivities incorporate both effects and as such often show very complex concentration dependence. It is also important to recognise that the Onsager reciprocal relationship also imposes a relationship between the four multicomponent diffusion coefficients and only three of these parameters can be considered independent.

In the mass transfer literature reference is often made to "thermodynamically corrected Fick diffusivity" or "mobility coefficients" [Mulder and Smolders, 1984; Mears, 1993; Shieh and Huang, 1998]. The relationship of these coefficients with the phenomenological coefficients is obtained by noting that at constant T and P:

$$d\mu_i = RT d \ln a_i \quad (2.30)$$

where a_i is the activity of component i. Using the activity a_i rather than the chemical potential μ_i , enables us to write (2.29) as:

$$\begin{bmatrix} (D_{11})_M & (D_{12})_M \\ (D_{21})_M & (D_{22})_M \end{bmatrix} = \begin{bmatrix} \frac{RT(\Omega_{11})_M}{C_1} & \frac{RT(\Omega_{12})_M}{C_2} \\ \frac{RT(\Omega_{21})_M}{C_1} & \frac{RT(\Omega_{22})_M}{C_2} \end{bmatrix} \begin{bmatrix} x_1 \frac{\partial \ln a_1}{\partial x_1} & x_1 \frac{\partial \ln a_1}{\partial x_2} \\ x_2 \frac{\partial \ln a_2}{\partial x_1} & x_2 \frac{\partial \ln a_2}{\partial x_2} \end{bmatrix} \quad (2.31)$$

The elements of $(D_{ij}^T)_M = RT(\Omega_{ij})_M / C_j$ are referred to as the thermodynamically corrected Fick diffusion coefficients. This is because the elements $x_i \partial \ln a_i / \partial x_j$ are directly related to the variation of the activity coefficients with composition and account for the thermodynamic non-ideality of the mixture. Noting that $a_i = \gamma_i x_i$, we can introduce the equilibrium interaction term Γ_{ij} , defined by:

$$\Gamma_{ij} = x_i \frac{\partial \ln a_i}{\partial x_j} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \quad (2.32)$$

where $\delta_{ij} = 1$ for $i=j$ and $\delta_{ij} = 0$ for $i \neq j$. The Fick diffusivity matrix can therefore be broken into two parts:

$$[D]_M = [D^T]_M [\Gamma] \quad (2.33)$$

where $(D_{ij}^T)_M = RT(\Omega_{ij})_M / C_j$ and the elements of Γ are given by (2.32). Given a model for the variation of the activity coefficients with composition we may calculate the matrix $[\Gamma]$ and recover the thermodynamically corrected diffusivities $[D^T]_M$, which should show a weaker concentration dependence than $[D]_M$.

2.2.4 The Stefan-Maxwell Formulation of Diffusion

The empirical generalisation of Fick's law and the phenomenological approach of irreversible thermodynamics lack a mechanistic model for the diffusion process. As a result, neither the Fick diffusivities nor the phenomenological coefficients may be directly interpreted in terms of the interaction between the i - j pairs in the mixture. There is in effect no relationship between the multicomponent diffusivities and those measured for the constituent binary pairs. Consequently, the binary diffusivities are of little value in describing multicomponent diffusion behaviour using either the generalised Fick's law or the irreversible thermodynamics approach. This would

require a mechanistic model for the diffusion process, which is provided by the Stefan-Maxwell formulation of diffusion based on the kinetic theory of gases.

To understand the basic idea of the Stefan-Maxwell theory, consider a binary system in which a molecule of species 1 has a velocity of u_1 and a molecule of species 2 has a velocity of u_2 . The momentum associated with these molecules is $m_1 u_1$ and $m_2 u_2$ where m_1 and m_2 are the masses of molecules 1 and 2, respectively. The average velocity after an *elastic* collision between these molecules is given by:

$$u_c = \frac{m_1 u_1 + m_2 u_2}{m_1 + m_2} \quad (2.34)$$

The momentum changed in a single collision between a molecule of species 1 and a molecule of species 2 is therefore:

$$\left[\begin{array}{l} \text{The momentum transferred from} \\ \text{a molecule of 1 to a molecule of 2} \\ \text{through a single collision} \end{array} \right] = m_1 (u_1 - u_c) = \frac{m_1 m_2 (u_1 - u_2)}{m_1 + m_2} \quad (2.35)$$

We note that no momentum is lost in a collision between two molecules of the same type. The total momentum lost by molecules of type 1 depends only on its collision with molecules of other types. Such molecules get in the way of a molecule of type 1 and exert a sort of frictional drag hindering its movement. Figure (2.2) shows pictorially the interaction between molecules of type 1 and type 2 in a binary system.

The rate at which the exchange of momentum of molecules of type 1 occurs also depends on the frequency of the collisions:

$$\left[\begin{array}{l} \text{The rate of change} \\ \text{of momentum for} \\ \text{molecules of type 1} \\ \text{per unit volume} \end{array} \right] = \left[\begin{array}{l} \text{Average amount of} \\ \text{momentum exchanged} \\ \text{in a single collision} \end{array} \right] \left[\begin{array}{l} \text{Number of collisions} \\ \text{between 1 - 2 molecules} \\ \text{per unit volume per unit time} \end{array} \right] \\ \propto (u_1 - u_2)(x_1 x_2) \quad (2.36)$$

Figure 2.2 Schematic presentation of interaction between different molecules in a binary system

The first term on the right hand side of (2.36) is given by (2.35) and depends on the velocity difference between the two molecules ($u_1 - u_2$). The second term is proportional to the concentration of the two molecules ($x_1 x_2$). Now according to the second law of motion:

$$\left[\begin{array}{c} \text{The sum of the} \\ \text{forces exerted on} \\ \text{a system} \end{array} \right] \propto \left[\begin{array}{c} \text{The rate of change} \\ \text{of the momentum} \\ \text{of the system} \end{array} \right] \quad (2.37)$$

An expression for the force can be developed for an ideal gas at constant pressure by considering the control volume shown in Figure (2.3), which is assumed to be moving with the molar average velocity of the mixture. There is therefore no net transfer of molecules across the bounding surfaces and no momentum enters or leaves the control volume, as a result of movement of molecules across its boundaries. Within the control volume molecules of type 1 exchange momentum as a result of collision with molecules of other types.

Figure 2.3 Control volume used for the derivation of the Stefan-Maxwell equations

The forces acting on the control volume include surface forces such as pressure forces, shear stresses caused by velocity gradients and body forces such as gravity. For the present discussion we consider only the pressure force exerted on the bounding surfaces of the control volume. The force exerted by molecules of type 1 striking the left-hand surface at position z is $AP_1|_z$ and that exerted at $z + \Delta z$ is $AP_1|_{z+\Delta z}$, where P_1 is the partial pressure of species 1. The net force acting on the species 1 is therefore $A(P_1|_z - P_1|_{z+\Delta z})$. Dividing by the volume $A \Delta z$ and taking the limit as $\Delta z \rightarrow 0$ we find that:

$$\left[\begin{array}{c} \text{Net force acting on molecules of} \\ \text{species 1 per unit volume in the} \\ \text{z direction} \end{array} \right] = \lim_{\Delta z \rightarrow 0} \frac{(P_1|_z - P_1|_{z+\Delta z})}{\Delta z} = -\frac{dP_1}{dz} \quad (2.38)$$

Adding the contribution from the other directions gives:

$$\left[\begin{array}{c} \text{Net force acting on molecules of} \\ \text{species 1 per unit volume} \end{array} \right] = -\nabla P_1 \quad (2.39)$$

Combining (2.36), (2.37) and (2.39) we may conclude that:

$$-\nabla P_1 \propto (u_1 - u_2)(x_1 x_2) \quad (2.40)$$

Introducing a proportionality constant, f_{12} , equation (2.40) can be written as:

$$-\nabla P_1 = f_{12} x_1 x_2 (u_1 - u_2) \quad (2.41)$$

Here ∇P_1 is a measure of the force exerted per unit volume of the mixture trying to move molecules of species 1 through the molecules of species 2 with a relative velocity of $(u_1 - u_2)$; $x_1 x_2$ is a concentration weight factor and f_{12} is a friction factor or drag coefficient. We are free to define the proportionality constant in any way that is convenient to us. Defining it as an inverse drag coefficient, $\mathfrak{D}_{12} = P/f_{12}$, enables us to rewrite (2.41) as:

$$d_1 = \left(\frac{1}{P}\right) \nabla P_1 = \frac{-x_1 x_2 (u_1 - u_2)}{\mathfrak{D}_{12}} \quad (2.42)$$

Here $d_1 = (1/P) \nabla P_1$ is the driving force for diffusion of species 1 in an ideal gas mixture at constant temperature and pressure. The coefficient $\mathfrak{D}_{12}$ is the Stefan-Maxwell diffusivity and has a clear physical interpretation as an inverse drag coefficient. For an ideal gas mixture, the driving force reduces to $d_1 = (1/P) \nabla P_1 = \nabla x_1$ and (2.42) can be simplified to:

$$-\nabla x_1 = \frac{x_1 x_2 (u_1 - u_2)}{\mathfrak{D}_{12}} \quad (2.43)$$

Repeating the same exercise for component 2 leads to:

$$-\nabla x_2 = \frac{x_1 x_2 (u_2 - u_1)}{\mathfrak{D}_{21}} \quad (2.44)$$

Noting that $\nabla x_1 + \nabla x_2 = 0$, it follows that the Stefan-Maxwell binary diffusion coefficients are symmetric: $\mathfrak{D}_{12} = \mathfrak{D}_{21}$ and as expected a single diffusivity suffices for a binary system.

For a mixture containing p species, (2.42) can be generalised as:

$$d_i = - \sum_{j=1}^p \frac{x_i x_j (u_i - u_j)}{\mathfrak{D}_{ij}} \quad (2.45)$$

Since the $\mathfrak{D}_{ij}$ are defined in terms of driving force, d_i , and the difference in components velocities, $(u_i - u_j)$, and both of these are independent of a frame of

reference, the $\mathfrak{D}_{ij}$ are also frame independent. Using the definition of molar fluxes relative to stationary co-ordinates, $N_i = C_i u_i$, the velocities can be eliminated from (2.45) to give:

$$d_i = \sum_{j=1}^p \frac{[x_i N_j - x_j N_i]}{C_t \mathfrak{D}_{ij}} \quad (2.46)$$

It should be noted that only $p-1$ of the driving forces are independent and the driving force for component p is obtained from the restriction:

$$\sum_{j=1}^p d_j = 0 \quad (2.47)$$

Equation (2.45) or (2.46) is the basic flux equation based on the Stefan-Maxwell formulation for a multicomponent mixture.

The driving force for an ideal gas mixture was shown to be the gradient in mole fraction. However, in liquids and solids we can no longer assume that only binary (two molecule) collisions takes place, three (or more) molecule collisions occur frequently in such systems and contribute to the momentum transfer process. Therefore, it is difficult to develop an analysis of liquid or solid diffusion in exactly the same form as that for ideal gases. However, the physical significance of (2.45) may be applied equally well to liquids or solids. It does not matter whether the frictional drag arises purely from intermolecular collisions as in the case of an ideal gas or from intermolecular forces between two sets of molecules which is the dominating factor in liquids and solids. The derivation of suitable expressions for the driving force in non-ideal fluids will be considered in chapter 5 of this thesis.

To summarise, three different approaches can be used to describe the multicomponent diffusion process. The various approaches are all equivalent and the choice depends on the practical problem at hand and the level of detail required. The Stefan-Maxwell diffusivities, $\mathfrak{D}_{ij} = \mathfrak{D}_{ji}$, are amenable to physical interpretation in terms of intermolecular friction or drag. This physical significance can be retained even when other external forces such as pressure gradients and electrostatic potential gradients are present. The Stefan-Maxwell coefficients are also independent of the

choice of reference frame, and this makes the analysis of mass transport much simpler. The Fick diffusion coefficients incorporate both the frictional and the thermodynamic interactions and in this sense can exhibit complex composition dependence. The elements of the Fick diffusivity matrix are not open to simple physical interpretation. On the other hand, the Fickian formulation is more easily introduced into the continuity equations and in this sense they are often referred to as 'practical'. The phenomenological coefficients introduced by the irreversible thermodynamic approach allow the separate evaluation of the kinetic and equilibrium coupling but like the Fick diffusivities do not present a clear picture of the transport behaviour. A major shortcoming of the phenomenological approach is that the binary diffusion coefficients can not be used to describe the multicomponent behaviour. In contrast, the binary Stefan-Maxwell diffusivities retain their physical significance in multicomponent mixtures and can be used in their description. A drawback of the Stefan-Maxwell formulation is that it delivers the driving forces in terms of fluxes, which makes its application less straightforward. In contrast, both the generalised Fick's law and the irreversible thermodynamic approach give the fluxes in terms of the driving forces and are therefore easier to apply.

2.2.5 Diffusion and Convection: *diffusion induced bulk flow*

For systems that exhibit a volume change on mixing unequal diffusive flow of the various species can induce an extra contribution to any hydrodynamic (non-selective) flow present. The diffusive flux $(J_i)_R$ for any frame of reference is unaffected by the magnitude of the hydrodynamic flow. An independent relationship for calculating the diffusion-induced contribution to the hydrodynamic flow was obtained by Kirkwood *et al* [1959]. We shall consider the volume-fixed frame, but the same treatment can be employed for any reference frame R. The flux relative to stationary co-ordinates is given by:

$$N_i = (J_i)_V + C_i u^V \quad (2.48)$$

Differentiating the above equation with respect to distance z , multiplying by $\bar{v}_i$ and

summing over all components and noting that $\sum_{i=1}^P \bar{v}_i C_i = 1$ leads to:

$$\sum_{i=1}^p \bar{v}_i \left(\frac{\partial N_i}{\partial z} \right) = \sum_{i=1}^p \bar{v}_i \left(\frac{\partial (J_i)_v}{\partial z} \right) + \left(\frac{\partial u^v}{\partial z} \right) + u^v \sum_{i=1}^p \bar{v}_i \left(\frac{\partial C_i}{\partial z} \right) \quad (2.49)$$

The left hand term and the last term on the right hand side of (2.49) are identically zero. Differentiating the relationship $\sum_{i=1}^p \bar{v}_i C_i = 1$ with respect to z leads to:

$$\sum_{i=1}^p \bar{v}_i \frac{\partial C_i}{\partial z} = - \sum_{i=1}^p C_i \frac{\partial \bar{v}_i}{\partial z} \quad (2.50)$$

The term on the right hand side of (2.50) is identically zeroed as a consequence of the Gibbs-Duhem equation. Similarly, using the Gibbs-Duhem equation, it can be shown that:

$$\sum_{i=1}^p \bar{v}_i \frac{\partial C_i}{\partial t} = - \sum_{i=1}^p C_i \frac{\partial \bar{v}_i}{\partial t} = 0 \quad (2.51)$$

The continuity equation for the cell co-ordinate system is:

$$\left(\frac{\partial C_i}{\partial t} \right) = - \left(\frac{\partial N_i}{\partial z} \right) \quad (2.52)$$

Multiplying (2.52) by $\bar{v}_i$ and summing over all components, we can conclude that the resulting term, $\sum_{i=1}^p \bar{v}_i \frac{\partial (N_i)}{\partial z}$ appearing on the left-hand side of (2.50) is zero. At any given instant the variation of u^v must therefore satisfy the partial differential equation:

$$\left(\frac{\partial u^v}{\partial z} \right) = - \sum_{j=1}^p \bar{v}_j \left(\frac{\partial (J_j)_v}{\partial z} \right) \quad (2.53)$$

To integrate the differential equation (2.53) we must specify the boundary conditions appropriate to the system at hand. As an illustrative example consider the diffusion cell shown in Figure 2.4 which is open at the top and has a tap at the bottom from which liquid is withdrawn at a volumetric flux (velocity) $q_0(t)$. The exit flow is clearly a function of time and depends on the liquid height remaining in the cell. If

there is no concentration gradient in the cell the diffusive fluxes $(J_i)_v$ are all zero.

Integration of (2.49) with the boundary condition $u^v(0, t) = q_0(t)$ then leads to:

$$u^v(z, t) = u^v(0, t) = q_0(t) \quad \text{see Figure 2.4B}$$

That is at any instant the hydrodynamic velocity is the same at every position z in the cell and equal to the exit velocity. If a concentration gradient is present, equation (2.53) can be integrated by parts from the exit $z=0$ to any position z to give:

Figure 2.4 Variation of the hydrodynamic velocity in a diffusion cell containing a boundary layer

$$u^v(z, t) - u^v(0, t) = -\sum_{i=1}^p \bar{v}_i (J_i)_v + \int_0^z \sum_{i=1}^p (J_i)_v \left(\frac{\partial \bar{v}_i}{\partial z} \right)_t dz$$

Noting that $-\sum_{i=1}^p \bar{v}_i (J_i)_v = 0$ and $u^v(0, t) = q_0(t)$ leads to:

$$u^v(z, t) = q_0(t) + \int_0^z \sum_{i=1}^p (J_i)_v \left(\frac{\partial \bar{v}_i}{\partial z} \right)_t dz \quad \text{see Figure 2.4A} \quad (2.54)$$

The integral on the right hand side of (2.54) is an extra contribution to the non-selective flow that may arise as a result of diffusion. For systems which do not exhibit a volume change on mixing, $\bar{v}_i$ is constant and this extra contribution is zero. For systems which exhibit a volume change on mixing, $\bar{v}_i$ is a function of composition and we may express (2.54) as:

$$u^V(z, t) = q_0(t) + \int_0^z \sum_{k=1}^p (J_i)_V \left(\frac{\partial \bar{v}_i}{\partial C_k} \right)_t \left(\frac{\partial C_k}{\partial z} \right)_t dz \quad (2.55)$$

Noting that $(J_i)_V \propto \Delta C_i / \Delta z$ we may conclude that the integral is of the order of $(\Delta C_i / \Delta z)^2$. Consequently, diffusion induced bulk flow can also be safely ignored when the gradients in concentration are sufficiently small.

2.2.6 Concentration Dependence of Membrane Diffusivity

Diffusion of small molecules in polymeric membranes can show strong concentration dependency. A relationship describing the variation of the diffusion coefficient with concentration is therefore desired to characterise the transport process. The concentration dependence of the diffusion coefficient in polymeric membranes is often expressed by an empirical relationship. An exponential form has been frequently used for transport of a single component across a membrane [Brun *et al* 1985, Sferrazza *et al* 1988]:

$$D_{ip} = D_{ip}^0 \exp(\zeta_i \phi_i) \quad (2.56)$$

Here D_{ip}^0 is the diffusion coefficient in a dilute solution, ϕ_i is the solute volume fraction and ζ_i is called the plasticisation factor. A positive (negative) value of ζ_i implies an increasing (decreasing) diffusion coefficient with concentration. Extension of this relationship to the transport of a binary liquid mixture was considered by Mulder and Smolders [1984]:

$$D_{ip} = D_{ip}^0 \exp[\zeta_i (\phi_i + B_{ij} \phi_j)] \quad (2.57)$$

Here B_{ij} is a parameter introduced to allow for potential diffusion coupling. For a ternary system, there are three empirical parameters for each solute, two of these (D_{ip}^0

and ζ_i) can be found from binary diffusion data but the third B_{ij} requires ternary diffusion data.

A number of empirical relationships have also been proposed to predict the binary mixture diffusivities from the infinite dilution diffusion coefficients in the form of a simple function of composition. For a binary system containing component 1 and 2, Caldwell and Babb [1956] proposed a linear expression:

$$D_{12} = x_2 D_{12}^0 + x_1 D_{21}^0 \quad (2.58)$$

where D_{ij}^0 is the diffusion coefficient of component i infinitely diluted in component j . The linear form (2.58) has limited applicability and a more flexible relationship was suggested by Vignes [1966]:

$$D_{12} = (D_{12}^0)^{x_2} (D_{21}^0)^{x_1} \quad (2.59)$$

The Vignes relationship has been applied to several binary liquid systems with some success [Kooijman and Taylor, 1991]. In addition, the form of Vignes relationship is such that it may be usefully extended to multicomponent systems. We shall defer a discussion of the multicomponent extension of the Vignes relationship to chapter 5.

A theoretical description of the concentration dependence of the diffusion coefficient is clearly desired since the number of parameters in the empirical expressions grows with the number of components. The key question is whether the thermodynamically corrected diffusion coefficient is a function of concentration. The best known theoretical approach available is the free volume theory developed by Fujita [1961], see also Masaro and Zhu [1999] and modified by Verentas and Duda [1977] and is considered next. Unfortunately, the free volume theory is often applied to the uncorrected diffusivities which as we shall show may lead to erroneous conclusions. Free volume theory also fails for diffusion of small polar solutes in hydrophobic polymers, which show a systematic deviation from this theory.

2.2.6.1 Free Volume Theory

The diffusion of small organic molecules in polymeric membranes is often described by the free volume theory of Fujita [1961] which is based on the work of

Doolittle [1951, 1952] on diffusion in liquids. Doolittle defined the free volume in a liquid as the difference between the total observed volume and the volume occupied by the constituent molecules. This free volume is generated randomly as a result of thermal expansion of the initial closed pack core volume at 0 °K. Fujita assumed that Doolittle's definition applies to each jumping unit in a polymer-solute system. A jumping unit was considered as a single molecule and a polymer segment of similar size. For a polymer above its glass transition temperature (rubbery state) a number of physical parameters change considerably faster with temperature in comparison to the glassy state. Figure 2.5 shows the variation of the specific volume of a typical polymer as a function of temperature. The free volume of the polymer above the glass transition temperature is taken as:

$$V_f = V_T - V_0 \quad (2.60)$$

Figure 2.5 Specific volume of a polymer above and below the glass transition temperature T_g

The total volume of a polymer at a particular temperature, V_T , is obtained from the polymer density whereas the volume occupied by the constituent molecules at 0 °K, V_0 , can be estimated by group contribution methods [Reid *etal*, 1987]. The dimensionless fractional free volume, v_f , is defined as:

$$v_f = \frac{V_f}{V_T} \quad (2.61)$$

For a binary polymer solution v_f is a function of the temperature T and the volume fraction ϕ ; $v_f = v_f(\phi, T)$. Fujita related the fractional free volume to the molar friction coefficient, f , which is in turn related to the thermodynamically corrected diffusion coefficient by the Stokes-Einstein expression:

$$D^T = RT/f(\phi, T) \quad (2.62)$$

The molar friction coefficient was related to the fractional free volume by a relationship of the form:

$$\ln f(\phi, T) = \ln A + Bv_f(\phi, T) \quad (2.63)$$

where A and B are constants. Combining (2.62) and (2.63) leads to:

$$\ln[D^T(\phi, T)/RT] = -\ln A - Bv_f(\phi, T) \quad (2.64)$$

For a pure polymer $\phi=0$ and D^T reduces to the diffusion coefficient of the solute at infinite solution D_0^T :

$$\ln[D_0^T(\phi, T)/RT] = -\ln A - Bv_f(0, T) \quad (2.65)$$

Combining (2.64) and (2.65) gives the working equation of the free volume theory for diffusion in polymers:

$$\ln(D^T/D_0^T) = B\left(\frac{1}{v_f(0, T)} - \frac{1}{v_f(\phi, T)}\right) \quad (2.66)$$

The advantage of Fujita's theory is that viscosity data for particular polymers can be used to evaluate the free volume parameters. Limited isothermal diffusion data are then needed to find D_0^T and B .

Free volume theory indicates that at a given temperature T the variation of the thermodynamically corrected diffusion coefficient, D^T , depends on the fractional free

volume of the solute in the polymer $v_f(\phi, T)$. For systems with $v_f(\phi, T) > v_f(0, T)$ the diffusion coefficient will increase with increasing uptake of solute. This is observed experimentally for many molecules that show a high affinity for the polymer matrix. The diffusion coefficient for some systems can exhibit a maximum with increasing concentration of solute in the membrane. This is due to volume change of mixing, which may cause $v_f(\phi, T)$ to fall below $v_f(0, T)$. Figure 2.6 compares the experimental data for diffusion coefficient of toluene in polystyrene with the predicted values based on Fujita's free volume theory. Vrentas and Duda [1977] have extended the free volume theory and a review of this extended theory is given by Mears [1993]. Further simplification is possible for systems exhibiting negligible volume change of mixing. Assuming volume additivity, we may set:

$$v_f(\phi, T) = v_f(0, T) + \phi [v_{fs}(0, T) - v_f(0, T)] \quad (2.67)$$

Figure 2.6 Concentration dependence of toluene diffusion coefficient in polystyrene at 110 °C. o: experimental data, dashed line: Fujita, solid line: Vrentas and Duda [reproduced from Mears, 1993]

where $v_{fs}(0, T)$ is the fractional free volume of the pure solute. Inverting equation (2.66) and substituting for $v_f(\phi, T)$ from (2.67) gives:

$$\frac{1}{\ln(D_0^T/D_0)} = \frac{v_f(0, T)}{B} \left[1 + \frac{1}{\phi} \frac{v_f(0, T)}{v_{fs}(0, T) - v_f(0, T)} \right] \quad (2.68)$$

The variation of the fractional free volume of pure polymers with temperature follows the relationship [Fox and Flory 1950]:

$$v_f(0, T) = v_f(0, T_g) + \Delta\alpha(T - T_g) \quad (2.69)$$

It turns out that the parameter $\Delta\alpha$ and $v_f(0, T_g)$ have similar values for most polymers and $v_f(0, T)$ is therefore easily accessible. Plotting the left-hand side of (2.68) against $1/\phi$ should give a straight line and the values of B and $v_{fs}(0, T)$ can be found from the intercept and slope of this line. As a typical example Figure 2.7 shows the variation of the diffusion coefficient of methanol in polyvinyl acetate (PVA) at several temperatures:

Figure 2.7 Concentration dependence of the diffusion coefficient of methanol in polyvinyl acetate at various temperatures. o: data, —: Eq. (2.68), (a) 45 °C, (b) 35 °C, (c) 25 °C, (d) 15 °C [reproduced from Mears, 1993]

2.2.6.2 Deviation from Free Volume Theory

The practical diffusion coefficient for many systems, particularly those involving hydrogen bonding molecules and hydrophobic polymers, shows a rapid initial fall with increasing solute volume fraction. This is usually taken as a deviation from the free volume theory, which suggests an initial increase in the diffusion coefficient. This deviation is usually attributed to the clustering of the solute within the polymer matrix. It must be noted, however, that the free volume theory deals with

the thermodynamically corrected rather than the practical diffusion coefficient. Clustering phenomena should only be considered after the practical diffusion coefficient has been corrected to account for thermodynamic non-idealities, a point that is frequently ignored. This is well demonstrated by the erroneous conclusions reached by Sun and Chen [1994] on the basis of the practical diffusion coefficients. The experimental data of Sun and Chen [1994] for diffusion of ethanol, xylene and toluene in silicone rubber is reproduced in Figure 2.8. The uncorrected ethanol diffusivity exhibits a marked maximum while those of xylene and toluene show a marked decrease with increasing solute volume fraction. Sun and Chen [1994] concluded that none of these systems follows the free volume theory. We have used the equilibrium data reported by Sun and Chen [1994] to correct the practical diffusion coefficients for thermodynamic nonideality and the results are also shown on Figure 2.8. It is notable that the corrected diffusion coefficient of ethanol does not exhibit a maximum and those of xylene and toluene are almost constant over the entire range of data. Within the accuracy of the data, the thermodynamically corrected diffusion coefficients do not contradict the free volume theory.

A genuine case of deviation from the free volume theory is shown by the data of Favre et al [1994] for diffusion of water and low molecular weight alcohols in silicone rubber. Figure 2.9 shows the practical diffusion coefficient reported by Favre et al [1994] for methanol and n-butanol in silicone rubber. The thermodynamically corrected values were also calculated using the equilibrium data reported by the same authors and are shown for comparison. Both the practical and the corrected diffusion coefficients decrease with the volume fraction of the solute in the polymer. The initial decrease in the corrected diffusion coefficient cannot be explained on the basis of the free volume theory. Favre *et al* [1994] suggested that this is due to the clustering of the polar solute molecules inside the non-polar polymer matrix.

It should also be noted that the application of the Fujita free volume theory is restricted to single component diffusion in polymers. An extension of the free volume theory to diffusion of binary mixtures in polymers was reported by Verentas and Duda [1977]. However, the application of the extended theory requires a large amount of data, which is not normally available. In the case of polar solutes and hydrophobic

polymers the free volume theory proves inadequate and we are forced to consider empirical relationships.

Figure 2.8 Variation of the practical and the corrected diffusion coefficient of (a) ethanol, (b) xylene and (c) toluene in silicone rubber at 40 °C; [∇ - practical diffusivity from Sun and Chen (1994), — thermodynamically corrected diffusivity]

Figure 2.9 Variation of the practical and the corrected diffusion coefficient of (a) methanol and (b) n-butanol in silicone rubber at 40 °C [---▽--- practical diffusivity from Favre *et al* (1994), — thermodynamically corrected diffusivity]

2.3 Multicomponent Sorption

Separate evaluation of the equilibrium and kinetic contribution to the transport process within a polymeric membrane demands an independent determination of the sorption equilibria. This requires both the measurement of the uptake by the membrane and the development of a suitable thermodynamic model of the sorption process. A major contribution to the driving force for transport is the chemical potential gradient and the chemical potential of all solutes contributes to the flux of an individual species:

$$(J_i)_m = -\sum_{j=1}^{p-1} (\Omega_{ij})_m \left(\frac{\partial \mu_j}{\partial z} \right) = -\sum_{j=1}^{p-1} \sum_{k=1}^{p-1} (\Omega_{ij})_m \left[\frac{\partial \mu_j}{\partial C_k} \right]_{T,P} \left(\frac{\partial C_k}{\partial z} \right) \quad (2.70)$$

A thermodynamic model of sorption is required to enable the direct evaluation of the $(\partial \mu_j / \partial C_k)$ terms appearing above.

Independent measurement of sorption equilibria for a gas or vapour is usually done with a vacuum microbalance [Chandak *et al*, 1997 and 1998] or pressure decay method [Bondar *et al*, 1999 and Hilic *et al*, 2000]. In the case of vapours, special attention should be paid to capillary condensation problems close to the saturation pressure. The measurement of uptake from liquids proves more difficult. In such measurements, a dry membrane of known mass is contacted with a liquid of known composition. At equilibrium, the membrane is *removed* from the liquid, its surface dried and the total uptake measured by weight. The composition of the sorbed phase can also be obtained using a thermal desorption apparatus [Mulder and Smolders, 1983]. This procedure suffers from the difficulty of obtaining a *clean* separation of the membrane from the free liquid. Evaporative loss of the sorbed liquid during handling is another source of error. In the case of volatile solutes with low uptake the above difficulties may lead to substantial error and limit the validity and thermodynamic consistency of the measured data.

A practical alternative for systems with small uptake is to determine the relative sorption isotherm, which can be measured without removing the membrane from the free liquid. The experimental relative sorption isotherm can be used to serve two useful purposes. First it provides a direct check on the reliability of the total

uptake measurement without the need for a priori theoretical assumptions. Second, if the measured total sorption is not available or is unreliable, the relative sorption isotherm can be used to establish the individual amount of the various species adsorbed using a suitable thermodynamic model.

A distinction must also be made between rigid and non-rigid sorbents. In the case of 'rigid' solids, such as molecular sieve crystals, the internal volume accessible to the solute is relatively easy to establish [Farhadpour and Bono 1988]. Polymeric matrices are not rigid and may swell as a result of sorption, which can alter the accessible volume within the matrix. For non-rigid matrices, it is also necessary to measure the equilibrium swelling of the polymer in addition to the amount and composition of the sorbed phase. However, accurate swelling measurement is only possible when the extent of swelling is considerable and becomes impractical for systems with low uptakes.

2.3.1 Relative and Total Sorption

Consider contacting a known mass M of a dry membrane with N_0 moles of a liquid with an initial mole fraction of x_{i0} and let x_i be the free liquid mole fraction at equilibrium. The easily accessible experimental quantity is the relative sorption η_i defined as [Kipling, 1965]:

$$\eta_i = \frac{N_0}{M} (x_{i0} - x_i) \quad (2.71)$$

The relative sorption η_i can be determined without removing the membrane from the free liquid. The total amount and composition of the sorbed phase are related to the relative sorption η_i by a simple material balance:

$$\eta_i = N^s (x_i^s - x_i) \quad (2.72)$$

where N^s is the total amount sorbed per unit of mass of the dry membrane and x_i^s is the binary mole fraction in the sorbed phase.

Two consequences of the definition of the relative sorption by (2.72) should be clearly appreciated. First, the relative sorption for a pure liquid is zero by definition.

Second, for a p-component mixture, only p-1 of the $\eta_1, \eta_2, \eta_3, \dots, \eta_p$ are independent; this is because $\sum \eta_i = 0$ by definition and one of the η_i is therefore fixed by this constraint. Consequently, the measurement of the relative sorption isotherm alone is not sufficient to establish the total amount and composition of the sorbed phase uniquely; an extra independent relationship is required for this purpose. Ideally this extra relationship should be obtained by direct experimental measurement of the total uptake N^s . However, for volatile solutes with low uptake the direct measurement of the total uptake becomes impractical. In such cases the extra relationship required could be obtained by adopting a model isotherm expression, which entails a priori assumptions about the nature of the sorbed phase. Here, we also note that the measurement of the relative sorption isotherm provides a simple but powerful check on the consistency of the total uptake data for any liquid/membrane system. This is simply because for any liquid membrane system, $N^s \geq 0$ and $|x_i^s - x_i| \leq 1$ by definition and therefore we must have:

$$|\eta_i| \leq N^s \quad \text{at all compositions}$$

The above constraint must be satisfied at any composition irrespective of the nature solutes and the membrane.

2.3.2 Thermodynamics of Sorption

In the absence of reliable total uptake data, a thermodynamic model is required to establish the extent and composition of the adsorbed phase. The general criterion for equilibrium between a liquid mixture and a polymer can be expressed as:

$$\mu_i^{\text{liq}}(T, P, x_i) = \mu_i^{\text{mem}}(T, P, x_i) \quad (2.73)$$

To develop a model we start by considering the relationship between the Gibbs free energy, enthalpy and entropy of mixing in a polymer solution:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.74)$$

where all quantities are expressed in molar units. Different models are obtained by adopting suitable expressions for the composition dependence of ΔH_m and ΔS_m . The chemical potential can then be simply obtained by differentiating the resultant ΔG_m :

$$\left[\frac{\partial(n\Delta G_m)}{\partial n_i} \right]_{T,P,n_j} = \mu_i = \mu_i^0 + RT \ln a_i \quad \text{at constant } T \text{ and } P \quad (2.75)$$

Here a_i denotes the activity of component i relative to a reference state with chemical potential μ_i^0 .

Systems containing molecules of widely different molar volume can exhibit non-ideality simply on the basis of size difference. In the case of a small solute and a large polymer molecule, therefore, mole fraction does not represent a convenient measure of concentration. Flory [1953] recognised this and suggested that a better measure of concentration for a polymer solution is the volume fraction:

$$\phi_i = \frac{n_i \bar{v}_i}{\sum_{i=1}^P n_i \bar{v}_i} = \frac{x_i \bar{v}_i}{\sum_{i=1}^P x_i \bar{v}_i}$$

Here n_i , x_i and $\bar{v}_i$ denote the number of moles, mole fraction and partial molar volume of component i , respectively.

2.3.2.1 The Classical Flory-Huggins Model

Flory considered a lattice with each solute molecule confined to a box and each polymer chain divided into segments with a size comparable to that of the solute molecule, see Figure 2.10. Segments of the polymer chain must occupy adjacent sites in the lattice, which restricts the number of possible configurations. Flory demonstrated that the configurational entropy of mixing, ΔS_{cf} , for a pure solute-polymer system (i.e. a binary solution) is given by:

$$\Delta S_{cf} = -R(x_1 \ln(\phi_1) + x_p \ln(\phi_p)) \quad (2.76)$$

where $z = (\bar{v}_p / \bar{v}_1)$. Flory (1953) recognised that the interaction between the polymer and the solute molecules can also contribute to the entropy of mixing. He suggested that the interaction parameter χ_{1p} might be considered as a free energy parameter. The main consequence of this argument is that despite the less well-defined physical meaning of the term ' $RT\chi_{1p}$ ' the form of equations (2.76) and (2.77) are preserved. The parameter χ_{1p} may in such cases show a dependence on concentration and can no longer be assumed constant.

The interaction parameter, χ_{1p} , can be obtained from a single experiment with a pure liquid. For a pure liquid in equilibrium with a polymer, $a_i^{liq} = a_i^{men} = 1$ and hence from (2.79):

$$\chi_{1p} = - \left[\frac{\ln(1 - \phi_p) + \phi_p}{\phi_p^2} \right] = - \left[\frac{\ln\phi_1 + (1 - \phi_1)}{(1 - \phi_1)^2} \right] \quad (2.80)$$

Note that as ϕ_1 diminishes the numerical value of χ_{1p} increases, indicating a decreasing affinity between the polymer and the solute.

The Flory-Huggins model can be easily extended to multicomponent systems. For a binary liquid mixture and a polymer (a ternary system), the free energy of mixing is given by:

$$\Delta G_m = RT[x_1 \ln \phi_1 + x_2 \ln \phi_2 + x_p \ln \phi_p + \chi_{12}x_1\phi_2 + \chi_{1p}x_1\phi_p + \chi_{2p}x_2\phi_p] \quad (2.81)$$

where subscripts 1 and 2 refer to the sorbed components and subscript p to the polymer. The solute-polymer interactions are characterised by χ_{1p} and χ_{2p} whilst χ_{12} is a measure of the interaction between the sorbed molecules within the matrix. The activities of the different components are again obtained by differentiating equation (2.81):

$$\begin{aligned} \ln a_1 = \ln \phi_1 + (1 - \phi_1) - \phi_2(\bar{v}_1 / \bar{v}_2) - \phi_p(\bar{v}_1 / \bar{v}_p) \\ + (\chi_{12}\phi_2 + \chi_{1p}\phi_p)(\phi_2 + \phi_p) - \chi_{2p}(\bar{v}_1 / \bar{v}_2)\phi_2\phi_p \end{aligned} \quad (2.82)$$

$$\begin{aligned} \ln a_1 = \ln \phi_2 + (1 - \phi_2) - \phi_1(\bar{v}_2 / \bar{v}_1) - \phi_p(\bar{v}_2 / \bar{v}_p) \\ + (\chi_{12}\phi_1(\bar{v}_2 / \bar{v}_1) + \chi_{2p}\phi_p)(\phi_1 + \phi_p) - \chi_{1p}(\bar{v}_2 / \bar{v}_1)\phi_1\phi_p \end{aligned} \quad (2.83)$$

The above equations can be further simplified by noting that $\bar{v}_i \ll \bar{v}_p$ and dropping terms involving $\bar{v}_i / \bar{v}_p$:

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) - \phi_2 (\bar{v}_1 / \bar{v}_2) + (\chi_{12} \phi_2 + \chi_{1P} \phi_P)(\phi_2 + \phi_P) - \chi_{2P} (\bar{v}_1 / \bar{v}_2) \phi_2 \phi_P \quad (2.84)$$

$$\ln a_1 = \ln \phi_2 + (1 - \phi_2) - \phi_1 (\bar{v}_2 / \bar{v}_1) + (\chi_{12} \phi_1 (\bar{v}_2 / \bar{v}_1) + \chi_{2P} \phi_P)(\phi_1 + \phi_P) - \chi_{1P} (\bar{v}_2 / \bar{v}_1) \phi_1 \phi_P \quad (2.85)$$

Given the liquid phase activities and the interaction parameters χ_{1P} , χ_{2P} and χ_{12} , the volume fraction in the membrane can be calculated by solving the above equations. The interaction parameter χ_{1P} and χ_{2P} can in principle be obtained from pure liquid/polymer data using equation (2.80). The solute-solute interaction within the polymer matrix χ_{12} can be determined from liquid/vapour equilibrium data.

For a pure vapour-polymer system, the sorption isotherm according to the Flory-Huggins model is:

$$\ln(a_1) = \ln(p/p_1^0) = \ln \phi_1 + (1 - \phi_1) + \chi_{1P}(1 - \phi_1)^2 \quad (2.86)$$

where p is the pressure and p_1^0 is the saturation vapour pressure of the solute. Figure 2.11 shows the pure vapour sorption isotherm for three different values of χ_{1P} .

Figure 2.11 Variation of pure vapour uptake with activity predicted by the classical Flory-Huggins model

Figure 2.12 shows the individual isotherms and the total uptake calculated from the Flory-Huggins model for sorption of a binary liquid mixture in two different polymers. Figure 2.12A is for a polymer showing a higher affinity for component 1, while Figure 2.12B is for a polymer with equal affinity for either solute. The bulk liquid is taken as {ethanol-water} solution at 25 °C in both cases.

Figure 2.12 Individual and total uptake of a binary mixture in a polymer with (A) higher affinity for component 1 and (B) equal affinity for either component

2.3.2.2 Modification of the Flory-Huggins Model

In the classical Flory-Huggins model the interaction parameters χ_{iP} are assumed to be constant. This assumption has proved appropriate for numerous

polymer-solvent systems, especially elastomeric polymers swollen by good solutes. However, the original Flory-Huggins model with constant χ_{iP} can not describe the experimental sorption data of certain systems, in particular the uptake of polar solutes by hydrophobic membranes [Favre *et al*, 1994]. In such cases it is necessary to employ a concentration dependent χ_{iP} in order to fit the observed data. Often a purely empirical approach is used and χ_{iP} is expressed in terms of a suitable function of the volume fraction, $\chi_{iP} = \chi_{iP}(\phi_1, \phi_2)$ [Mulder and Smolders, 1984]. The empirical approach is unsatisfactory as it lacks predictive power and the number of parameters grows with the number of components. A number of attempts have been made to provide usable theoretically based modifications of the classical Flory-Huggins model. These are based on the modification of the enthalpic and/or the entropic terms in the classical Flory-Huggins model. It must be recognised, however, that such modifications will inevitably introduce additional model parameters.

Modified enthalpic contribution:

Koningsveld and Kleinjens [1971] proposed a modification based on the assumption that the enthalpy of mixing is related to the surface fraction rather than the volume fraction of the solute. This modification leads to the following expression for the variation of χ_{iP} with the polymer volume fraction:

$$\chi_{iP} = \alpha + \frac{\beta(1-\omega)}{(1-\omega\phi_p)^2} \quad (2.87)$$

The above equation contains three adjustable parameters (α, β, ω) which can be determined by a fit of the experimental sorption data for a pure solute. The modified equation has proved adequate for a number of systems [Favre *etal*, 1994]. This is demonstrated in Figure 2.13, which compares the classical Flory-Huggins isotherm with a constant interaction parameter with one based on the above enthalpic modification.

Figure 2.13 Sorption isotherm of (A) methanol and (B) butanol in silicone rubber at 40 °C calculated by the classical model and the enthalpic modification of the Flory-Huggins model [reproduced from Favre *et al*, 1994]

A) Classical: $\chi_{1P} = 1.84$, Modified: $\alpha = 1.562$, $\beta = 0.147$, $\omega = 0.943$

B) Classical: $\chi_{1P} = 1.33$, Modified: $\alpha = 0.942$, $\beta = 0.254$, $\omega = 0.883$

Modified entropic contribution:

Lichtenthaler [1974] proposed a modification of the entropic term in the classical Flory-Huggins model aimed at accounting for the differences between size and the surface/volume ratio of the polymer and the solute molecules. The resulting isotherm expression takes the form:

$$\ln a_1 = \left[\ln \phi_1 + \phi_p - k(\ln \phi_1 + k' \phi_p) + (1 - k')\phi_p \right] + \chi_{1P} \phi_p^2 \quad (2.88)$$

This expression contains two additional constants k and k' which are related to the molecular size and shape. Favre *et al* [1993] have demonstrated that this entropic modification is incapable of describing the sorption data of polar solutes in non-polar polymers.

Finally, we should mention that the sorption data for a number of systems can not be explained by either the enthalpic or the entropic modifications of the classical Flory-Huggins model. Notable amongst these is the uptake of water by hydrophobic polymers, which exhibits the general shape shown in Figure 2.14.

Figure 2.14 Sorption isotherm of water in silicone rubber at 40 °C [Naguyen *et al*, 1996]

The value of χ_{1P} required so that the classical Flory-Huggins model fits the experimental isotherm exactly at any (a_1, ϕ_1) can be calculated from:

$$\chi_{1P} = \left[\frac{\ln \phi_1 + (1 - \phi_1) - \ln(a_1^v)}{-(1 - \phi_1)^2} \right] \quad (2.89)$$

and is shown in Figure 2.15 as a function of the solute volume fraction. It is evident that a simple relationship $\chi_{1P} = \chi_{1P}(\phi_1)$ capable of describing such complex behaviour is unlikely.

Figure 2.15 Interaction parameter χ_{1P} as a function of volume fraction in polymer (water/silicone rubber system)

A practical alternative is to relate the liquid/polymer interaction parameter χ_{1P} to the activity a_1 rather than the volume fraction ϕ_1 . This leads to the relatively simple variation shown in Figure 2.16. It should be noted, however, that this procedure produces an implicit equation,

$$\ln(a_1) = \ln \phi_1 + (1 - \phi_1) + \chi_{1P}(a_1)(1 - \phi_1)^2 \quad (2.90)$$

which must be solved iteratively to establish the isotherm.

Figure 2.16 Interaction parameter χ_{1p} as a function of activity for the (water/silicone rubber system)

2.4 Summary

The analysis of multicomponent diffusion requires careful attention to a number of points. First, diffusive fluxes and diffusion coefficients can be defined using a variety of reference velocities. The most appropriate choice is dictated by the physical situation at hand and must be clearly stated for a given problem. Second, diffusion in multicomponent systems exhibits a number of effects that are absent in a binary system. In particular, the flux of each species is driven not only by its own composition gradient but also by the gradient in the composition of other species. Consequently, the diffusive fluxes in multicomponent systems may be strongly coupled due to thermodynamic non-ideality (equilibrium coupling) and frictional interactions caused by the relative movement of the species (kinetic coupling). The analysis of multicomponent diffusion is complicated by the need to account for the potential coupling of fluxes. Third, unequal diffusive fluxes may induce an extra non-selective contribution to any bulk movement present. Finally, in the case of diffusion in polymeric systems the diffusion coefficients are usually a very strong function of composition that makes the analysis difficult.

Three different approaches, the empirical generalisation of Fick's law, the phenomenological approach of irreversible thermodynamics and the mechanistic Stefan-Maxwell formulation of multicomponent diffusion were briefly reviewed. The three approaches are largely equivalent and interrelated and the choice depends on the problem at hand and the level of detail required. In the empirical generalisation of Fick's law, the driving force is taken as the composition gradient and this approach is most easily introduced into the continuity equations. The multicomponent Fick diffusivities must, however, account for both equilibrium and kinetic coupling effects and as such show very complex composition dependence. The irreversible thermodynamic approach recognises that the true driving force for diffusion is the gradient in chemical potential. This enables the separate evaluation of equilibrium and kinetic coupling effects but requires independent information on the thermodynamic non-ideality of the multicomponent mixture. Using such information it is possible to develop the thermodynamically corrected multicomponent Fick diffusivities which are intended to account for kinetic coupling alone. We shall use the irreversible thermodynamic approach in Chapter 4 to develop a phenomenological model and test its performance for transient dialysis and pervaporation of {ethanol-water} mixtures across a silicon rubber membrane.

A major draw back of both the generalised Fick's law and the irreversible thermodynamic approach is that the associated diffusion coefficients are not open to simple physical interpretation. For example, there is no simple relationship between the multicomponent diffusivities and those measured for the binary pairs in the mixture. In addition, the multicomponent diffusivities defined in either approach depend on the choice of the mixture reference velocity employed. The inclusion of the diffusion-induced contribution to the non-selective bulk flow is also difficult within the formulation of the generalised Fick's law or irreversible thermodynamic approach. This contribution is often ignored but can play a significant role in systems with large uptake [Kamaruddin and Koros, 1997].

Such difficulties are largely overcome by the mechanistic Stefan-Maxwell formulation of multicomponent diffusion that is based on the kinetic theory of gases. The Stefan-Maxwell diffusivities are frame independent and have a clear physical interpretation in terms of the frictional interaction between the molecules within the

mixture. In particular, the binary Stefan-Maxwell diffusion coefficients retain their physical significance and may be used directly to interpret complex multicomponent behaviour. The Stefan-Maxwell formulation gives the fluxes relative to the stationary co-ordinates directly and any contribution to the non-selective bulk flow is automatically included. In many membrane separation processes an external potential is employed to assist the separation, for example a large pressure difference is employed in reverse osmosis and an electrical potential is applied across the membrane in electro-dialysis. A significant advantage of the Stefan-Maxwell formulation is that both external and internal (chemical potential gradient) driving forces can be easily accommodated without affecting the physical significance of the diffusion coefficients. A disadvantage of the Stefan-Maxwell formulation is that it delivers the driving forces in terms of the fluxes that makes its application in the continuity equations less straightforward. We shall use the Stefan-Maxwell formulation in chapter 5 to develop a *generic* model of multicomponent membrane transport and assess its performance for dialysis and pervaporation of the {ethanol-water}/silicon rubber system.

The transport of small solutes through nonporous polymeric membranes also raises a number of specific issues. In particular the diffusion coefficients in such systems are known to be a strong function of composition. Ideally such composition dependence should be catered for theoretically. The free volume theory of Fujita [1961] is often used for this purpose and was briefly reviewed. This theory can provide a good description for diffusion of single non-polar solutes in non-polar polymers but fails in the case of polar molecules diffusing in hydrophobic polymers, for example the {ethanol-water}/silicon rubber system considered in this study. In such cases, we are forced to resort to an empirical description of the concentration dependence of the diffusion coefficients. Among the various empirical relationships available, the Vignes [1966] relationship used for binary systems is identified as a procedure which can be naturally extended to multicomponent systems.

Irrespective of the procedure used for describing the diffusion process, the separate evaluation of the equilibrium and kinetic contributions to the mass transport process within the membrane requires an independent measurement of the multicomponent sorption equilibria and its description in terms of a suitable

thermodynamic model. Accurate swelling and uptake measurement are only possible when the extent of swelling is considerable and become impractical for systems with low uptake. A practical alternative for such systems is to measure the relative sorption isotherm, which can be obtained without removing the polymer from the liquid. A thermodynamic model can then be used to characterise the multicomponent sorption using only the relative sorption isotherm.

The basic sorption process in polymeric systems, in particular elastomers, is usually described in terms of the classical Flory-Huggins model [1953], which accounts for the large size difference between the solute and polymer molecules. The basic concepts underpinning the classic model were briefly reviewed and the enthalpic and entropic modifications proposed to improve its performance for the uptake of polar solutes were highlighted using a number of practical examples. These modifications prove unsatisfactory for the uptake of water and ethanol in silicon rubber. It was demonstrated that a semi-empirical modification of the classic model using activity dependent interaction parameters gives a good description of such systems and may be used to describe the sorption equilibria for systems such as the {ethanol-water}/silicon rubber system considered in this study.

CHAPTER 3

TRANSIENT DIALYSIS AND PERVAPORATION: DATA FOR {ETHANOL-WATER}/SILICONE RUBBER SYSTEM AND NUMERICAL PROCEDURES

3. Transient Dialysis and Pervaporation: data for {ethanol -water}/silicone rubber system and numerical procedures.

3.1 Introduction

The description of multicomponent transport across nonporous polymers is based on a variety of solution-diffusion models which contain a large number of equilibrium and diffusive parameters [eg Lee 1975, Mulder and Smolders 1984, Bansal 1988, Doong *etal* 1995, Shieh and Huang 1998]. Furthermore, both the equilibrium and diffusive parameters appearing in the model are usually highly concentration dependent. The evaluation of the model parameters and discrimination between the various models of membrane transport require substantial amount of experimental data, which is not normally available. The model parameters are also often highly system specific and small changes in the polymer material can cause radical changes in the solubility and/or diffusivity of the permeating species. Consequently, the data measured using a silicon/rubber membrane supplied by one manufacturer cannot be confidently used to describe the behaviour of one supplied by another manufacturer. Indeed, measurable differences are often observed even for different batches of a polymeric membrane supplied by the same manufacturer.

A critical theoretical examination of multicomponent transport demands experimental data measured for the same polymer under various operating conditions. The conventional techniques for the experimental investigation of multicomponent membrane transport are usually based on the measurement of the steady state fluxes. Such measurements do not, in general, carry sufficient information to enable the confident evaluation of the individual contributions to the overall transport process. In addition, the resistance to transport across the stagnant boundary layer adjacent to the membrane often exerts a marked influence on the overall performance. In many cases the external boundary layer resistance is either ignored completely or is treated on the basis of an assumed shape for the boundary layer concentration profile. Consequently, different sets of parameter values or even different theoretical models can often be used to "fit" the measured steady state flux data to the same accuracy. Conventional steady state techniques also frequently require large membrane area and large volume

of feedstock; which can become limiting in the case of expensive or experimental membranes or pharmaceutical and biotechnology products.

The experimental measurement of transient fluxes coupled with transient models of the transport process within the polymer enables a more critical assessment of the membrane transport phenomena. We are fortunate in having access to transient data measured for {ethanol(1)-water(2)} mixtures by previous workers [Bansal 1988, Abdel-Ghani 1992] in our research group for the same 143 μm thick silicon rubber membrane supplied by Dow-Corning (Silastic 500-1). Bansal [1988] used a novel non-intrusive laser interferometer to measure the evolution of the concentration profiles in the liquid bathing the membrane under transient dialysis conditions. Subsequently, Abdel-Ghani [1992] measured the transient pervaporation flux of pure water, pure ethanol and their mixtures using the same polymeric membrane.

The transient methods and procedures developed by Bansal [1988] and Abdel-Ghani [1992] are rather unusual and their interpretation requires a clear understanding of the apparatus employed and will be described in sufficient detail in this chapter. In particular, the interpretation of the interferometric data demands a rigorous treatment of the path of light rays in a medium of varying refractive index. Failure to account for deflection of light in such a medium can cause substantial error and is dealt with rigorously in this chapter. Transient models of multicomponent dialysis and pervaporation constitute a highly coupled set of partial differential equations that do not admit an analytical solution. The numerical solution of these partial differential equations is a major source of resistance to the development and acceptance of the more informative transient experimental techniques. A general procedure based on the method of lines is described which can handle the multicomponent transient models of membrane transport in their full complexity. The chapter is closed with a sensitivity analysis for a hypothetical model system, which serves to describe the parameter extraction procedures.

3.2 Transient Pervaporation Measurements of Abdel-Ghani [1992]

The measurement of pervaporation flux is usually carried out under steady state conditions by pulling a vacuum at the lower membrane interface and attempting to maintain a constant composition at the upper membrane interface. The total mass flux is measured by weighing the permeate collected in a nitrogen cold trap and its composition is obtained by analysis. This procedure suffers from two drawbacks. First, a cross-flow of liquid must be maintained across the top membrane interface which inevitably leads to the formation of a hydrodynamic boundary layer and a stationary concentration profile close to the upper membrane surface. There is, therefore, an additional resistance to mass transfer in the upper liquid which is often ignored altogether or at best is treated using an assumed shape for the stationary concentration profile. Second, the total flux measured by collection in the cold trap is prone to error due to the potential carry over of condensable material through the cold trap. Abdel-Ghani [1992] developed an alternative procedure that eliminates the cross-flow altogether and allows a transient, rather than stationary, concentration profile to develop in a closed liquid compartment. The total transient mass flux of the permeating species was measured directly and continuously by a novel arrangement measuring the fall in the liquid level. The composition of the permeate was measured by analysing the contents of material collected in a cold trap.

A schematic of the apparatus used by Abdel-Ghani [1992] is shown in Figure 3.1. The pervaporation cell was constructed by modifying a high vacuum flange with a copper o-ring seal (supplied by Edwards High Vacuum, UK) and is also shown schematically in Figure 3.1. The flange was machined to accept an open sintered disc which supported the membrane and gave a free area of 10 cm diameter. Provisions were also made for attaching a thermocouple and a capacitance manometer to the vapour chamber. Two capacitance manometers (Edwards High Vacuum, UK) were used by Abdel-Ghani [1992] to cover the 0-10 mbar and the 0-1000 mbar ranges accurately. The pressure in the vapour chamber was closely controlled using a PID controller and control valve (Edwards High Vacuum) that adjusted the flow of a nitrogen gas leak into the vacuum line. The permeate was collected in two nitrogen cold traps placed in series using a by-pass arrangement which enabled the removal of the first cold trap without interrupting the process. The permeate composition was

determined by analysing the contents of this cold trap by gas chromatography. All the experiments were conducted in a temperature controlled room maintained at 25 ± 0.05 °C.

Figure 3.1 Schematic of pervaporation apparatus used by Abdel-Ghani [1992]

A special mercury seal was constructed by Abdel-Ghani [1992] to enable the precise measurement of the transient total mass flux from the movement of the liquid in the upper compartment. A schematic of the seal is shown in Figure 3.2 and is essentially a hollow cylinder with a 0.5 mm deep groove machined on its outer surface. The cylinder fitted tightly in a 2 cm diameter precision bore glass tube leaving a small gap. The seal is obtained by filling the hollow cylinder with mercury, which flows to the outside rim filling the gap between the cylinder and the glass and provides a gas and liquid tight seal. The total mass leaving the upper compartment was measured continuously by monitoring the movement of the cylinder using a Linear Voltage Displacement Transducer (LVDT) supplied by Schlumberger Industries, UK which was accurate to better than $0.15\ \mu\text{m}$

Figure 3.2 Special Mercury Seal and Level Measurement Device of Abdel-Ghani [1992]

The silicon rubber membrane was supplied by Dow-Corning (Silastic 500-1) in flat sheet form and was pre-equilibrated with the feed solution before use. To start a run, the membrane was clamped in the pervaporation cell and the top chamber and the precision bore glass tube were filled with the feed liquid. The empty seal cylinder was inserted in the glass tube and mercury introduced to form the seal. The run was

started by turning on the vacuum pump and nitrogen gas supply and recording the fall in the liquid level continuously. Abdel-Ghani [1992] reports that the permeate pressure settled to the desired set-point in under 100 second for all the runs. After 1 hour, the removable cold trap was isolated and the composition of the permeate was determined by gas chromatography. Table 3.1 shows the results obtained by Abdel-Ghani [1992] for pervaporation of different feed mixtures at a permeate pressure of 0.5 mbar. Table 3.2 gives the variation of the pure pervaporation flux with the permeate pressure measured by Abdel-Ghani [1992].

Table 3.1 Total permeation flux and permeate composition at 3600 s [Abdel-Ghani, 1992]

Feed Ethanol wt %	Flux (g/m ² h)	Permeate Ethanol wt %
0.000	13.78	0.000
0.030	16.21	0.195
0.060	18.88	0.324
0.199	31.33	0.616
0.300	41.28	0.738
0.450	51.82	0.804
0.600	62.44	0.837
0.800	77.50	0.875
0.900	96.72	0.924
0.950	119.88	0.962
1.000	181.19	1.000

Table 3.2 Variation of pure component pervaporation flux with permeate pressure
Abdel-Ghani, 1992]

Ethanol		Water	
Permeate pressure Mbar	Flux (g/m ² h)	Permeate pressure mbar	Flux (g/m ² h)
0.5	181.19	0.5	13.78
2.0	180.95	2.0	11.28
5.0	175.70	5.0	8.98
10.0	171.45	10.0	6.98
25.0	150.87		
50.0	121.11		
60.0	90.37		

3.3. Transient Interferometric Measurements of Bansal [1988]

Interferometry has long been used for the quality control of optical components, the precise measurement of distances, the accurate measurement of refractive indices [Baird and Hanes 1967] and also provides a highly accurate and non-intrusive technique for the examination of diffusive phenomena [Cussler 1976]. The application of this technique to the measurement of liquid phase diffusion coefficients, particularly for macromolecules, dates back to the elegant studies of Gosting *etal* [1949]. Table 3.3 lists the reported applications of interferometry to mass transport across membrane interfaces. A major obstacle to the quantitative application of interferometry in membrane transport is the interpretation of the interference pattern, which is severely complicated by the deflection of light in a medium of varying refractive index. Consequently, the majority of the reported interferometric investigations of membrane transport have been largely confined to the observation of the fringe pattern and stop short of a quantitative analysis. In particular, the influence of light deflection is either ignored altogether or is accounted for under assumptions which can not be justified a priori; see Table 3.3.

A variety of interferometers differing in mechanical design [Baird and Hanes 1967] can be used in the examination of membrane transport phenomena. These have been classified by Muller [1973] who has also discussed the relative merits of using one type over another. Most interferometers are capable of measuring one and two dimensional refractive index fields but the majority of practical applications have dealt with only a one-dimensional field. From a practical point of view, the two most important criteria in selecting a particular interferometer are the ease of alignment and the accuracy attainable. The Twyman-Green interferometer employed by Bansal [1988] is particularly easy to align. It is, however, a two-pass interferometer in which the light beam traverses the liquid medium twice. This, as pointed out by Muller [1973], complicates the analysis beyond that needed with a single pass interferometer.

Table 3.3 Interferometric investigation of membrane transport phenomena

Authors	Process	Interferometer	Light Deflection
Robinson (1950)	Sorption	Fabry-Perot	NO
Crank & Robinson (1950)	Sorption	Fabry-Perot	NO
Sargent & Ashbee (1982)	Sorption	Fizeau	NO
Stamatialis <i>etal</i> (1997)	Sorption	Fizeau	NO
Spiegler <i>etal</i> (1965)	Electrodialysis	Fabry-Perot	NO
O'Brien (1975)	Electrodialysis	Holographic	NO
Clifton (1982)	Electrodialysis	Holographic	YES♣
Langer (1982)	Electrodialysis	Mach-Zehnder	YES♣
Shaposhnik <i>etal</i> (1995)	Electrodialysis	Mach-Zehnder	NO
Shaposhnik <i>etal</i> (1997)	Electrodialysis	Mach-Zehnder	NO
Shaposhnik <i>etal</i> (2000)	Electrodialysis	Mach-Zehnder	NO
Johnson (1971)	Reverse Osmosis	Mach-Zehnder	NO
Welinder (1974)	Reverse Osmosis	Holographic	NO
Belfort <i>etal</i> (1976)	Reverse Osmosis	Mach-Zehnder	NO
Mahlab <i>etal</i> (1978)	Reverse Osmosis	Mach-Zehnder	YES♣
Lerche & Kott (1971)	Dialysis	Mach-Zehnder	NO
Lerche & Wolf (1971)	Dialysis	Mach-Zehnder	NO
Lerche (1976)	Dialysis	Mach-Zehnder	NO
Bollenbeck (1973)	Dialysis	Rayleigh	YES♣
O'Brien & Zhao (1984)	Dialysis	Holographic	NO
Bansal (1988)	Dialysis	Twyman-Green	YES
Vasil'eva <i>etal</i> (2001)	Dialysis	Mach-Zehnder	NO

♣ Under simplifying assumption

A schematic of the Twyman-Green interferometer used by Bansal [1988] is shown in Figure 3.3. The light source is a He/Ne laser with a wavelength of $\lambda=0.6328 \mu\text{m}$. The light from the aperture A1 is collimated by the lens L1 and is then split into two beams at the partially reflecting surface of the beam splitter S1. The two resultant coherent beams travel to the mirrors M1 and M2 respectively and are reflected back so that they return and recombine at S1 to produce an interference pattern. One arm of the interferometer, S1M1, contains the optical diffusion cell OC through which the

light beam passes twice. The interference fringes obtained depend at any given point on the relative phase retardation between the sample and reference beams. The phase retardation depends in turn on the optical path length difference between the two arms, which is due primarily to the passage of one beam through the optical cell. The optical components used in Bansal's instrument were of a quality better than $\lambda/10$ and were mounted on high precision adjustable mounts (all were supplied by SPECAC, UK). The entire optical assembly was mounted on a single polished stone block supported on a rigid steel framework mounted on anti-vibration pads (TICO pads).

Figure 3.3 Schematic diagram of the Twyman-Green interferometer and associated equipment used by Bansal [1988]

The Twyman-Green interferometer can be arranged to produce different types of interference fringe pattern [Baird and Hanes 1967]. In Bansal's study [1988] the apparatus was set up so that in the absence of a refractive index gradient straight identical fringes were obtained. This is achieved by keeping the reference mirror M2 perpendicular to the axial ray from the collimating lens L1 while the other mirror M1 is kept at a slight angle to this ray. The orientation of the fringes can be changed by tilting the mirror M1 in the X-Z plane and the fringe spacing (i.e. the number of fringes observed) can be altered independently by tilting the mirror M1 in the X-Y plane. If the optical cell contains a medium of varying refractive index, the fringes appear curved as shown in Figure 3.3. The task of the theoretical analysis, which will be described subsequently, is to recover the refractive index profile in the optical cell from the extent of deflection of the original straight fringes.

The optical diffusion cell employed by Bansal [1988] is shown schematically in Figure 3.4 and was constructed from a single sheet of 5 mm thick borosilicate optical glass (refractive index 1.4720). The cell consisted of two separate halves each equipped with capillary inlet and outlet flow lines. The membrane sample used was a rectangular (12mm x 60mm) strip of a 143 μm thick unsupported silicon rubber membrane (Silastic 500-1) supplied by Dow-Corning. The membrane strip was placed between the two halves of the cell, which were then clamped together in a specially designed holder. This gave a 2mm wide exposed membrane surface with the unexposed area acting as a gasket, which obviated the need for any sealant or grease. The diffusion cell was manufactured by a specialist optical firm (Optiglass, UK) with parallel walls and highly polished flat surfaces to reduce edge diffraction effects. The holder containing the optical diffusion cell was mounted on a precision translation table, which enabled the positioning of the membrane relative to the light beam with accuracy better than 2 μm .

All experiments were conducted in a temperature controlled room maintained at 25 ± 0.05 $^{\circ}\text{C}$ and the ethanol/water mixtures were made up by weight using Anal-R grade ethanol (>99.7 %) and double distilled de-ionised water. Prior to each run, the membrane sample was soaked for a prolonged period in the solution to be used in the top half of the cell. It was then clamped in the optical cell and the same solution was passed through both halves of the cell for a further six hours to ensure equilibrium

was fully established. All flows through the cell were gravity controlled using the arrangement shown in Figure 3.4. At this stage the cell should contain a uniform solution and the interference fringes corresponding to either half must therefore appear straight. The interferometer was used to confirm that this was the case and minor adjustments were made to mirror M1 to orient the fringes vertically; this mirror was then locked into position and was not further disturbed.

Figure 3.4 The optical diffusion cell and the filling arrangement used by Bansal [1988]

To initiate a run, the solution in the lower half of the cell was replaced with a mixture of lower composition by connecting the bottom inlet capillary line to the second solution reservoir. The time delay in replacing the bottom solution must be kept to a minimum to avoid excessive mass transfer during the filling period. The volume of the lower half of the cell was about 2.5 cm^3 and a flow rate of about $150 \text{ cm}^3/\text{min}$ was used to minimise the filling time. The interferometer was again used to check this stage of operation and in all cases the fringes corresponding to the lower half of the cell re-stabilised to straight lines in less than 10 seconds. At this point all flows through the cell were stopped and diffusion across the membrane was allowed to proceed between two static liquids of differing composition. Four experiments were conducted by Bansal [1988] with 0-3, 0-6, 15-20 and 25-30 wt%, starting ethanol concentration in the bottom and top halves of the cell respectively and each individual run was allowed to proceed for at least 1 hour.

The variation of the fringe pattern with time was monitored continuously via a camera and recorded on a video system with a real time clock and an electronic grid superimposed on the image. The clock was accurate to 0.01 s and the fringe pattern could be recorded at 25 frames/s. The continuous monitoring and recording of the fringe pattern offers significant advantages over the traditional method based on discrete photographic exposure. In particular, each stage of the experiment can be checked on-line and any spurious disturbances caused by convection currents and unwanted leaks from the diffusion cell are immediately apparent. With photographic techniques such artifacts can only be detected after the film has been developed and then only if a sufficient number of sequential exposures are available.

Figure 3.5 shows selected interference patterns recorded by Bansal [1988] for a typical run with the {ethanol-water}/silicon rubber system. The instantaneous fringe pattern is presented at successively longer time to highlight the fringe deflection. Initially, the interference pattern consists of two sets of straight equidistant fringes with a dividing grey area corresponding to the membrane shadow, see Figure 3.5a. As diffusion is allowed to proceed a concentration (and hence a refractive index) profile develops close to the membrane surfaces which causes the deflection of the fringes from their original position. In theory the fringes on a given instantaneous interference pattern should be identical. In practice, however, there is a variation in

intensity and minor differences between individual fringes: this is due to imperfections in the optical components and the presence of dust particles on the optical surfaces. Such statistical errors were minimised by considering 5-10 fringes to establish the location of an "average" fringe. Each fringe corresponds to a contour of constant optical path; the fringe deflection is therefore a measure of the optical path length difference caused by the presence of a refractive index profile in the cell. Experimental data from an interference fringe is obtained by measuring the extent of the fringe deflection at various heights above the membrane shadow.

(a) $t = 7$ seconds

(b) $t = 601$ seconds

(c) $t = 756$ seconds

(d) $t = 1213$ seconds

(e) $t = 3012$ seconds
top half

(f) $t = 3150$ seconds
bottom half

Figure 3.5 Selected interference patterns for diffusion of ethanol-water across silicon-rubber at 25°C reproduced from Bansal [1988]
(top liquid: 6 wt% ethanol, bottom liquid: water)

The image analysis and digitisation of the fringe pattern exerts a critical influence on the accuracy of the results recovered from interferometric techniques. In particular, direct visual measurement of the fringe deflection is prone to substantial error and must be avoided; the best visual resolution attainable is about $0.1f$ where f represents the distance between successive fringes. The resolution can be improved through a variety of sophisticated photographic techniques and Muller [1973] reports that resolutions approaching $0.001f$ can be obtained by such methods. Photographic techniques are however extremely time consuming and demand considerable expertise. Fortunately, the development of modern electronic image analysis equipment has largely obviated the need for such laborious methods. Bansal [1988] employed a Quantimet 920 image analyser (Cambridge instruments, UK) and details of the image analysis procedure are given in his PhD thesis. With this instrument Bansal [1988] was able to achieve a routine resolution better than $0.02f$ and in many cases the resolution obtained was better than $0.005f$.

3.4 Theoretical Interpretation of the Fringe Patterns

The rigorous and accurate interpretation of the fringe pattern is the key to the quantitative application of interferometry in membrane transport phenomena. In the majority of previous applications (see Table 3.3) this has been based on oversimplistic assumptions which can cause substantial error and ambiguity in the results obtained. The purpose of this section is to point out the potential sources of error and present a rigorous analysis that avoids such errors. The theory presented in this section was used to develop a self-standing ray tracing programme which generates the theoretical fringe corresponding to a given refractive index profile in the diffusion cell. Matching of the theoretical and experimental fringes offers an opportunity for extracting the model parameters.

Consider Figure 3.6 which compares the idealised fringe pattern corresponding to the top half of the optical cell at the start of an experiment $t=0$ with that at time t . For the present we need only consider the path of light through the cell liquid. The contribution from the cell walls and the air gaps separating the optical components will be considered subsequently. At the start of the experiment the light beam traverses a medium of constant refractive index n_b and all the rays pass through undeflected. For a two-pass system, the geometric path length of each ray is then

identical and equal to twice the cell width $2L$. The fringes observed at this time are identical vertical lines and we may therefore concentrate on any one of them. Let us consider the fringe labelled $\lambda=0$ on Figure 3.6, the optical path length $P(Y)$ at a vertical height Y above the top edge of the membrane shadow is therefore:

$$P(Y) = 2Ln_b \quad \text{for any } Y \text{ at time } t=0$$

Next let us consider the same fringe (labelled $\lambda=0$) at time t and examine its deflection from its original vertical position at $t=0$. The light arriving at height $Y > Y_b$ has again traversed through a medium with a constant refractive index and its optical path length is therefore unaltered:

$$P(Y_b) = 2Ln_b \quad \text{for any } Y > Y_b \text{ at time } t$$

The light arriving at height Y_1 (i.e. point m_1) is however deflected by one fringe spacing and its optical path length is therefore:

$$P(Y_1) = 2Ln_b + \lambda \quad \text{for } Y=Y_1 \text{ at time } t$$

Figure 3.6 Comparison of idealised straight fringes at time $t=0$ with those after some time t

Similarly, the light arriving at height Y_2 (ie point m_2) is deflected by two fringe spacing so that:

$$P(Y_2) = 2Ln_b + 2\lambda \quad \text{for } Y=Y_2 \text{ at time } t$$

It follows that the optical path length of the light arriving at an arbitrary height $Y < Y_b$ is given by:

$$P(Y) = 2Ln_b + \left(\frac{M}{f}\right)_Y \lambda \quad \text{for } Y < Y_b \text{ at time } t \quad (3.1)$$

where $(M/f)_Y$ is the extent of fringe deflection measured at height Y relative to the fringe spacing f . Thus given the cell width L and the bulk liquid refractive index n_b , the variation in the optical path length $P(Y)$ can be calculated from the deflection measured on the experimental interference pattern. The remaining task is to recover the unknown refractive index profile in the liquid $n(Y)$ from the experimentally determined optical path length variation $P(Y)$.

3.4.1 Simplified Analysis: no light deflection

The calculation of the refractive index profile $n(Y)$ is greatly simplified if the deflection of light in a medium of varying refractive index is ignored. The geometric path of each ray can then be equated to twice the cell width $2L$, and the refractive index profile is simply given by:

$$n(Y) = \frac{P(Y)}{2L} = n_b + \frac{1}{2L} \left(\frac{M}{f}\right)_Y \lambda \quad (3.2)$$

The majority of reported interferometric studies of membrane transport have used the above simple and highly convenient expression. Unfortunately, this simplistic approach incurs substantial error which invalidates the results obtained. This is because (3.2) is only valid in the presence of very small refractive index gradients. In membrane transport, however, the concentration (hence the refractive index) gradient

increases as the liquid/membrane interface is approached and is at its highest at the interface.

Before discussing the influence of light deflection it is instructive to consider the resolution attainable with the Twyman-Green interferometer. From (3.2) the detectable refractive index change δn is given by:

$$\delta n = \frac{\lambda}{2L} \delta \left(\frac{M}{f} \right)$$

The image analysis procedure used by Bansal [1988] provided a routine resolution of $0.02f$ in the fringe deflection, ie $\delta(M/f)=0.02$. For a He/Ne laser ($\lambda=0.6328 \mu\text{m}$) and a 2 mm wide cell, the detectable refractive index change is therefore $\delta n=3 \times 10^{-6}$. Evidently, the Twyman-Green interferometer is a highly sensitive instrument capable of measuring minute refractive index variations. Another important factor is the closest distance to the membrane surface at which a measurement can be made. This is limited only by edge diffraction from the flat surfaces of the optical diffusion cell, which is largely confined to a distance equivalent to 5-10 wavelengths of the incident beam [Born and Wolf 1965]. For the simple cell design and the He/Ne laser ($\lambda=0.6328 \mu\text{m}$) used in Bansal's work [1988] measurement could be made at distances as close as $5 \mu\text{m}$ from the membrane surface. This was confirmed by Bansal [1988] by measuring the thickness of the membrane in-situ from its shadow on the interference pattern and comparing the result with the independently measured physical dimensions of the membrane.

3.4.2 Errors Caused by Ignoring Light Deflection

Consider a medium in which the index of refraction varies in the Y direction as shown in Figure 3.7. A given ray passing through this medium is deflected towards regions of higher refractive index and follows a curved geometric path. According to Fermat's principal of least time [Born & Wolf 1965] this geometric path is uniquely determined by the extremum of the integral:

$$P(Y) = \int n(Y) ds \quad (3.3)$$

Expressing the differential arc length, ds , in terms of the cell co-ordinates allows us to write:

$$P(Y) = \int_0^{2L} n(Y) \left[1 + \left(\frac{dY}{dX} \right)^2 \right]^{1/2} dX \quad (3.4)$$

A classical application of the calculus of variation reveals that the extremum of integral (3.4) occurs for a geometric path which must satisfy the non-linear differential equation:

$$\frac{d^2Y}{dX^2} = \frac{1}{n(Y)} \left[1 + \left(\frac{dY}{dX} \right)^2 \right] \frac{dn(Y)}{dY} \quad (3.5)$$

The detailed derivation of equation (3.5) can be found in most textbooks on optics [eg Born and Wolf 1965] and a lucid interpretation is given by Feynman [1964].

Figure 3.7 Geometric path of a light ray in a medium of varying refractive index

We can now quantify the error caused by ignoring light deflection for a known refractive index profile. For a given profile $n(Y)$, the differential equation (3.5) can be integrated numerically and the result substituted in (3.4) to determine the optical path length variation $P(Y)$. This can then be compared with the values calculated through equation (3.2), which ignores light deflection. A general error analysis can be easily performed for a semi-infinite medium with a linear refractive index $n(Y) = kY$ where k is an arbitrary constant, see Figure 3.8. Muller [1973] has reported such

calculations for a single pass interferometer. In the case of a two pass interferometer however, the path taken through the cell walls and air gaps must also be accounted for. In particular, Snell's law of refraction must be applied at all liquid/glass and air/glass interfaces to determine the direction of a given ray on its return journey through the cell.

Figure 3.8 Geometric path of a light ray through a diffusion cell with a linear refractive profile (—true path, ---- no light deflection)

Figure 3.9 presents the results of an error analysis for various cells with identical wall thickness but different widths as a function of the refractive index gradient k . The ordinate on this graph is the difference in the optical path lengths calculated with and without light deflection expressed in terms of the fringe spacing f . It is clear that the error grows with both the cell width and the sharpness of the refractive index profile. The magnitude of the error is substantial when we consider that for a 2mm wide cell the deflection observed on the experimental fringes shown in Figure 3.5 does not exceed 2 fringe spacing.

Figure 3.9 General plot of error caused on ignoring light deflection in a semi-infinite medium with a linear refractive index profile

Ignoring light deflection causes two types of error. The first is an error in the optical path length because a deflected ray travels longer and encounters a variable refractive index on its path. A second less obvious error is revealed on considering a medium with a more realistic curved refractive index profile. This is depicted schematically in Figure 3.10 where for simplicity only a single path is shown. In the absence of light deflection (*dashed line*) the entire region above the membrane surface is illuminated and is open to observation. Now consider the true path of a ray (*solid line*) entering at the liquid/membrane interface. This ray is deflected away from the membrane towards regions of higher refractive index and exits the cell at some distance above the membrane; consequently, the region of the liquid lying below this exit point will not be illuminated. The fringes in the top half of the cell are therefore shifted vertically and the upper edge of the membrane shadow does not correspond to the true position of the top liquid/membrane interface. Failure to recognise this optical shift will invalidate the deflection measured on the experimental fringe pattern. We should also note that this optical shift is a transient error and its magnitude depends on the slope of the refractive profile close to the liquid/membrane interface.

Figure 3.10 Optical Shift of interference fringes in a medium with a refractive index profile decreasing away from the membrane surface (Top cell half)

The behaviour in the lower half of the cell is slightly different. In this half the refractive index increases as the membrane is approached and the light is therefore bent towards the membrane, see Figure 3.11. The rays striking the lower membrane surface may be absorbed and lost or reflected back into the liquid. In the latter case we could expect to see a diffuse lower edge to the shadow of the membrane as a result of interference between the transmitted and reflected rays. However, close examination of the experimental interference pattern (see Figure 3.5 f) shows a sharp lower edge to the membrane shadow. We can therefore conclude that for the system shown on Figure 3.5, the rays striking the membrane are largely absorbed and lost and not reflected. In addition, the bottom half of the cell is always fully illuminated since, irrespective of the magnitude refractive index gradient, there is always a ray which just clears the bottom right hand edge of the membrane. Consequently, the position of the lower edge of the membrane shadow remains virtually stationary in the course of the diffusion process and is a measure of the true physical location of the membrane.

Figure 3.11 Path of light rays in a medium with variable refractive profile increasing towards the membrane surface (Bottom cell half)

Another optical feature, which was not prominent in the liquid/membrane experiments with a 2 mm cell but was clearly observed for liquid/liquid experiments reported by Bansal [1988], is a severe distortion of the fringes caused by 'ray cross-over' [Muller 1973, Bansal 1988]. For a sufficiently large refractive index gradient at the interface, a ray entering close to the interface is severely deflected and may cross another ray which enters at a higher position but sees a lower refractive index gradient, see Figure 3.12. Such ray cross over can lead to a severe distortion of the observed interference fringes. However, this is again a transient phenomenon which fades away as diffusion is allowed to proceed and the refractive index gradients are reduced. According to Bansal [1988] ray cross over effects were not observed for the {ethanol-water}/silicon rubber system but may occur for other liquid/membrane systems exhibiting a sharper interfacial concentration gradient.

Figure 3.12 Schematic presentation of the “ray cross-over” effect in a medium with a sharp refractive index gradients

3.4.3 Rigorous Analysis: light deflection

We now turn to the more difficult task of recovering an *unknown* refractive index profile $n(Y)$ from the optical path length variation $P(Y)$ determined from the experimental fringes. From the above discussion it is evident that the simplistic approach based on neglecting light deflection [cf Eq.2] can lead to significant error. A more rigorous approach allowing for light deflection is, however, complicated because the refractive index profile must be known before the true geometric path can be calculated [cf Eq.5]. We therefore face an implicit problem, which demands an iterative solution. The most obvious procedure is to assume an a priori parametric expression for the shape of the *unknown* refractive index profile. The optimal parameter values can then be found by matching the theoretical optical path lengths with those measured experimentally. This is invariably the approach adopted by the few authors who have taken light deflection into account (see Table 3.3) and some of the empirical expressions used are given in Table 3.4. The serious objection to this procedure arises because the empirical expressions used have little theoretical basis and can not distinguish between the possible diffusive mechanisms within the membrane. For example, different empirical expressions can fit the fringes obtained at a given time to the same degree of accuracy. In addition, time dependent empirical

parameters are needed to fit the fringes observed at different times with a given expression.

Table 3.4 Empirical expressions used to characterise the laminar boundary layer refractive index profile

$n(Y) = a_0 + a_1 Y + a_2 Y^2 + a_3 Y^3 + a_4 Y^4$	Langer (1982)
$n(Y) = a_0 + a_1 \exp(a_2 Y^2)$	Mahlab et al (1978)
	Clifton (1982)
$n(Y) = a_0 + a_1 \operatorname{erf}(a_2 Y)$	Bollenbeck (1973)
$\theta(Y) = a_0 + a_1 Y$	Bollenbeck (1973)
where	
$\theta(Y) = \frac{Y - a_2}{\log\left(\frac{20n(Y)}{\log[100 - n(Y)]}\right)}$	

A more logical but substantially more complex alternative is to adopt a suitable theoretical model to describe the transient transport phenomena across the membrane. For a given set of parameters, the model can be solved to determine the boundary layer concentration profiles which can in turn be used to generate the corresponding set of theoretical fringes. The best values for the model parameters can then be found by matching the calculated and experimental fringes. The significant advantage of this approach is that the model parameters have a well-defined physical meaning. In addition, many of the parameters involved for instance the bulk liquid diffusion coefficient and the liquid/membrane equilibrium parameters can be obtained by independent experimentation. In principle, therefore, only the membrane phase diffusivities need to be recovered from the experimental interference fringes. The overall parameter estimation procedure is shown schematically in Figure 3.13. The successful implementation of this procedure requires a stable and efficient technique for the numerical solution of the transient model equations and a robust method for parameter adjustment.

Figure 3.13 Flow Chart of the Overall Parameter Estimation Procedure

The major obstacle to this approach arises because a realistic model of transient multicomponent mass transfer across membranes constitutes a set of highly coupled non-linear partial differential equations. Such equations do not in general admit an analytical solution and the computational burden involved in their numerical solution appears to have deterred the application of the procedure outlined. The practical feasibility of this approach is confirmed in the next section through a theoretical sensitivity analysis for a hypothetical system; its practical application to {ethanol-water}/silicon rubber will be described subsequently.

3.5 Sensitivity Analysis

The purpose of this section is to establish the practicality of recovering the membrane phase diffusion coefficients from the interferometric measurement of the transient refractive index profile in the liquid boundary layers. To perform this task unambiguously, we choose a hypothetical model system depicting the transfer of a

flowing binary liquid across a membrane to a second stationary liquid. Under suitable boundary conditions this system admits an analytical solution which can be used to assess the accuracy of the numerical technique needed for the solution of the partial differential equations describing more complex situations. This is an important step because the Twyman-Green interferometer is capable of very high resolution and the numerical procedure must deliver the solution to at least the same accuracy. The model system is also used to calculate the theoretical fringes for a given set of parameters by tracing the path of a large number of rays ($\cong 300$) taking full account of light deflection. Random noise corresponding to the level observed on an experimental interference pattern (ie 0.02 f) is then superimposed on a theoretical fringe to simulate an "experimental" fringe. This enables an unambiguous appraisal of the accuracy and reliability of recovering the membrane phase diffusion coefficients from the "experimental" fringes with and without accounting for light deflection.

3.5.1 Numerical Solution of Transient Diffusion Equations

The basic equation describing diffusion through a stagnant medium takes the following parabolic form:

$$\frac{\partial U}{\partial t} = \frac{\partial}{\partial Y} \left(D \frac{\partial U}{\partial Y} \right) \quad (3.6)$$

A general procedure (Method of Lines) for the solution of diffusion equations involves the discretisation of the spatial derivatives on a predetermined grid. This transforms equation (3.6) to a set of coupled ordinary differential equations which can be solved using readily available general purpose integration packages.

To illustrate the procedure, consider the grid shown in Figure 3.14 and let us assume that the dependent variable U is known at all positions at time level m and is also specified at the boundary points $i=1$ and $i=N$. To ease the notation we denote $U(m, i)$ by U_i and remembering that all spatial derivatives are evaluated at time level m drop specific reference to time. Consider the expansion of U_{i-1} and U_{i+1} about U_i :

$$U_{i-1} = U_i + \frac{1}{1!} \frac{\partial U_i}{\partial Y} (-\Delta Y) + \frac{1}{2!} \frac{\partial^2 U_i}{\partial Y^2} (-\Delta Y)^2 + \frac{1}{3!} \frac{\partial^3 U_i}{\partial Y^3} (-\Delta Y)^3 + \dots \quad (3.7a)$$

$$U_{i+1} = U_i + \frac{1}{1!} \frac{\partial U_i}{\partial Y} (+\Delta Y) + \frac{1}{2!} \frac{\partial^2 U_i}{\partial Y^2} (+\Delta Y)^2 + \frac{1}{3!} \frac{\partial^3 U_i}{\partial Y^3} (+\Delta Y)^3 + \dots \quad (3.7b)$$

An approximation to $(\partial U_i / \partial Y)$ is obtained by multiplying equations (3.7a) and (3.7b) with unknown constants A and B and adding the result to form a linear combination:

$$\begin{aligned} AU_{i-1} + BU_{i+1} = (A+B)U_i - (A-B) \left(\frac{\partial U_i}{\partial Y} \right) \Delta Y \\ + \frac{1}{2} (A+B) \frac{\partial^2 U_i}{\partial Y^2} (\Delta Y)^2 - \frac{1}{6} (A-B) \frac{\partial^3 U_i}{\partial Y^3} (\Delta Y)^3 \dots \end{aligned} \quad (3.8)$$

A finite difference approximation of high accuracy is obtained by choosing A and B such that the coefficients of the desired first derivative are unity and that of as many of the higher derivatives as possible is zero. In the case of equation (3.8), we must have $A+B=0$ and $A-B=1$, which can be solved to give $A=1/2$ and $B=-1/2$. Back substitution of these values in (3.8) leads to the familiar central difference formula:

$$\frac{dU_i}{dY} = \frac{U_{i-1} - U_{i+1}}{2\Delta Y} + O(\Delta Y)^2 \quad i = 2, 3, 4, \dots, n-1$$

The boundary points $i=1$ and $i=N$ require a different treatment. Using a forward difference approximation for the left hand boundary and a backward difference approximation for the right hand boundary leads to:

$$\frac{\partial U_1}{\partial Y} = \frac{-3U_1 + 4U_2 - U_3}{2\Delta Y} + O(\Delta Y)^2 \quad \text{left boundary, } i=1$$

$$\frac{\partial U_N}{\partial Y} = \frac{3U_N - 4U_{N-1} + U_{N-2}}{2\Delta Y} + O(\Delta Y)^2 \quad \text{right boundary, } i=N$$

time t

Figure 3.14 Discretisation grid used for the numerical solution of the diffusion equations by the method of lines

More accurate higher order formulae are obtained using the same procedure but carrying further terms of the Taylor series expansion. Details of the relevant formulae are given by Schiesser (1976) and general implementation of the method of lines is also available from the same author. For our purposes we have retained derivatives of up to sixth order, which yields the finite difference formula [Schiesser 1976]:

$$\frac{\partial U_i}{\partial Y} = \frac{1}{6! \Delta Y} (-12U_{i-3} + 108U_{i-2} - 540U_{i-1} + 0U_i + 540U_{i+1} - 108U_{i+2} + 12U_{i+3}) + 0(\Delta Y)^6; i = 4, \dots, N-3 \quad (3.9)$$

Points close to the left boundary ($i=1, 2$ and 3) require a different treatment employing forward difference approximation which leads to the following approximations:

$$\frac{\partial U_1}{\partial Y} = \frac{1}{6! \Delta Y} (-1764U_1 + 4320U_2 - 5400U_3 + 4800U_4 + 2700U_5 + 864U_6 + 120U_7) + 0(\Delta Y)^6 \quad (3.10a)$$

$$\frac{\partial U_2}{\partial Y} = \frac{1}{6! \Delta Y} (-120U_1 - 924U_2 + 1800U_3 - 1200U_4 + 600U_5 - 180U_6 + 24U_7) + 0(\Delta Y)^6 \quad (3.10b)$$

$$\frac{\partial U_3}{\partial Y} = \frac{1}{6! \Delta Y} (24U_1 - 288U_2 - 420U_3 + 960U_4 - 360U_5 + 96U_6 - 12U_7) + 0(\Delta Y)^6 \quad (3.10c)$$

Similarly, points close to the right hand boundary ($i=N-2, N-1$ and N) require the use of backward difference approximation which result in:

$$\frac{\partial U_{N-2}}{\partial Y} = \frac{1}{6! \Delta Y} (12U_{N-6} - 96U_{N-5} + 360U_{N-4} - 960U_{N-3} + 420U_{N-2} + 288U_{N-1} - 24U_N) + 0(\Delta Y)^6 \quad (3.11a)$$

$$\frac{\partial U_{N-1}}{\partial Y} = \frac{1}{6! \Delta Y} (-24U_{N-6} + 180U_{N-5} - 600U_{N-4} + 1200U_{N-3} + 1800U_{N-2} + 924U_{N-1} + 120U_N) + 0(\Delta Y)^6 \quad (3.11b)$$

$$\frac{\partial U_N}{\partial Y} = \frac{1}{6! \Delta Y} (120U_{N-6} - 864U_{N-5} + 2700U_{N-4} - 4800U_{N-3} + 5400U_{N-2} - 4320U_{N-1} + 176U_N) + 0(\Delta Y)^6 \quad (3.11c)$$

The above formulae are first used to approximate the spatial derivatives ($\partial U/\partial Y$) at each point on the grid shown in Figure 3.14. The resultant equations are then multiplied by the corresponding values of D (which may or may not depend on concentration) to yield the product $D (\partial U/\partial Y)$ at each grid point. This product is then discretised once again using the above approximations to result in a set of highly coupled ordinary differential equations with the following general structure which can be solved by a general purpose integration package:

$$\frac{dU_i}{dt} = f_i(U_{i-6}, \dots, U_{i+6}) \quad i=i, \dots, N \quad (3.12)$$

To summarize, by dividing the space domain into $N-1$ equal increments, the single partial differential (3.6) is transformed into a system of N ordinary differential equations (3.12). Some care needs to be exercised in choosing a numerical package for the solution of these equations; this is because the discretised equations are frequently 'stiff' and contain elements which vary on radically different time scales. For instance, immediately following a sharp change at a boundary, the points close to the boundary will exhibit very large gradients whereas those far away from the boundary are yet to sense the sharp variation introduced. Because of this inherent stiffness, explicit integration techniques, such as Euler or Runge-Kutta methods, may either require very small time increments or may fail to converge due to instability [Gear 1971]. This problem is best avoided by choosing a numerical package based on implicit methods which are specially designed for stiff equations. For our work we used the variable-step variable-order implicit method developed by Gear [1971].

The above discussion was limited to diffusion across a single spatial domain or phase but is easily extended to interphase diffusion across a membrane; eg top liquid/membrane/ bottom liquid diffusion. In such cases an equation similar to (3.6) is used to describe the diffusion processes in each phase. The connection between the phases is determined through the boundary conditions prescribed at the phase boundaries. These may specify the value of the dependent variable at the phase interface, U_1 or U_N , which can be inserted directly in the finite difference approximations. Alternatively, the gradient ($\partial U/\partial Y$) may be specified at the interface. In this case, the boundary condition is discretised and transformed to an algebraic equation which, is solved along with the system of ordinary differential equations

describing the diffusion process in each phase. The method of lines is highly flexible and can handle the membrane transport equations in their full complexity, it is also easily applied and its implementation is readily available from various sources [Schiesser 1976].

3.5.2 A Hypothetical Model System

The model system is shown schematically in Figure 3.15 and consists of a membrane of thickness L_m initially in equilibrium with a semi-infinite liquid of composition C_L^0 .

Figure 3.15 Schematic of the model system used for the sensitivity analysis of the interferometric method.

The differential equations describing this system may be stated as:

$$\frac{\partial C_L}{\partial t} = \frac{\partial}{\partial Y} (D_L \frac{\partial C_L}{\partial Y}) \quad 0 \leq Y \quad \text{liquid} \quad (3.13a)$$

$$\frac{\partial C_M}{\partial t} = \frac{\partial}{\partial Y} (D_M \frac{\partial C_M}{\partial Y}) \quad -L_M \leq Y \leq 0 \quad \text{membrane} \quad (3.13b)$$

We consider the evolution of the transient profile when the concentration at the lower membrane surface is suddenly dropped and maintained at zero. The above equation must then be solved subject to initial conditions,

$$C_L(0, Y) = C_L^0 \quad (3.14a)$$

$$C_M(0, Y) = g(C_L^0) \quad (3.14b)$$

where the function $g(\cdot)$ represents the equilibrium isotherm. The boundary conditions may be expressed as:

$$C_L(\infty, t) = C_L^0 \quad (3.15a)$$

$$D_L \frac{\partial C_L}{\partial Y} = D_M \frac{\partial C_M}{\partial Y} \quad \text{at } Y=0 \quad (3.15b)$$

$$C_M(0, t) = g[C_L(0, t)] \quad \text{at } Y=0 \quad (3.15c)$$

$$C_M(-L_M, t) = 0 \quad (3.15d)$$

Boundary condition (3.15b) arises from the assumption of no accumulation at the interface and condition (3.15c) implies that equilibrium is achieved instantaneously at the interface.

If we further assume that the diffusivities D_L and D_M are constant and the equilibrium isotherm is linear with a slope h ,

$$C_M = g(C_L) = hC_L \quad (3.16)$$

Equations (3.13) to (3.16) admit the following analytical solution [Carslaw and Jaeger 1959]:

$$C_L(t, Y) = C_L^0 \left[1 - \frac{2}{1+\sigma} \sum_n \alpha^n \operatorname{erfc} \left[\frac{(2n+1)L_m + \beta Y}{2(D_M t)^{1/2}} \right] \right] \quad (3.17)$$

$$C_M(t, Y) = hC_L^0 \left[1 - \sum_n \alpha^n \left[\operatorname{erfc} \left[\frac{(2n+1)L_m + Y}{2(D_M t)^{1/2}} \right] - \alpha \operatorname{erfc} \left[\frac{(2n+1)L_m - Y}{2(D_M t)^{1/2}} \right] \right] \right]$$

where $\sigma = h^{-1}(D_L/D_M)^{1/2}$, $\beta = (D_L/D_M)^{1/2}$ and $\alpha = (\sigma - 1)/(\sigma + 1)$. The availability of an analytical solution for the hypothetical model system chosen facilitates the critical assessment of the accuracy of the numerical procedure over a wide range of parameter values.

The model equations (3.13-3.16) were solved numerically for a 150 μm thick membrane and a wide range of parameter values: $8 \times 10^{-6} \leq D_L \leq 3 \times 10^{-5} \text{ cm}^2/\text{sec}$; $1 \times 10^{-10} \leq D_M \leq 1 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $4 \times 10^{-4} \leq h \leq 1$. Excellent agreement between the analytical and numerical solution was obtained in all cases when the membrane

and the first 2 cm of the 'stagnant liquid were each divided into 30 or more equal increments. The maximum discrepancy in the concentration and concentration gradient at the interface (where the largest errors are expected) were less than 0.005% and 0.6% respectively. Figure 3.16a and 3.16b show typical transient profiles in the liquid and the membrane phases respectively; different time scales are used to highlight the development of the profiles in each phase more clearly.

Figure 3.16a Transient concentration profile for the model system for liquid phase (1:1s, 2:2s, 3:5s, 4:20s, 5:600s, 6:1200s, 7:3600s)

Figure 3.16b Transient concentration profile for the model system for membrane phase (1:30s, 2:300s, 3:600s, 4:1200s, 5:1800s, 6:2400s, 7:3600s)

3.5.3 Recovery of Membrane Diffusivity from Experimental Fringe Patterns

With the accuracy and reliability of the numerical technique established we can now turn to the main task at hand; namely the recovery of the membrane phase diffusion coefficients from the experimental interference patterns. To achieve an unambiguous appraisal, the concentration profiles in Figure 3.16a were used to generate the corresponding theoretical fringes by tracing the path of 300 rays taking full account of light deflection. For the purposes of this illustration the liquid was taken as {ethanol-water} mixture. The variation of the refractive index with composition for this system is shown in Figure 3.17 and is well fitted with the polynomial:

$$n = 1.33828 + 0.179258x_1^L - 0.380008(x_1^L)^2 + 0.351867(x_1^L)^3 + 0.124503(x_1^L)^4$$

where x_1^L is the mole fraction of ethanol in the liquid.

Figure 3.17 Variation of refractive index with composition for {ethanol-water} mixtures at 25 °C and a wavelength of 0.6328 μm .

The fringes obtained are shown in Figure 3.18 and it is interesting to note that they are vertically shifted by about 0.3 mm due to the light deflection caused by the sharp gradient at the interface. The discrepancy between the fringes obtained using the analytical and numerical fringes was less than $0.0001f$ which is substantially better than the $0.02f$ resolution attainable experimentally. Random noise of the level expected in practice (ie $0.02 f$) was added to the theoretical fringes calculated for a *known* set of parameters ($D_L = 1.13 \times 10^{-5} \text{ cm}^2 / \text{s}$, $h=0.03$ and $D_M = 2.0 \times 10^{-6} \text{ cm}^2 / \text{s}$) to simulate a set of “experimental” fringes which were then used to back extract the model parameters.

Figure 3.18 Theoretical interference fringes corresponding to the concentration profiles of Figure 3.16a. (—light deflection, ---- no light deflection)
{1: 30s, 2: 300s, 3: 1500s, 4: 3600s}

In general the models used to describe the membrane transport phenomena contain several parameters which have to be systematically adjusted to obtain the best fit between the calculated and experimental fringes. It is also often necessary to bound the model parameters and impose constraints to ensure physically realistic values are recovered. An excellent treatment of constrained non-linear programming

is available in the text by Gill *et al* [1981]. The basic mathematical problem in its most general form can be stated as:

“Find the values $v_1^*, v_2^*, \dots, v_n^*$ which

$$\min_{\mathbf{v}} F(v_1, v_2, \dots, v_n)$$

subject to:

$$v_i^{\text{Low}} \leq v_i \leq v_i^{\text{High}} \quad ; i = 1, 2, \dots, n \quad n \text{ bound constraints}$$

$$\sum_{j=1}^{m_L} a_{ij} v_j \geq 0 \quad m_L \text{ linear inequality constraints}$$

$$g_j(v_1, v_2, \dots, v_n) \geq 0 \quad , j = 1, \dots, m_N \quad m_N \text{ non-linear inequality constraints}”$$

An effective procedure for handling the above problem is obtained by assuming an initial guess and expanding the non-linear objective function to second order and the non-linear inequality constraints to first order. This results in a linearly constrained quadratic optimisation sub-problem that has well known convergence properties and a guaranteed solution. The repeated solution of this quadratic sub-problem will in principle converge to the solution of the original non-linear programming problem. In our applications we employed the constrained sequential quadratic programming procedure developed and implemented by Chen and Macchietto [1991]. It suffices to say that optimisation is itself a vast subject and practical applications must often be “nursed” to convergence. An excellent discussion of the scaling of the variables, the gradients and the objective function which help the convergence of constrained non-linear optimisation problems is given by Gill *et al* [1981].

As a first test, the values of $D_L = 1.13 \times 10^{-5} \text{ cm}^2/\text{s}$ and $h=0.03$ were fixed at their a priori known theoretical values and a one parameter search was conducted to recover the value of D_M using the simplified analysis based on equation (3.2) which ignores light deflection. The best values of D_M recovered for cells of various thickness based on the instantaneous “experimental” fringes at various times are summarised in Table 3.5. The membrane phase diffusivity recovered exhibits substantial error

compared to its a priori known value. For the 2 and 5 mm wide cells the error diminishes with time, this is to be expected as the gradients giving rise to light deflection also decrease with time. The errors for the 10 mm wide cell are erratic due to the intrusion of ray-cross over effects.

Table 3.5 Membrane Phase Diffusion Coefficient Recovered from a Single Parameter Optimisation Search Under the Assumption of No Light Deflection.

Fringe Time (s)	2 mm cell		5mm cell		10 mm cell	
	$10^6 D_M$ (cm ² /s)	% err	$10^6 D_M$ (cm ² /s)	% err	$10^6 D_M$ (cm ² /s)	% err
300	2.31	15.5	2.96	47.5	2.42	21.0
900	2.24	12.0	2.71	33.5	3.08	54.0
900	2.19	9.6	2.58	29.0	3.04	52.0
3600	2.10	5.0	2.27	13.5	2.54	27.0

Parameters used to simulate the experimental fringes:

$$D_L = 1.13 \times 10^{-5} \text{ cm}^2 / \text{s}, h=0.03 \text{ and } D_M = 2.0 \times 10^{-6} \text{ cm}^2 / \text{s}$$

The same analysis was then repeated but this time with light deflection taken into account. The values of D_M recovered from the transient fringes at various times are given in Table 3.6 for a 2 mm wide cell. The membrane diffusivity recovered by this procedure was independent of the fringe time and in almost perfect agreement with the *a priori* known value of D_M employed to generate the “experimental” fringes. We can therefore conclude that each instantaneous interference pattern contains sufficient information to enable a highly accurate recovery of the membrane diffusivity provided light deflection is taken into account; failure to account for light deflection can lead to significant error.

Table 3.6 Membrane Phase Diffusion Coefficient Recovered from a Single Parameter Optimisation Search Accounting for Light Deflection in a 2 mm Cell.

Fringe Time (s)	Membrane phase diffusivity $10^6 D_M$ (cm ² /s)	% error
300	2.00020	0.0100
600	2.00010	0.005
900	2.00008	0.004
3600	2.00003	0.0015

Parameters used to simulate the experimental fringes:

$$D_L = 1.13 \times 10^{-5} \text{ cm}^2 / \text{s}, h=0.03 \text{ and } D_M = 2.0 \times 10^{-6} \text{ cm}^2 / \text{s}$$

As a more severe test, only the value of the liquid phase diffusivity was fixed at its a priori known value, $D_L = 1.13 \times 10^{-5} \text{ cm}^2/\text{s}$ and an attempt was made to recover both h and D_M from the “experimental” fringes using a two-parameter search. The parameters recovered were again independent of the fringe time and are shown in Table 3.7. As expected it is more difficult to recover two rather than one parameter from the experimental fringes; even so the average error in D_M and h values recovered are 0.5% and 0.6% respectively. This indicates that each instantaneous fringe contains sufficient information to allow the accurate recovery of both the membrane diffusivity D_M and the membrane solubility h . We can therefore conclude that the experimental fringes measured by the Twyman-Green interferometer can be confidently used to recover the model parameters provided light deflection is taken into account; failure to account for light deflection will cause substantial error in the parameters recovered.

Table 3.7 Membrane Phase Diffusion and Solubility Coefficients Recovered from a Two Parameter Optimisation Search Accounting for Light Deflection in a 2 mm Cell.

Fringe Time Sec	Membrane phase diffusivity		Membrane Phase Solubility	
	$10^6 D^M (\text{cm}^2/\text{s})$	% error	$h(-)$	%error
300	2.014	0.71	0.02987	-0.75
600	2.012	0.60	0.02986	-0.80
900	1.994	-0.30	0.03015	0.50
3500	2.010	0.50	0.02985	-0.50

Parameters used to simulate the experimental fringes:

$$D_L = 1.13 \times 10^{-5} \text{ cm}^2/\text{s}, h=0.03 \text{ and } D_M = 2.0 \times 10^{-6} \text{ cm}^2/\text{s}$$

3.6 Summary

The measurement of transient fluxes coupled with transient models of membrane transport allows a more critical evaluation of membrane separation performance. Transient pervaporation data for {ethanol-water} mixtures measured by Abdel-Ghani [1992] and transient dialysis data measured by Bansal [1988] using the same membrane were described. Interpretation of the interference fringes produced by the non-intrusive laser interferometer used by Bansal [1988] requires careful attention. In particular, it is essential to make proper allowance for the deflection of light in a medium of varying refractive index. Failure to account for light deflection can result in substantial error. A detailed analysis of the optical effects was presented and led to the development of a ray tracing programme capable of generating a

theoretical fringe which may be compared with the experimental fringes reported by Bansal [1988].

Transient models of membrane transport constitute a highly coupled set of partial differential equations. A numerical procedure, the method of lines, which is capable of handling the transient models in their full complexity was described. The stability and accuracy of the numerical procedure was tested over a wide range of conditions by comparison with a hypothetical model membrane system that has an analytical solution. The same hypothetical model system was used to test a constrained sequential quadratic programming procedure for estimation of the model parameters. The results obtained confirm that both the diffusive and equilibrium parameters may be confidently recovered from the interference fringes. The transient data for the {ethanol-water}/silicon rubber system coupled with the numerical procedures developed in this chapter offer a unique opportunity for a critical assessment of theoretical models of membrane transport.

CHAPTER 4

A PHENEMENOLOGICAL MODEL OF MEMBRANE TRANSPORT: TRANSIENT DIALYSIS AND PERVAPORATION OF {ETHANOL /WATER}/SILICONE RUBBER

4. A Phenomenological Model of Membrane Transport: transient dialysis and pervaporation of {ethanol-water}/silicon rubber

4.1 Introduction

Selective multicomponent transport in processes such as dialysis, pervaporation and vapour permeation is driven by chemical potential gradients and external driving forces make an insignificant contribution. A molecule within the polymeric membrane moves in response to the *local* chemical potential gradients and has no memory of how it entered the membrane or how the local gradients were generated. This means that a properly formulated model of transport within the membrane should be equally applicable to dialysis, pervaporation or vapour permeation. This has important practical implications in as far as it allows the evaluation of the model parameters from experimental data gathered under different processing conditions. Such a model and its parameters can be used for the design, scale-up and optimisation of dialysis, pervaporation or vapour permeation processes employing the same polymeric membrane. The major difference between such processes lies in the manner in which the driving force for separation is generated. In dialysis the membrane is maintained between liquids of differing composition. In pervaporation the upper membrane interface is in contact with a liquid while the activities at the lower interface are maintained at a low value by pulling a vacuum or using a sweep gas. In vapour permeation the driving force is generated by contacting the membrane with vapours maintained at different pressures. The basic transport processes occurring within the polymeric matrix are, however, the same in all cases.

The primary objective of this chapter is to develop and test a general model of membrane transport based on the phenomenological approach of irreversible thermodynamics. In particular, we would like to test the potential of such a model for *predicting* the pervaporation performance using the model parameters recovered from measurements made under dialysis conditions. The practical system chosen is the transport of {ethanol-water} mixtures across a homogeneous silicon rubber membrane. This is a difficult system in as far as the bulk liquid is highly non-ideal and the transport of polar molecules through the hydrophobic silicon rubber matrix may lead to intricate coupling of the fluxes of the permeating species. We are also

fortunate in having available the transient dialysis data measured by Bansal [1988] and the transient pervaporation data measured for the same membrane by Abdel-Ghani [1992].

The success or failure of a general model depends in the first instance on the validity and accuracy of the assumptions used to describe the multicomponent transport process within the polymeric membrane. Early attempts in this direction ignored the kinetic coupling of fluxes and assumed that the flux of each permeating species is driven by its own chemical potential gradient [eg Lee, 1975; Mulder and Smolders, 1984; Wijmans and Baker, 1995]. A more comprehensive model using thermodynamically corrected multicomponent Fick diffusivities was used by Bansal [1988] to fit his interferometric data for the {ethanol-water}/silicon rubber system. The diffusive parameters reported by Bansal [1988] fail to even predict the general trends observed by Abdel-Ghani [1992] for the pervaporation of {ethanol-water} mixtures using the same membrane. A careful analysis of the assumptions used by Bansal [1988] is undertaken in this chapter to pinpoint the reasons for the failure of his model. In particular, it is shown that Bansal's assumptions violate the Onsager reciprocal relationships. Imposing the reciprocal relationship reduces the number of parameters involved and at the same time provides a much better prediction of the pervaporation data.

In this chapter we develop a general model of membrane transport based on the irreversible thermodynamic approach described in chapter 2. This model is used to set up the continuity equations and boundary conditions pertinent to the transient dialysis and pervaporation experiments reported by Bansal [1988] and Abdel-Ghani [1992]. The resultant equations constitute a set of coupled non-linear partial differential equations, which do not admit an analytical solution. A stable and robust procedure based on the method of lines described in chapter 3 is developed and used to obtain the transient concentration profiles within the membrane and the bulk liquid bathing the membrane. Separate evaluation of equilibrium and kinetic contributions to the transport process requires a thermodynamic model of multicomponent sorption in the membrane. For the purposes of this chapter, the phase equilibria of {ethanol-water}/silicone rubber system is described by the classical Flory-Huggins model

using constant interaction parameters recovered from a match with the relative sorption data reported by Bansal [1988].

Average values of the thermodynamically corrected diffusivities, satisfying the Onsager reciprocal relationships, are obtained from a match with the interference fringes measured by Bansal [1988] under dialysis conditions. The parameters obtained differ markedly from those reported by Bansal [1988] and provide a much better prediction for the pervaporation of {ethanol-water} mixtures across the silicon rubber membrane. The chapter is closed by a discussion of the underlying reasons for the remaining discrepancies between the predicted and measured pervaporation data. These may be traced to the need for a more accurate description of phase equilibria than is offered by the classical Flory-Huggins model, the need for the explicit inclusion of the concentration dependence of the polymer phase diffusivities and a better description of the kinetic coupling effects. Such modifications are best achieved using the mechanistic Stefan-Maxwell formulation of multicomponent diffusion and are deferred to the next chapter.

4.2 The Transient Transport Equations

In this section we develop the continuity equations and boundary conditions which together constitute the transport equations describing transient dialysis and pervaporation. The model equations will be presented for the transport of a binary bulk phase which together with the polymer constitute a ternary system but extension to four or more components is straightforward. The close similarity between the dialysis and pervaporation experiments is highlighted by the schematic of the diffusion cells shown in Figure 4.1. The upper surface of the liquid in the top half of either cell is closed to diffusive mass transfer. The liquid level in the top half of the cell may fall (or rise) depending on the net amount of material entering (or leaving) the upper membrane interface at L_{mem} but there is no diffusive flux across the upper interface at $L_{TOP}(t)$. From a modelling viewpoint, the behaviour and boundary conditions are identical for the upper liquid and the membrane in the dialysis and pervaporation cells. The bottom half of the dialysis cell is filled with liquid and is closed to either convective or diffusive mass transport. The bottom half of the pervaporation cell is filled with a vapour at low pressure and is open to convective

mass transport through the vacuum pump. The extent of diffusive flux in the lower half of the pervaporation cell is negligible in comparison to the convective flux. The vapour can therefore be assumed well mixed and its dynamics described in terms of a lumped parameter model. This is in contrast to the lower half of the dialysis cell where the diffusive flux dominates and the behaviour in the lower liquid must therefore be described in terms of a distributed parameter model.

Figure 4.1 Schematic of the dialysis and pervaporation cells

4.2.1 Transport Equations for the Membrane

The continuity equation for a component i in the membrane is obtained from a differential material balance,

$$\frac{\partial C_i}{\partial t} = -\frac{\partial}{\partial z}(N_i) ; \quad i = 1, 2 \text{ or } p \quad (4.1)$$

where C_i is the molar concentration and N_i is the molar flux relative to stationary co-ordinates. To proceed further we must *choose* a reference velocity for the mixture and relate the flux N_i to the diffusive fluxes (and hence the diffusion coefficients) defined for the *chosen* frame of reference. Polymeric membranes may expand or contract as a

result of diffusion and the most convenient choice is therefore a polymer-fixed frame of reference,

$$N_i = (J_i)_p + u_p C_i ; \quad i = 1, 2 \text{ or } p \quad (4.2)$$

where u_p represents the velocity of the polymer component relative to stationary co-ordinates. We note here that $(J_p)_p = 0$ by definition and

$$u_p = \frac{N_p}{C_p} \quad (4.3)$$

Recalling the discussion in section 2.2.5, the determination of an independent equation for the variation of u_p requires detailed information on the volume change of mixing and the composition dependence of the partial molar volumes in the polymer network, which is not normally available. In the absence of such information we are forced to adopt suitable *a priori* assumptions and two extreme situations can be envisaged:

- (i) **Volume Additivity:** *the partial molar volumes of the polymer and the permeating species are assumed constant and independent of composition. Under this assumption the membrane must expand (or contract) by an amount exactly equal to the net volume of the diffusing species entering (or leaving) the membrane. This is a good assumption for polymeric systems exhibiting a large degree of swelling as a result of the diffusion process. The boundaries of the membrane move appreciably with time and there is a flux of the polymer component relative to the cell, $N_p \neq 0$. Diffusion within the membrane must therefore be treated as a moving boundary problem and appropriate (jump) mass balances are required to track the movement of the membrane interfaces.*
- (ii) **Negligible Swelling:** *alternatively, we may assume that the partial molar volumes of the permeating species remain constant but the partial molar volume of the polymer adjusts such that there is no expansion or contraction and therefore no flux of the polymer component relative to the cell, $N_p = 0$. This represents a good assumption for systems with low uptake, which show a negligible degree of swelling as a result of the diffusion process. In this case*

the polymer velocity is identically zero $u_p = 0$ and $N_i = (J_i)_p$ which simplifies the analysis.

The behaviour of a real system will in fact lie somewhere between these two extreme conditions. In the case of the {ethanol-water}/silicon rubber system the level of uptake is so small that measurable swelling is not observed even when the polymer is immersed in pure ethanol. We shall therefore assume that the polymer is stationary and base the analysis in this thesis on the assumption of no swelling. The continuity equations in the membrane can therefore be written as:

$$\begin{aligned}\frac{\partial C_i}{\partial t} &= -\frac{\partial}{\partial z}(N_i) = -\frac{\partial}{\partial z}[(J_i)_p]; \quad i=1, 2 \\ \frac{\partial C_p}{\partial t} &= -\frac{\partial}{\partial z}(N_p) = 0\end{aligned}\tag{4.4}$$

This implies that the molar concentration of the polymer C_p is constant and does not change in the course of diffusion. The location of the top and bottom membrane interfaces are also time invariant and the membrane thickness does not change with time.

Using the procedures outlined in chapter 2, the diffusive fluxes in the polymer-fixed frame of reference can be expressed as,

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix}_p = \begin{bmatrix} (\Omega_{11})_p & (\Omega_{12})_p \\ (\Omega_{21})_p & (\Omega_{22})_p \end{bmatrix} \begin{pmatrix} \frac{\partial \mu_1}{\partial z} \\ \frac{\partial \mu_2}{\partial z} \end{pmatrix}\tag{4.5}$$

where the $(\Omega_{ij})_p$ are a set of phenomenological coefficients which satisfy the Onsager reciprocal relationship,

$$(\Omega_{12})_p = (\Omega_{21})_p\tag{4.6}$$

Noting that $d\mu_i = RT d \ln(a_i)$ and the activity a_i is a function of the concentrations C_1 and C_2 , we may express the diffusive fluxes in terms of composition gradients by:

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix}_P = \underbrace{\begin{bmatrix} \frac{RT(\Omega_{11})_P}{C_1} & \frac{RT(\Omega_{12})_P}{C_2} \\ \frac{RT(\Omega_{21})_P}{C_1} & \frac{RT(\Omega_{22})_P}{C_2} \end{bmatrix}}_{\text{Kinetic Coupling}} \underbrace{\begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix}}_{\text{Equilibrium Coupling}} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \quad (4.7)$$

The off diagonal elements of the first matrix on the left hand side of (4.7) give a measure of the extent of kinetic coupling of fluxes. The second matrix accounts for the equilibrium coupling of fluxes and its elements may be computed from a thermodynamic model, for example the Flory-Huggins model, describing the concentration dependence of the activities.

We may define a set of thermodynamically corrected diffusivities in the polymer-fixed frame of reference by $(D_{ij}^T)_P = RT(\Omega_{ij})_P / C_j$ and write (4.7) as:

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix}_P = \underbrace{\begin{bmatrix} (D_{11}^T)_P & (D_{12}^T)_P \\ (D_{21}^T)_P & (D_{22}^T)_P \end{bmatrix}}_{\text{Kinetic Coupling}} \underbrace{\begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix}}_{\text{Equilibrium Coupling}} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \quad (4.8)$$

In view of the Onsager reciprocal relationship (4.6), the off-diagonal thermodynamically corrected diffusivities are not independent and are subject to the following constraint,

$$C_2 (D_{12}^T)_P = C_1 (D_{21}^T)_P \quad (4.9)$$

Combining (4.2) and (4.8) and noting that under the assumption of negligible swelling $u_P = 0$ enables us to express the continuity equation for the membrane as:

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left\{ \begin{bmatrix} (D_{11}^T)_P & (D_{12}^T)_P \\ (D_{21}^T)_P & (D_{22}^T)_P \end{bmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \right\} \quad (4.10)$$

The connection between the membrane and bulk phases is obtained through the boundary conditions specified at the upper and lower membrane interfaces. One

set of boundary conditions is obtained on the assumption that equilibrium is established instantaneously and the activities are equal at the interfaces:

Equilibrium Boundary Conditions:

$$\begin{aligned} a_i(t, L_{\text{mem}}) &= a_i^b(t, L_{\text{mem}}) \\ a_i(t, 0) &= a_i^b(t, 0) \end{aligned} \quad (4.11)$$

The equilibrium boundary conditions enable the calculation of the membrane phase interface concentrations from those in the bulk phase indicated by a superscript b. Activities in the membrane may be related to composition using the Flory-Huggins model. The vapour phase may be assumed ideal and its activity is simply, $a_i^v = P_i / P_i^0$, where P_i is the partial pressure and P_i^0 the saturation vapour pressure of component i. For the liquid phase activities we may resort to a variety of thermodynamic models, for example the Wilson, NRTL or UNIQUAC equations [Reid et al 1987, Taylor and Kooijman, 1991].

A second set of boundary conditions is obtained by assuming that there is no material accumulation at an interface and the molar fluxes are continuous across an interface:

Flux Boundary Conditions:

$$\begin{aligned} N_i(t, L_{\text{mem}}) &= N_i^b(t, L_{\text{mem}}) \\ N_i(t, 0) &= N_i^b(t, 0) \end{aligned} \quad (4.12)$$

The flux boundary conditions enable us to relate the interfacial concentration gradient in the liquid to those within the polymer. Equations (4.10) and boundary conditions (4.11) and (4.12) constitute the transient transport equations for the membrane.

It is instructive at this point to note that the diffusive fluxes and the diffusion coefficients are frequently reported in other frames of reference. It may therefore become necessary to convert from one reference to another to make comparison between reported diffusion coefficients. For example, the diffusive fluxes relative to the volume-average reference velocity are related to those in the polymer-fixed frame by,

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix}_V = \begin{bmatrix} 1 - C_1 \bar{v}_1 & -C_1 \bar{v}_2 \\ -C_2 \bar{v}_1 & 1 - C_2 \bar{v}_2 \end{bmatrix} \begin{pmatrix} J_1 \\ J_2 \end{pmatrix}_P \quad (4.13)$$

where $\bar{v}_i$ is the partial molar volume of component i . Combining (4.8) and (4.13) and introducing a set of thermodynamically corrected diffusion coefficients defined for the volume-fixed frame of reference,

$$\begin{bmatrix} \left(D_{11}^T \right)_V & \left(D_{12}^T \right)_V \\ \left(D_{21}^T \right)_V & \left(D_{22}^T \right)_V \end{bmatrix} = \begin{bmatrix} 1 - C_1 \bar{v}_1 & -C_1 \bar{v}_2 \\ -C_2 \bar{v}_1 & 1 - C_2 \bar{v}_2 \end{bmatrix} \begin{bmatrix} \left(D_{11}^T \right)_P & \left(D_{12}^T \right)_P \\ \left(D_{21}^T \right)_P & \left(D_{22}^T \right)_P \end{bmatrix} \quad (4.14)$$

Inverting (4.14) yields the diffusion coefficients in the polymer fixed frame in terms of those in the volume fixed frame:

$$\begin{bmatrix} \left(D_{11}^T \right)_P & \left(D_{12}^T \right)_P \\ \left(D_{21}^T \right)_P & \left(D_{22}^T \right)_P \end{bmatrix} = \begin{bmatrix} \frac{1 - C_2 \bar{v}_2}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} & \frac{C_1 \bar{v}_2}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} \\ \frac{C_2 \bar{v}_1}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} & \frac{1 - C_1 \bar{v}_1}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} \end{bmatrix} \begin{bmatrix} \left(D_{11}^T \right)_V & \left(D_{12}^T \right)_V \\ \left(D_{21}^T \right)_V & \left(D_{22}^T \right)_V \end{bmatrix} \quad (4.15)$$

We are of course entirely free to work either in the polymer fixed or the volume fixed frame of reference. In the latter case, however, careful attention must be paid to the proper inclusion of the non-selective contribution caused by bulk flow, a point that is often ignored. We may express the diffusive fluxes in the volume fixed-frame of reference by,

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix}_V = \begin{bmatrix} \left(D_{11}^T \right)_V & \left(D_{12}^T \right)_V \\ \left(D_{21}^T \right)_V & \left(D_{22}^T \right)_V \end{bmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \quad (4.16)$$

Kinetic Coupling Equilibrium Coupling

The flux relative to stationary co-ordinates appearing in the continuity equation (4.1) is given by $N_i = (J_i)_V + u^V C_i$ where u^V is the volume-average velocity within the membrane. The continuity equation in this frame of reference is therefore given by:

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left\{ \begin{bmatrix} (D_{11}^T)_v & (D_{12}^T)_v \\ (D_{21}^T)_v & (D_{22}^T)_v \end{bmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} + u^v \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \right\} \quad (4.17)$$

The last term on the right hand side of (4.17) represents a non-selective contribution to the flux and is often ignored. Kamaruddin and Koros [1997] have demonstrated that this is only justified under special circumstances and may, in general, lead to significant error.

It is also important to recognise that in view of the Onsager reciprocal relationship, equations (4.6) or (4.9), the elements of the diffusivity matrix $[D^T]_v$ are not independent of each other and must satisfy the constraint,

$$C_2 \{ (1 - C_2 \bar{v}_2) (D_{12}^T)_v + C_1 \bar{v}_2 (D_{22}^T)_v \} = C_1 \{ C_2 \bar{v}_1 (D_{11}^T)_v + (1 - C_1 \bar{v}_1) (D_{21}^T)_v \} \quad (4.18)$$

Only three of the four coefficients $(D_{11}^T)_v$, $(D_{12}^T)_v$, $(D_{21}^T)_v$ and $(D_{22}^T)_v$ can therefore be considered as independent, the fourth coefficient is fixed by constraint (4.18) derived from the Onsager reciprocal relationship. This constraint is also often ignored and all four coefficients are treated as independent parameters, which as we shall show later may lead to seriously inconsistent results.

4.2.2 Transport Equations for the Bulk Phases

The continuity equation in the liquid phases bathing the membrane is given by,

$$\frac{\partial C_i^L}{\partial t} = - \frac{\partial}{\partial z} (N_i^L); \quad i = 1, 2 \quad (4.19)$$

The superscript L is used to distinguish the molar concentration C_i^L and the molar flux N_i^L in the liquid from those within the membrane. In the case of the binary liquids it is more convenient to employ the volume average velocity $(u^v)^L$,

$$N_i^L = (J_i^L)_V + (u^V)^L C_i^L; \quad i = 1, 2 \quad (4.20)$$

and express the diffusive fluxes $(J_i)_V$ in terms of a single practical diffusion coefficient,

$$\begin{aligned} (J_1^L)_V &= -D_V^L \frac{\partial C_1^L}{\partial z} \\ (J_2^L)_V &= -\frac{\bar{v}_1^L}{\bar{v}_2^L} (J_1^L)_V \end{aligned} \quad (4.21)$$

This is because both the partial molar volumes and the practical diffusion coefficient in the liquid phase are open to direct measurement, the relevant data for the {ethanol-water} mixture considered in this study is available in the literature [Hansen and Miller, 1954; Hammond and Stokes, 1954]. Equation (4.21) recognises that there is only a single independent diffusive flux and a single diffusion coefficient suffices in a binary system. In contrast, the fluxes relative to stationary co-ordinates N_1^L and N_2^L are independent and their magnitude depends on the volume average velocity in the liquid, $(u^V)^L$.

The volume average velocity $(u^V)^L$ may in general have a convective contribution and there may also be an extra diffusion induced contribution caused by volume changes of mixing in the liquid. An independent expression for the diffusion-induced contribution to non-selective bulk flow was developed in section 2.2.5 and can be used if so desired. In practical terms, however, the volume change of mixing in liquids is normally small, it is less than 3% for the mixing of pure ethanol with pure water. In addition, the concentration changes in the liquid phase encountered in both the transient dialysis and pervaporation experiments are also quite small and we may safely ignore the volume change of mixing in the liquid phases bathing the membrane.

The lower liquid compartment in the dialysis cell is closed at the bottom and, ignoring volume changes of mixing, we may conclude that,

$$\bar{v}_1^L N_1^L + \bar{v}_2^L N_2^L = 0 \quad \text{no bulk movement in bottom liquid}$$

The top liquid compartment in the dialysis and pervaporation cell is open to convection, the level in the top compartment may fall (or rise) as a result of the movement of material across the top membrane interface. Ignoring the small volume change of mixing in the liquid, the velocity $(u^v)^L$ is independent of position and exactly equal to the net volume crossing the top membrane interface. In view of the flux boundary condition we may conclude that:

$$\frac{dL_{\text{Top}}}{dt} = \bar{v}_1^L N_1(t, L_{\text{mem}}) + \bar{v}_2^L N_2(t, L_{\text{mem}}) \quad \text{bulk movement in top liquid}$$

The model equations for transient dialysis are now complete and are summarised in Figure 4.2

The model equation for the top liquid and the membrane in the pervaporation cell are identical to those given for the dialysis cell. However, the vapour compartment in the pervaporation cell can be treated more simply. The vapour phase is at low pressure and can be considered as ideal. In addition convective flux dominates in the vapour chamber and the vapour may be treated as well mixed. There are therefore no concentration gradients in the vapour chamber and its dynamics may be described by a simple lumped material balance:

$$\frac{dC_1^v}{dt} = \frac{1}{L_v} N_1^v(t, 0) - \frac{1}{\tau_v} C_1^v \quad (4.22A)$$

$$\frac{dC_2^v}{dt} = \frac{1}{L_v} N_2^v(t, 0) - \frac{1}{\tau_v} C_2^v \quad (4.22B)$$

where L_v is the length of the vapour chamber and τ_v is its residence time. For an ideal vapour phase $P_1 = C_1 / RT$, $P_2 = C_2 / RT$, and the downstream pressure is given by $P = RT(C_1^v + C_2^v)$. The transient model equations for the pervaporation cell are summarised in Figure 4.3.

Top half

$$z = L_{\text{Top}} \quad \frac{\partial C_i^L}{\partial z}(t, L_{\text{Top}}) = 0 \quad \text{closed to diffusion}$$

$$\frac{dL_{\text{Top}}}{dt} = \bar{v}_1^L N_1^L(t, L_{\text{mem}}) + \bar{v}_2^L N_2^L(t, L_{\text{mem}}) \quad \text{open to convection}$$

$$\frac{\partial C_i^L}{\partial t} = -\frac{\partial}{\partial z} \left[D_V^L \frac{\partial C_i^L}{\partial z} + \frac{dL_{\text{Top}}}{dt} C_i^L \right]$$

Membrane

$$z = L_{\text{mem}} \quad a_i(t, L_{\text{mem}}) = a_i^L(t, L_{\text{mem}}) \quad \text{instantaneous equilibrium}$$

$$N_i^L(t, L_{\text{mem}}) = N_i(t, L_{\text{mem}}) \quad \text{no accumulation}$$

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left[\begin{pmatrix} (D_{11}^T)_P & (D_{12}^T)_P \\ (D_{21}^T)_P & (D_{22}^T)_P \end{pmatrix} \begin{pmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{pmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \right]$$

$$z=0 \quad a_i(t, 0) = a_i^L(t, 0) \quad \text{instantaneous equilibrium}$$

$$N_i^L(t, 0) = N_i(t, 0) \quad \text{no accumulation}$$

Bottom half

$$\frac{\partial C_i^L}{\partial t} = -\frac{\partial}{\partial z} \left[D_V^L \frac{\partial C_i^L}{\partial z} \right]$$

$$z = L_{\text{bot}} \quad \frac{dL_{\text{bot}}}{dt} = 0 \quad \text{closed to convection}$$

$$\frac{\partial C_i^L}{\partial z}(t, L_{\text{bot}}) = 0 \quad \text{closed to diffusion}$$

Figure 4.2 Continuity equations and boundary conditions for the dialysis cell.

(Polymer fixed frame with negligible swelling)

Top half

$$z = L_{\text{Top}} \quad \frac{\partial C_i^L}{\partial z}(t, L_{\text{Top}}) = 0 \quad \text{closed to diffusion}$$

$$\frac{dL_{\text{Top}}}{dt} = \bar{v}_1^L N_1^L(t, L_{\text{mem}}) + \bar{v}_2^L N_2^L(t, L_{\text{mem}}) \quad \text{open to convection}$$

$$\frac{\partial C_i^L}{\partial t} = -\frac{\partial}{\partial z} \left[D_v^L \frac{\partial C_i^L}{\partial z} + \frac{dL_{\text{Top}}}{dt} C_i^L \right]$$

Membrane

$$z = L_{\text{mem}} \quad a_i(t, L_{\text{mem}}) = a_i^L(t, L_{\text{mem}}) \quad \text{instantaneous equilibrium}$$

$$N_i^L(t, L_{\text{mem}}) = N_i(t, L_{\text{mem}}) \quad \text{no accumulation}$$

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left[\begin{pmatrix} (D_{11}^T)_P & (D_{12}^T)_P \\ (D_{21}^T)_P & (D_{22}^T)_P \end{pmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \right]$$

$$z=0 \quad a_i(t, 0) = a_i^V(t, 0) \quad \text{instantaneous equilibrium}$$

$$N_i^V(t, 0) = N_i(t, 0) \quad \text{no accumulation}$$

Bottom half

$$\frac{dC_1^V}{dt} = \frac{1}{L_v} N_1^V(t, 0) - \frac{1}{\tau_v} C_1^V ; p_1 = \frac{C_1^V}{RT} \quad \text{well mixed ideal vapour}$$

$$\frac{dC_2^V}{dt} = \frac{1}{L_v} N_2^V(t, 0) - \frac{1}{\tau_v} C_2^V ; p_2 = \frac{C_2^V}{RT} \quad \text{well mixed ideal vapour}$$

Figure 4.3 Continuity equations and boundary conditions for the pervaporation cell.

(Polymer fixed frame with negligible swelling)

4.3 Phase Equilibria for the {ethanol-water}/ silicon rubber System

The solution of the transient transport equations requires information on the properties of the bulk fluid as well as a thermodynamic model for the polymer/permeant sorption equilibria. The bulk phase properties of aqueous ethanol are well studied and readily available in the literature. The liquid phase non-ideality is well described by a variety of thermodynamic models, for example the Wilson, NRTL and UNIQUAC models [Reid *etal*, 1987]. The vapour/liquid data available at 25 °C [Hansen and Miller, 1954] and 50 °C and 60 °C [Jones *etal*, 1943] were correlated by Fong [1992] for a variety of models satisfying the Gibbs-Duhem equation. There was little to choose between the various expressions in the mid composition range but close to infinite dilution the best results were obtained with the correlation suggested by Hansen and Miller [1954],

$$\begin{aligned} \ln \gamma_1^L &= [1 - (x_1^L)^2] [A_0 + A_1 x_1^L + A_2 \exp(-A_3 x_1^L)] \\ \ln \gamma_2^L &= (x_1^L)^2 \left[A_0 - \frac{1}{2} A_1 + A_1 x_1^L + A_2 \exp(-A_3 x_1^L) + \right. \\ &\quad \left. \frac{A_2}{A_3 (x_1^L)^2} (1 - \exp(-A_3 x_1^L))(1 + A_3 x_1^L) \right] \end{aligned} \quad (4.23A)$$

using the following temperature dependent parameters:

$$\begin{aligned} A_0 &= 2.0612 - 0.00178T ; A_1 = -2.1792 + 0.0030T \\ A_2 &= -2.9607 + 0.0092T ; A_3 = 11.0000 \end{aligned} \quad (4.23B)$$

Figure 4.4 shows the variation of the ethanol and water activity coefficients calculated from the above correlation at 25 °C.

Diffusion in aqueous ethanol is also well studied and Hammond and Stokes [1953] report accurate results for the variation of the practical binary diffusivity at 25 °C. Figure 4.5 shows the variation of the binary diffusivity with liquid composition, which is well fitted by the following polynomial:

$$\begin{aligned} 10^5 D_v (\text{cm}^2 / \text{s}) &= 1.240 - 0.179x_1^L + 18.825(x_1^L)^2 \\ &\quad - 18.297(x_1^L)^3 + 6.557(x_1^L)^4 \end{aligned} \quad (4.24)$$

Figure 4.4 Liquid phase activity coefficients for ethanol(1) and water(2) at 25 °C calculated from the correlation of Fong (1992).

Figure 4.5 Liquid phase diffusivity for {ethanol(1)-water(2)} mixtures at 25 °C.

[correlated from data of Hammond and Stokes , 1953]

Description of the sorption equilibria for the {ethanol(1)-water(2)}/silicon rubber system presents a major challenge. The difficulty inherent in the experimental measurement of the total uptake and the degree of swelling for systems with low uptake were discussed in chapter 2. In the absence of reliable total uptake data, we may choose a model and attempt to recover its parameters from a match with the relative sorption isotherm, which can be measured with relative ease. Evidently, this procedure would incorporate the *a priori* assumptions inherent in the thermodynamic

model employed. The Flory-Huggins model [1953] which recognises the large size difference between the permeant and polymer molecules offers a suitable starting point for sorption in elastomers.

In this section we use the classical Flory-Huggins model with constant interaction parameters to model the sorption equilibria, modifications of the classic model will be considered in the next chapter. According to the Flory-Huggins model, the activity of the solutes in the polymer are given by:

$$\ln(a_1) = \ln \phi_1 + (1 - \phi_1) - \phi_2 (\bar{v}_1 / \bar{v}_2) + (\chi_{12} \phi_2 + \chi_{1P} \phi_P)(\phi_2 + \phi_P) - \chi_{2P} (\bar{v}_1 / \bar{v}_2) \phi_2 \phi_P \quad (4.25A)$$

$$\ln(a_2) = \ln \phi_2 + (1 - \phi_2) - \phi_1 (\bar{v}_2 / \bar{v}_1) + (\chi_{12} \phi_1 (\bar{v}_2 / \bar{v}_1) + \chi_{2P} \phi_P)(\phi_1 + \phi_P) - \chi_{1P} (\bar{v}_2 / \bar{v}_1) \phi_1 \phi_P \quad (4.25B)$$

The parameter χ_{12} represents penetrant-penetrant interactions within the polymer matrix. Assuming that such interactions are similar to that observed in the bulk liquid, the value of χ_{12} can be obtained from the Gibbs free energy change of mixing in the liquid. The excess Gibbs free energy of mixing for a binary system is given by (see chapter 2):

$$\frac{\Delta G_m^{ex}}{RT} = x_1 \ln(\phi_1 / x_1) + x_2 \ln(\phi_2 / x_2) + \chi_{12} x_1 \phi_2 \quad (4.26)$$

The above equation was fitted to the experimental excess Gibbs free energy of mixing at 25 °C reported by Hansen and Miller [1954] using a non-linear regression procedure which gave a value of $\chi_{12} = 3.65$. We remark here that this parameter has a small influence on the sorption characteristic in elastomers, which is dominated by polymer-permeant interactions characterised by χ_{1P} and χ_{2P} . Assuming χ_{1P} and χ_{2P} are independent of composition, their value can be obtained from a match with the relative sorption isotherm reported by Bansal [1988]. The best values obtained using non-linear regression were $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$ and are identical to those reported by Bansal [1988] who employed a similar procedure. The fit to the experimental data at 25 °C with $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$ and $\chi_{12} = 3.65$ is shown in Figure 4.6.

Figure 4.6 Relative isotherm for the {ethanol(1)-water(2)}/silicon rubber system at 25 °C predicted from the classical Flory-Huggins model with $\chi_{12} = 3.65$, $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$.

The individual and total uptake isotherms predicted with the classical Flory-Huggins model are shown in Figure 4.7. Unlike the bulk liquid, the sorbed phase does not exhibit an azeotrope and the silicon rubber membrane is selective towards ethanol over the entire range of liquid composition. We shall demonstrate later in this chapter that the χ_{1P} and χ_{2P} parameters should in fact be considered as composition dependent but retain the constant values for the present purposes.

Figure 4.7 Individual uptake isotherms of the {ethanol(1)-water(2)}/silicon rubber system at 25 °C predicted from the classical Flory-Huggins model with $\chi_{12} = 3.65$, $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$.

4.3.1 Equilibrium and Kinetic Coupling of Fluxes

It is instructive at this point to consider the magnitude of the elements of the equilibrium-coupling matrix $C_i \partial \ln(a_i) / \partial C_j$. Figure 4.8 shows the diagonal (main) and off-diagonal (cross) equilibrium terms calculated from the classical Flory-Huggins model as a function of the ethanol concentration in the membrane. Ignoring any kinetic-coupling effects, the diffusive fluxes in the membrane are given by,

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix}_P = \begin{bmatrix} (D_{11}^T)_P & 0 \\ 0 & (D_{22}^T)_P \end{bmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \quad (4.27)$$

No kinetic Coupling Equilibrium Coupling

From Figure 4.8, as the ethanol concentration is diminished the cross term $C_1 \partial \ln(a_1) / \partial C_2$ tends to zero while the main term $C_1 \partial \ln(a_1) / \partial C_1$ approaches unity. This implies that at low ethanol concentration the diffusive flux of ethanol is largely unaffected by the concurrent diffusive flux of water. In contrast, the cross term $(C_2 \partial \ln(a_2) / \partial C_1)$ does not approach zero but takes on a finite value comparable to the main term $(C_2 \partial \ln(a_2) / \partial C_2)$. This implies that the diffusive flux of water is strongly coupled to that of ethanol and a large concentration gradient of ethanol may induce an additional flux of water due to equilibrium coupling alone. The extent of the coupling of fluxes observed will of course depend on the magnitude of the local concentration gradients and may also be affected by kinetic-coupling effects.

The influence of kinetic coupling is most easily brought out by considering the diffusive flux equations in the following unexpanded form and conducting a simple numerical exercise:

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix}_P = \begin{bmatrix} (\Omega_{11}^T)_P & (\Omega_{12}^T)_P \\ (\Omega_{21}^T)_P & (\Omega_{22}^T)_P \end{bmatrix} \begin{pmatrix} \frac{\partial \mu_1}{\partial z} \\ \frac{\partial \mu_2}{\partial z} \end{pmatrix} \quad (4.28)$$

kinetic Coupling

Figure 4.8 Variation of the elements of the equilibrium matrix with ethanol concentration in the silicon rubber membrane at 25 °C calculated from the classical Flory-Huggins model with $\chi_{12} = 3.65$, $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$.

We note here that the influence of equilibrium coupling is inherent in the composition dependence of the chemical potentials.

Consider a point within the membrane and assume that the local chemical potential gradient of component 2 is r times that of component 1:

$$\frac{\partial \mu_2}{\partial z} = r \frac{\partial \mu_1}{\partial z}$$

The diffusive fluxes can then be expressed as:

$$-(J_1)_P = \left\{ 1 + r \frac{(\Omega_{12}^T)_P}{(\Omega_{11}^T)_P} \right\} (\Omega_{11}^T)_P \frac{\partial \mu_1}{\partial z} \quad (4.29A)$$

$$-(J_2)_P = \left\{ 1 + \frac{1}{r} \frac{(\Omega_{21}^T)_P}{(\Omega_{22}^T)_P} \right\} (\Omega_{22}^T)_P \frac{\partial \mu_2}{\partial z} \quad (4.29B)$$

The bracketed terms in equation (4.29A) and (4.29B) are the ratio of fluxes with and without kinetic coupling. Table 4.1 shows the influence of the cross term diffusion coefficients on the fluxes of species 1 and 2 for two different values of r . The gradients are assumed opposite to each other, $r < 0$, as would be expected in dialysis. With $r = -0.1$ the flux of component 1 is unaffected by the smaller chemical potential gradient of component 2 for values of $(\Omega_{12})_P / (\Omega_{11})_P$ as high as 0.5. In contrast, the flux of component 2 is halved for a value of $(\Omega_{21}^T)_P / (\Omega_{22}^T)_P$ as small as 0.05 due to coupling with component 1. A value of $(\Omega_{21}^T)_P / (\Omega_{22}^T)_P = 0.1$ will stop the flux of component 2 altogether and larger values $(\Omega_{21}^T)_P$ will cause component 2 to diffuse against its own chemical potential gradient. Similar but stronger coupling effects are indicated for $r = -0.01$. It is evident that kinetic coupling of fluxes may have a significant effect on the flux of the less preferentially adsorbed species.

Table 4.1 Ratio of kinetically coupled and uncoupled diffusive fluxes for a

membrane system with $\frac{\partial \mu_2}{\partial z} = r \frac{\partial \mu_1}{\partial z}$

Ratio of cross and main term diffusivities $(\Omega_{ij}^T)_P / (\Omega_{ii}^T)_P$	$r = -0.10$		$r = -0.01$	
	comp 1	comp 2	comp 1	comp 2
	$1 + r \frac{(\Omega_{12}^T)_P}{(\Omega_{11}^T)_P}$	$1 + \frac{1}{r} \frac{(\Omega_{21}^T)_P}{(\Omega_{22}^T)_P}$	$1 + r \frac{(\Omega_{12}^T)_P}{(\Omega_{11}^T)_P}$	$1 + \frac{1}{r} \frac{(\Omega_{21}^T)_P}{(\Omega_{22}^T)_P}$
0.00	1.0000	1.0000	1.0000	1.0000
0.05	0.9950	0.5000	0.9995	-4.0000
0.10	0.9900	0.0000	0.9990	-9.0000
0.25	0.9750	-1.5000	0.9975	-24.0000

4.4 Parameter Estimation Procedures

The transient model of dialysis and pervaporation shown in Figures 4.2 and 4.3 contain a large number of parameters that must be estimated from experimental data. The bulk phase properties are usually available in the literature and the equilibrium parameters may be estimated separately as shown in section 4.3. This leaves the membrane phase diffusion coefficients, which must be recovered from the interference patterns measured under dialysis conditions. The recovered parameters can then be used to *predict* the transient pervaporation data.

The diffusion coefficients of ethanol and water in the silicone rubber membrane are recovered from the deflection of the experimental interference fringes measured in the liquid boundary layers. The basic principles of the Twyman-Green interferometer and the experimental and theoretical procedures for recovering the membrane phase diffusion coefficients were detailed in chapter 3. In particular the essential requirement of accounting for light deflection in a medium of varying refractive index was clearly established. The partial differential equations constituting the model must first be solved for an assumed set of diffusivities to establish the concentration (hence refractive index) profile in the liquid bathing the membrane. This information must then be translated into an associated theoretical interference fringe that can be tested against the experimental fringe. This was accomplished by tracing the paths of a large number light rays (≈ 200) through the optical cell and the various components of the interferometer to build up the theoretical fringes associated with an assumed set of membrane phase diffusivities. The final step in the analysis is the adjustment of the assumed diffusivities to obtain the best match between the theoretical and experimental interference fringes.

4.4.1 Numerical Solution and Boundary Conditions

An essential first step is the development of a stable and accurate numerical technique for the solution of the coupled non-linear partial differential equations constituting the transient model of dialysis and pervaporation. The model equations were solved using the method of lines described in detail in chapter 3. The spatial derivatives were discretised using a seven-point finite difference formula, which transforms the partial differential equations into a much larger stiff set of ordinary

differential equations. The latter equations were integrated in time using the variable step, variable order method of Gear [1971] which can handle the integration of stiff equations efficiently.

The correct implementation of the boundary conditions specified at the membrane interfaces plays an important role in the numerical stability of the solution procedure. The interfacial concentrations in the bulk and membrane phases are assumed to achieve instantaneous equilibrium. This implies for example that at the lower interface:

$$\begin{aligned} \ln[a_1^L(t,0)] &= \ln \phi_1 + (1 - \phi_1) - \phi_2 (\bar{v}_1 / \bar{v}_2) + (\chi_{12} \phi_2 + \chi_{1P} \phi_P)(\phi_2 + \phi_P) \\ &\quad - \chi_{2P} (\bar{v}_1 / \bar{v}_2) \phi_2 \phi_P \\ \ln[a_2^L(t,0)] &= \ln \phi_2 + (1 - \phi_2) - \phi_1 (\bar{v}_2 / \bar{v}_1) + (\chi_{12} \phi_1 (\bar{v}_2 / \bar{v}_1) + \chi_{2P} \phi_P)(\phi_1 + \phi_P) \\ &\quad - \chi_{1P} (\bar{v}_2 / \bar{v}_1) \phi_1 \phi_P \end{aligned} \quad (4.30)$$

A Newton-Raphson procedure was used to solve the above non-linear algebraic equations to obtain the interfacial concentrations within the membrane from those in the bulk liquid. A similar procedure was employed for the upper interface at $z = L_{\text{mem}}$.

The flux boundary conditions relate the single independent interfacial concentration gradient in the binary liquid to the two independent interfacial concentration gradients of the permeating species in the membrane. The flux is continuous across the phase interfaces, for example,

$$N_i(t,0) = N_i^L(0,t)$$

Noting that $N_i^L = (J_i^L)_V + (u^V)^L C_i^L$, $N_i = (J_i)_P + u_P C_i$ and the polymer is assumed stationary $u_P = 0$, the continuity of fluxes requires that:

$$[u^V(t,0)]^L = \frac{[J_1(t,0)]_P - [J_1^L(t,0)]_V}{C_1^L(t,0)} = \frac{[J_2(t,0)]_P - [J_2^L(t,0)]_V}{C_2^L(t,0)} \quad (4.31)$$

Since there is only a single independent diffusive flux in the binary liquid, $(J_2^L)_V = -(\bar{v}_1^L / \bar{v}_2^L)(J_1^L)_V$, we may eliminate $(J_2^L)_V$ from (4.31) to yield:

$$[J_1^L(t,0)]_V = \bar{V}_2^L \{ C_2^L(t,0)[J_1(t,0)]_P - C_1^L(t,0)[J_2(t,0)]_P \} \quad (4.32)$$

Substituting for $(J_1)_P$ and $(J_2)_P$ from (4.8) and noting that $(J_1^L)_V = -D_V \partial C_1^L / \partial z$ enables us to relate the interfacial concentration gradient in the liquid phase to the interfacial concentration gradients in the membrane by:

$$\begin{aligned} \left\{ \frac{1}{\bar{V}_2^L} D_V \right\} \frac{\partial C_1^L(t,0)}{\partial z} = & \left\{ \left(C_1 \frac{\partial \ln(a_1)}{\partial C_1} \right) [C_2^L(D_{11}^T)_P - C_1^L(D_{21}^T)_P] \right. \\ & \left. + \left(C_2 \frac{\partial \ln(a_2)}{\partial C_1} \right) [C_2^L(D_{12}^T)_P - C_1^L(D_{22}^T)_P] \right\} \frac{\partial C_1(t,0)}{\partial z} \\ & + \left\{ \left(C_1 \frac{\partial \ln(a_1)}{\partial C_2} \right) [C_2^L(D_{11}^T)_P - C_1^L(D_{21}^T)_P] \right. \\ & \left. + \left(C_2 \frac{\partial \ln(a_2)}{\partial C_2} \right) [C_2^L(D_{12}^T)_P - C_1^L(D_{22}^T)_P] \right\} \frac{\partial C_2(t,0)}{\partial z} \end{aligned} \quad (4.33)$$

where the terms in the braces $\{ \}$ must all be evaluated at the lower membrane interface at $z = 0$. A similar expression holds at the upper membrane interface at $z = L_{mem}$.

A stable numerical solution was obtained by first using the equilibrium boundary conditions to calculate the interfacial concentrations in the membrane from those in the bulk liquid. The flux boundary conditions were then used to relate the interfacial concentration gradient in the bulk liquid to those in the membrane. A series of runs over a wide range of equilibrium and diffusivity parameters was conducted to confirm the stability of the numerical solution. Accurate and stable results were obtained in all cases when the 143 μm thick membrane and the first 2-cm of the upper and lower liquid compartments were each divided into 30 or more equal increments.

The membrane phase diffusion coefficients are, in general, a strong function of composition. The explicit inclusion of concentration dependent diffusivities in the numerical procedure requires knowledge of the specific functional form of the concentration dependency, which is not normally available. For the analysis of the transient dialysis process we may resort to constant "average diffusivities". This is motivated by the fact that in the dialysis experiments of Bansal [1988] the concentration difference between the two parts of the cell was kept deliberately small

(less than 5 wt%). The diffusive parameters recovered should be considered as "integral" diffusion coefficients and will be denoted by $\hat{D}_{ij}^T$ to distinguish them from point values D_{ij}^T . Figure 4.9 shows a typical example for the evolution of the concentration profiles with time and distance in the upper liquid and the membrane. The membrane phase diffusivities $(\hat{D}_{ij}^T)_P$ were assumed independent of composition for the purpose of this illustration and kinetic coupling was also ignored $(\hat{D}_{12}^T)_P = (\hat{D}_{21}^T)_P = 0$. Note that different time scales are used to demonstrate the evolution of the profiles in each phase more clearly. The concentration profile in the "thin" membrane develops rapidly and after a short time assumes a practically linear form. The profile in the liquid phase expands gradually with the diffusion front only advancing to about 1.2 cm from the interface after 1 hour.

Figure 4.9 Development of concentration profiles in the liquid (top panel) and the membrane (bottom panel) calculated with no kinetic coupling and $(\hat{D}_{11}^T)_P = 2 \times 10^{-6}$, $(\hat{D}_{22}^T)_P = 1 \times 10^{-4} \text{ cm}^2 / \text{s}$.
 {Top liquid: 3 wt%, Bottom Liquid: 0 wt % ethanol,
 Time scale for top liquid : 1:30s, 2:300s, 3:600s, 4:1800s, 5:3600s
 Time scale for membrane: 1:5 s, 2:15 s, 3:30 s, 4:600 s, 5:3600s}

The calculated concentration (refractive index) profile in the top liquid layer can be used to generate the corresponding interference fringe by tracing the path of a number light rays. Figure 4.10 shows the experimental interference fringe together with the theoretical fringe calculated for a particular set of membrane phase diffusivities at 1800 seconds. The values of the membrane phase diffusivities can be determined by adjusting the parameters to match the experimental and theoretical fringes shown on Figure 4.10.

Figure 4.10 Experimental and theoretical fringes calculated at 1800 seconds with $(\hat{D}_{11}^T)_P = 2 \times 10^{-6}$, $(\hat{D}_{22}^T)_P = 1 \times 10^{-4} \text{ cm}^2/\text{s}$ and no kinetic coupling. {other parameters as in Figure 4.9}

We are of course free to work with diffusivities defined for the polymer or the volume fixed frame of reference, the connection between these is given by equations 4.14 and 4.15. For the purpose of this chapter we choose to work in the volume fixed frame of reference, so that we can compare our results directly with those reported by Bansal [1988]. The objective function to be minimised was defined as:

$$F\left\{(\hat{D}_{11}^T)_V, (\hat{D}_{12}^T)_V, (\hat{D}_{21}^T)_V, (\hat{D}_{22}^T)_V\right\} = \sum_{r=1}^{200} (S_r - S_r^{\text{exp}})^2 + (Y_r - Y_r^{\text{exp}})^2 \quad (4.34)$$

where S_r and Y_r represent the optical path length and the distance above the interface for the r^{th} ray. Each element of the objective function (4.34) is a measure of the distance between the corresponding points on the fringes, indicated by the lines on Figure 4.10. The minimisation of (4.34) represents a complex constrained non-linear programming problem. This is because the matrix $[\hat{D}^T]_v$ must be positive definite and its diagonal elements also be positive. Furthermore, the elements of the matrix $[\hat{D}^T]_v$ are not independent of each other and must satisfy the Onsager reciprocal relationship (4.18). We may also need to place bounds on the individual elements $[\hat{D}^T]_v$ to constrain them to physically reasonable values. The constrained sequential quadratic programming procedure outlined in chapter 3 was used to adjust the parameter values.

4.5 Results and Discussion

Given sufficient parameters, the measured interference fringes can be equally well fitted by a variety of diffusion models. A critical test of the model, and its parameters, can therefore only be obtained by its ability to predict unseen experimental data measured under different operating conditions. To this end we shall attempt to recover the membrane phase diffusivities from transient dialysis data of Bansal[1988]. The model, and its parameters, will then be judged against its ability to *predict* the transient pervaporation fluxes reported by Abedl-Ghani [1992] for the same membrane.

The critical importance of the basic assumptions made in the development of the membrane transport model is brought out by considering the results reported by Bansal [1988]. The starting point for Bansal's analysis was the transport equation in the volume-fixed frame of reference written as:

$$\begin{pmatrix} -N_1 \\ -N_2 \end{pmatrix} = \begin{bmatrix} (D_{11}^T)_v & (D_{12}^T)_v \\ (D_{21}^T)_v & (D_{22}^T)_v \end{bmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} + u^v \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad (4.35)$$

Bansal [1988] assumed that the contribution of non-selective bulk flow is negligible, $u^v = 0$, and also set the cross-coefficients arbitrarily to zero, $(D_{12}^T)_v = (D_{21}^T)_v = 0$. The simplified membrane phase continuity equations considered by Bansal reduce to:

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left\{ \begin{bmatrix} (D_{11}^T)_v & 0 \\ 0 & (D_{22}^T)_v \end{bmatrix} \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \right\} \quad (4.36)$$

and a two parameter search may be conducted to obtain the $(\hat{D}_{11}^T)_v$ and $(\hat{D}_{22}^T)_v$ values by matching the theoretical and experimental fringes. As an initial test of our procedures we simulated the model and assumptions used by Bansal to fit the experimental fringes measured at different times. The results are summarised in Table 4.2 and are virtually identical to those reported by Bansal [1988] who used a different optimisation routine. The fit to the experimental fringes was excellent in all cases and the diffusion coefficients recovered were independent of the fringe time for each of the four separate experiments reported by Bansal [1988]. It is clear that an "average" $\hat{D}_{ij}^T$ value can be used for each particular experimental run but different values are required for different runs, which is a consequence of the concentration dependence of the diffusivities.

The basic transport processes occurring within the polymer are the same in dialysis and pervaporation. The validity of Bansal's model may therefore be critically tested by its ability to predict the transient pervaporation fluxes measured by Abdel-Ghani [1992] for the same silicon rubber membrane. Figure 4.11 compares the experimental pervaporation fluxes with those *predicted* by Bansal's model with the diffusion coefficients set at the mean of the values reported in Table 4.2. It is clear that the model proposed by Bansal, and the associated parameters, cannot even predict the general trend observed in pervaporation. In particular, the hydrophobic silicon rubber membrane is predicted to be selective towards water at feed ethanol concentrations approaching 80 wt%. Evidently, the assumptions inherent in the simplified model proposed by Bansal [1988] are in serious error and must be re-appraised.

Table 4.2 Average diffusion coefficient of ethanol and water in silicone rubber at 25 °C (Reproduction of the results obtained by Bansal, 1988)

Fringe Time S	Ethanol $10^6 (\hat{D}_{11}^T)_V \text{ cm}^2/\text{s}$			
	Concentration difference			
	0-3wt%	0-6wt%	15-20wt%	25-30wt%
600	2.08	1.34	0.56	0.53
900	1.94	1.34	0.57	0.54
1200	2.06	1.41	0.56	0.54
1500	1.98	1.40	0.59	0.55
1800	1.97	1.39	0.61	0.50
Mean	2.01	1.38	0.58	0.53
STD	0.061	0.034	0.022	0.019
Fringe time S	Water $10^4 (\hat{D}_{22}^T)_V \text{ cm}^2/\text{s}$			
	Concentration difference			
	0-3wt%	0-6wt%	15-20wt%	25-30wt%
600	1.10	0.69	0.28	0.18
900	1.07	0.69	0.26	0.19
1200	1.09	0.68	0.27	0.19
1500	1.06	0.69	0.26	0.18
1800	1.10	0.68	0.26	0.19
Mean	1.08	0.69	0.27	0.19
STD	0.018	0.005	0.009	0.005

Figure 4.11 Pervaporation of {ethanol-water}/silicone rubber at 25 °C predicted with $(\hat{D}_{12}^T)_V = (\hat{D}_{21}^T)_V = 0$ and $(\hat{D}_{11}^T)_V = 1 \times 10^{-6}$, $(\hat{D}_{22}^T)_V = 0.5 \times 10^{-4} \text{ cm}^2/\text{s}$ {data from Abdel-Ghani, 1992}

4.5.1 Non-Selective Bulk Flow

There may be several separate reasons for the extremely poor prediction of pervaporation results by Bansal's model. The first issue to be considered is the contribution of non-selective bulk flow within the polymer. There are few studies that have dealt explicitly with this problem and this contribution is usually ignored. A rare and notable exception is a recent article by Kamaruddin and Koros [1997] aimed specifically at the importance of diffusion induced non-selective bulk flow. Starting from an empirical generalisation of Fick's law Kamaruddin and Koros [1997] clearly demonstrate that non-selective bulk flow can affect the flux of the less preferentially sorbed species. The extent of this non-selective contribution depends primarily on the level of uptake and we shall now demonstrate that it has a small influence for the {ethanol-water}/silicon rubber system.

The correct continuity equation incorporating the influence of non-selective bulk flow is obtained by substituting for $[D^T]_p$ in terms of $[D^T]_v$ from (4.15) into (4.10):

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left[\begin{array}{cc} \frac{1 - C_2 \bar{v}_2}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} & \frac{C_1 \bar{v}_2}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} \\ \frac{C_2 \bar{v}_1}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} & \frac{1 - C_1 \bar{v}_1}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} \end{array} \begin{bmatrix} (D_{11}^T)_v & 0 \\ 0 & (D_{22}^T)_v \end{bmatrix} \right] + \begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix} \quad (4.37)$$

We note here that in keeping with Bansal's [1988] assumptions we have arbitrarily set the cross coefficients $(\hat{D}_{12}^T)_v = (\hat{D}_{21}^T)_v = 0$. A series of optimisation runs were conducted to recover the diffusion coefficients by matching the theoretical and experimental fringes using (4.37) instead of (4.36). The values recovered differed by less than 1% from those shown in Table 4.2, which suggests that diffusion induced bulk flow has a small contribution in the dialysis experiments of Bansal [1988]. This may be because the initial concentration difference in each experiment was kept to less than 5 wt% or it may be due to the small uptakes observed for the {ethano-

water}/silicon rubber system. To resolve this issue the transient dialysis model based on (4.38) was solved for a large initial concentration difference between top and bottom liquids (30-0wt% ethanol). Table 4.3 compares the contribution of the selective diffusive flux and the non-selective diffusion induced bulk flux to the total flux of ethanol and water within the membrane at 1800 seconds. It is clear from Table 4.3 that even for a 30% initial concentration difference the contribution of the diffusion induced bulk flow is small (less than 1%) and cannot be responsible for the failure of Bansal's model and parameters to predict the pervaporation flux. The uptake for the {ethanol-water}/silicon rubber system is small and diffusion induce bulk flow has a small influence. This is in agreement with the conclusion by Kamaruddin and Koros [1997] that bulk flow may only be ignored for systems exhibiting low sorption level for all permeating components.

Table 4.3 Contribution of non-selective bulk flow to the total flux ($\text{g/m}^2 \text{ h}$) within the membrane at 1800 s for an initial concentration difference of 0-30wt%

$$[\hat{D}_{11}^T = 1.0 \times 10^{-6}, \hat{D}_{22}^T = 0.5 \times 10^{-4} \text{ cm}^2 / \text{s}]$$

Position	Ethanol				Water			
z/L_{mem}	Total N_1	Diffusive $(J_1)_v$	Bulk flow $C_1 u^v$	% bulk	Total N_2	Diffusive $(J_2)_v$	Bulk flow $C_2 u^v$	% bulk
0.0	-29.901	-30.076	0.175	0.58	38.570	38.785	-0.215	0.56
0.1	-29.907	-30.082	0.175	0.58	38.570	38.785	-0.215	0.56
0.2	-29.915	-30.090	0.175	0.58	38.570	38.786	-0.216	0.56
0.3	-29.921	-30.095	0.174	0.58	38.570	38.786	-0.216	0.56
0.4	-29.925	-30.099	0.174	0.58	38.571	38.787	-0.216	0.56
0.5	-29.927	-30.100	0.173	0.58	38.571	38.787	-0.216	0.56
0.6	-29.927	-30.100	0.173	0.58	38.571	38.788	-0.217	0.56
0.7	-29.925	-30.098	0.173	0.58	38.571	38.788	-0.217	0.56
0.8	-29.922	-30.094	0.172	0.57	38.571	38.789	-0.218	0.57
0.9	-29.917	-30.089	0.172	0.57	38.571	38.790	-0.219	0.57
1.0	-29.910	-30.081	0.171	0.57	38.571	38.790	-0.219	0.57

4.5.2 Onsager Reciprocal Relationship

The primary reason for the failure of Bansal's simplified model (4.36) and the improved model (4.37) can be traced to the violation of the Onsager reciprocal relationship. The correct formulation of the phenomenological model of membrane transport indicates that the elements of the diffusivity matrix $[\hat{D}^T]_v$ are not independent of each other and must satisfy the constraint:

$$C_2 \left\{ (1 - C_2 \bar{v}_2) (\hat{D}_{12}^T)_v + C_1 \bar{v}_2 (\hat{D}_{22}^T)_v \right\} = C_1 \left\{ C_2 \bar{v}_1 (\hat{D}_{11}^T)_v + (1 - C_1 \bar{v}_1) (\hat{D}_{21}^T)_v \right\} \quad \text{cf (4.18)}$$

In view of this restriction, the arbitrary assumption of $(\hat{D}_{12}^T)_v = (\hat{D}_{21}^T)_v = 0$ imposes a definite relationship between the main term diffusion coefficients:

$$\frac{(\hat{D}_{11}^T)_v}{(\hat{D}_{22}^T)_v} = \frac{\bar{v}_2}{\bar{v}_1} \quad (4.38)$$

This means that there is only a single independent diffusivity; searching for two parameters, as was done by Bansal[1988] and in section 4.3.1, gives an excellent fit of the experimental interference fringes. This is, however, at the expense of violating the fundamental constraint imposed by the Onsager reciprocal relationship and leads to a very poor prediction of the pervaporation data.

Imposing the Onsager reciprocal relationship reduces the number of adjustable parameters by one and at the same time leads to better prediction. Setting $(\hat{D}_{12}^T)_v = (\hat{D}_{21}^T)_v = 0$ and noting (4.38), the continuity equation takes the form,

$$\begin{pmatrix} \frac{\partial C_1}{\partial t} \\ \frac{\partial C_2}{\partial t} \end{pmatrix} = \frac{\partial}{\partial z} \left[\begin{bmatrix} \frac{1 - C_2 \bar{v}_2}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} & \frac{C_1 \bar{v}_2}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} \\ \frac{C_2 \bar{v}_1}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} & \frac{1 - C_1 \bar{v}_1}{1 - C_1 \bar{v}_1 - C_2 \bar{v}_2} \end{bmatrix} \begin{bmatrix} (\hat{D}_{11}^T)_v & 0 \\ 0 & \frac{\bar{v}_1}{\bar{v}_2} (\hat{D}_{11}^T)_v \end{bmatrix} \right] \quad (4.39)$$

$$\begin{bmatrix} C_1 \frac{\partial \ln(a_1)}{\partial C_1} & C_1 \frac{\partial \ln(a_1)}{\partial C_2} \\ C_2 \frac{\partial \ln(a_2)}{\partial C_1} & C_2 \frac{\partial \ln(a_2)}{\partial C_2} \end{bmatrix} \begin{pmatrix} \frac{\partial C_1}{\partial z} \\ \frac{\partial C_2}{\partial z} \end{pmatrix}$$

The above equation accounts for non-selective bulk flow explicitly, it also satisfies the Onsager reciprocal relationship and contains a single adjustable diffusivity $(\hat{D}_{11}^T)_v$. Table 4.4 shows the result of single parameter searches conducted to match the experimental fringes reported by Bansal [1988] using a transient model based on (4.39). The values reported for water were calculated directly from $(\hat{D}_{22}^T)_v = \bar{v}_1(\hat{D}_{11}^T)_v / \bar{v}_2$. The fit to the experimental fringes was excellent in all cases and the parameters for each run were again independent of fringe time.

Table 4.4 Average diffusion coefficients of ethanol and water in silicone rubber at 25 °C (satisfying the Onsager reciprocal relationship)

Fringe Time S	Ethanol $10^6 (\hat{D}_{11}^T)_v \text{ cm}^2/\text{s}$			
	Concentration difference			
	0-3wt%	0-6wt%	15-20wt%	25-30wt%
600	3.30	2.83	2.43	2.28
900	3.30	2.83	2.44	2.29
1200	3.32	2.93	2.43	2.30
1500	3.31	2.92	2.45	2.29
1800	3.31	2.91	2.46	2.31
Mean	3.31	2.88	2.44	2.29
STD	0.008	0.050	0.013	0.011

Fringe time S	Water $10^5 (\hat{D}_{22}^T)_v \text{ cm}^2/\text{s}$			
	Concentration difference			
	0-3wt%	0-6wt%	15-20wt%	25-30wt%
600	1.07	0.92	0.79	0.74
900	1.07	0.92	0.77	0.74
1200	1.08	0.91	0.78	0.75
1500	1.07	0.95	0.77	0.74
1800	1.09	0.91	0.78	0.75
Mean	1.07	0.92	0.78	0.74
STD	0.005	0.016	0.008	0.005

Comparison of the entries in Tables 4.2 and 4.4 shows that the diffusion coefficients satisfying the Onsager reciprocal relationship are substantially different from those which do not. The model based on (4.36) with the parameters reported in Table 4.2 gives an excellent fit of the experimental fringes. An equally good fit is also obtained with the model based on (4.39) and the parameters reported in Table 4.4. A distinction between these models cannot therefore be made based on their ability to fit the experimental dialysis data used to recover the diffusive parameters. Their reliability can, however, be critically assessed by comparison of the *prediction* made of the pervaporation performance. Figure 4.12 shows the pervaporation flux predicted using the transient model satisfying the Onsager reciprocal relationship with the diffusivities set at the mean of the values reported in Table 4.4. It is clear that this model predicts the qualitative trends observed in the pervaporation of {ethanol-water} mixtures across silicon rubber faithfully. This is in contrast to the model of Bansal [1988] and its improvement based on (4.37), both of which violate the Onsager reciprocal relationship, see Figure 4.11.

Figure 4.12 Pervaporation of {ethanol-water}/silicone rubber at 25 °C predicted with

$$(\hat{D}_{12}^T)_v = (\hat{D}_{21}^T)_v = 0 \text{ and } (\hat{D}_{11}^T)_v = 2.7 \times 10^{-6}, (\hat{D}_{22}^T)_v = 0.88 \times 10^{-5} \text{ cm}^2/\text{s}$$

{data from Abdel-Ghani,1992}

The quantitative differences observed in Figure 4.12 may be attributed to the concentration dependence of the equilibrium and diffusive parameters that have been ignored up to this point. In particular, the same classical Flory-Huggins model with constant interaction parameters has been used in the description of both the dialysis and the pervaporation processes. In the case of pervaporation the membrane is in contact with a vapour at its lower interface and there is a much larger concentration change within the membrane compared to dialysis. As demonstrated in chapter 2, the classical Flory-Huggins model cannot accurately describe the sorption of water and ethanol vapours by silicon rubber. Figure 4.13 shows the vapour uptake predicted at 25 °C using the classical Flory-Huggins model with constant interaction parameters, the experimental data available at 40 °C [Ngueyn 1996] are also shown for comparison purposes. It is clear that the vapour uptake at low pressure is seriously overestimated and this may be partly responsible for the larger pervaporation fluxes predicted.

Figure 4.13 Sorption of ethanol and water vapour in silicone rubber at 25 °C predicted with constant Flory-Huggins interaction parameters $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$.
{• data of Nguyen *etal* ,1996 at 40 °C}

We should emphasise here that, despite the quantitative differences observed in Figure 4.12, the predictions made by the correctly formulated phenomenological model are quite impressive. First, the model contains only a single adjustable membrane diffusivity parameter whose value is determined from only four experiments conducted under dialysis conditions. Second, the pervaporation data is not used in any way to adjust the model parameters. Third, the cross-term diffusivities $(\hat{D}_{12}^T)_v$ and $(\hat{D}_{21}^T)_v$ were set to zero arbitrarily, which in turn implies that the *diffusive* fluxes in the silicon rubber membrane are not kinetically coupled. Fourth, the predictions made in Figure 4.12 are obtained with constant diffusion coefficients, whereas the results shown in Table 4.4 indicate that the average main-term diffusivities are concentration dependent.

It is clear that a much better quantitative prediction can be obtained by using a better description of the phase equilibria and allowing for the concentration dependence of the diffusivities. For example we could conduct a three parameter search by adjusting $(D_{11}^T)_v, (D_{22}^T)_v, (D_{12}^T)_v$ with $(D_{21}^T)_v$ obtained from the Onsager reciprocal relationship (4.18). This procedure could, in principle, establish the actual magnitude of kinetic coupling between the diffusive fluxes which was assumed negligible in Figure 4.12. This approach is complicated because the multicomponent phenomenological coefficients do not have a clear physical basis. For example, there is no simple relationship between the binary phenomenological coefficients and their multicomponent counterparts. As a result, the concentration dependence of the phenomenological coefficients is usually rather complex and its determination demands substantial multicomponent data over a wide range of concentrations which is not available to us. This is in contrast to the Stefan-Maxwell formulation of multicomponent diffusion, which is based on a clearly defined mechanistic model of the diffusion process. The latter approach provides a more convenient vehicle for the examination of concentration dependence of diffusive parameters and will be considered in the next chapter.

CHAPTER 5

A GENERIC MODEL FOR MULTICOMPONENT TRANSPORT ACROSS NONPOROUS MEMBRANES

5. A Generic Model for Multicomponent Transport across

Nonporous Membranes

5.1 Introduction

A molecule diffusing within a homogeneous nonporous polymer moves in response to the sum of forces exerted on it. Such forces may arise as a result of local chemical potential gradients caused by departure from equilibrium or may be due to an external potential imposed across the polymeric matrix. In principle, a properly formulated transport model accounting for the various driving forces should be equally applicable to any separation process employing a homogeneous nonporous polymer as the selective separation barrier. Examples of such processes include dialysis, electrodialysis, pervaporation, vapour permeation and reverse osmosis. The primary purpose of this chapter is to present a "generic" model of membrane transport with physically well defined equilibrium and kinetic parameters. Such a model has great practical utility in as far as the parameters recovered under one processing condition can be used for the design, scale-up and optimisation of other processes employing the same membrane. There have been numerous attempts over the years to develop mathematical models of membrane separation processes. The majority of these models were, however, aimed at the description of specific examples and only a handful of studies have focused on formulating a general model capable of handling different membrane processes. [Lee, 1975; Kataoka *et al*, 1982; Mulder and Smolders, 1984; Wijman and Baker, 1995].

The aim of this chapter is to develop a general mathematical model applicable to a wide range of membrane separation processes. To this end we first develop the flux equations based on the Stefan-Maxwell formulation of multicomponent diffusion. A general expression accounting for the internal and external driving forces is then derived through consideration of irreversible thermodynamics culminating in a "generic" set of membrane transport equations. The chief advantage of the generic model, over the phenomenological approach of chapter 4, is that the diffusive parameters and driving forces are well defined and retain their physical significance in diverse processes such as reverse osmosis, electrodialysis, dialysis, pervaporation and vapour permeation which employ a nonporous polymeric membrane.

Selective transport across nonporous membranes can arise as a result of differences in the solubility and/or diffusivity of the permeating species in the polymer matrix. Separate evaluation of the equilibrium and kinetic contributions to the transport process is complicated by the strong concentration dependence of the parameters involved. In most practical applications the detailed experimental data necessary for the direct evaluation of the model parameters is not available. The practical utility of the “generic” transport model is tested using the limited data available to us for the transient dialysis and pervaporation of the {ethanol-water}/silicone rubber system. External forces play a minor role in dialysis or pervaporation and the driving force for transport is the local chemical potential gradient. In principle, therefore, the parameters recovered using data for dialysis (pervaporation) should be equally applicable to pervaporation (dialysis).

In this chapter we present modifications of the classical Flory-Huggins model which enable the description of the pure and binary uptake of ethanol and water from both liquid and vapour mixtures using an identical set of parameters. A systematic procedure is then developed which enables the simultaneous extraction of the binary equilibrium and the binary Stefan-Maxwell diffusivities from the variation of the pure liquid pervaporation fluxes with the permeate pressure. The binary Stefan-Maxwell diffusivities recovered retain their physical significance and can be used directly in multicomponent systems. The concentration dependence of the Stefan-Maxwell diffusivity in binary and ternary systems are related by a natural extension of the binary Vignes relationship [1966] to multicomponent systems. The results obtained confirm that transient dialysis and pervaporation can both be described by the generic model using the same set of model parameters.

5.2 A “Generic” Model of Membrane Transport

In this section we develop the transport equations describing the fluxes in terms of the driving forces using the Stefan-Maxwell formulation. The development is limited to a ternary system but its extension to any number of components is straightforward. The Stefan-Maxwell formulation offers three distinct advantages over the irreversible thermodynamics approach used in the previous chapter. First, the Stefan-Maxwell diffusivities have a well-defined physical meaning in terms of intermolecular friction, which is lacking with the phenomenological coefficients of

chapter 4. Second, the Stefan-Maxwell diffusivities are by definition frame independent whereas the phenomenological coefficients require the careful definition of the frame of reference. Finally, the ternary Onsager phenomenological coefficients have no obvious relationship with their binary counterparts. Consequently the phenomenological coefficients recovered from binary experiments are of little value in predicting the multicomponent diffusive behaviour. In contrast, the binary Stefan-Maxwell diffusivities retain their physical significance and can be used directly in the description of complex multicomponent systems.

5.2.1 Stefan-Maxwell Formulation of the Flux Equations

An introduction to the Stefan-Maxwell formulation of diffusion was presented in Chapter 2. For a mixture containing p species, the general driving force for component i , d_i , is related to the velocity difference between different species by:

$$d_i = - \sum_{j=1}^p \frac{x_i x_j (u_i - u_j)}{\bar{D}_{ij}} \quad (5.1)$$

where x_i and u_i denote the mole fraction and velocity of component i respectively and $\bar{D}_{ij}$ is the binary diffusion coefficient for the i - j pair. A more useful form of (5.1) is obtained by using the definition of the molar flux, $N_i = C_i u_i$,

$$d_i = \sum_{j=1}^p \frac{(x_i N_j - x_j N_i)}{C_t \bar{D}_{ij}} \quad (5.2)$$

where C_t is the total molar concentration. Equation (5.2) enables the calculation of the driving force for component i in terms of the molar fluxes of the various species present. It is important to recognise that only $(p-1)$ of the driving forces are independent and the sum of all driving forces is by definition zero:

$$\sum_{i=1}^p d_i = 0 \quad (5.3)$$

In contrast, the p molar fluxes $N_1, N_2, \dots, N_p$ are all independent. Consequently, the description of the molar fluxes in terms of the independent driving forces demands an additional restriction. This additional restriction must be obtained by considerations

other than diffusion and depends on the particular problem at hand. Using the arguments advanced in chapter 4, we shall again assume negligible swelling so that the polymer is stationary and does not move in the course of the diffusion process. This implies that $N_p = 0$ and enables us to express (5.2) as:

$$C_t d_i = - \sum_{j=1}^{p-1} B_{ij} N_j \quad (5.4)$$

with the B_{ij} defined by:

$$B_{ii} = \sum_{k=1}^p \frac{x_k}{D_{ik}} \quad (5.5)$$

$$B_{ij} = - \frac{x_i}{D_{ij}}$$

It is convenient to define a $(p-1) \times (p-1)$ matrix B with elements B_{ij} and the vectors

$\underline{d} = [d_1, d_2, \dots, d_{p-1}]^T$, $\underline{N} = [N_1, N_2, \dots, N_{p-1}]^T$ and express (5.4) in the compact form,

$$C_t \underline{d} = -[B] \underline{N}$$

which may be inverted to give,

$$\underline{N} = -C_t [B]^{-1} \underline{d} \quad (5.6)$$

The Stefan-Maxwell formulation (5.6) delivers the fluxes relative to stationary coordinates, N_i , in terms of the independent driving forces. The diffusivities, D_{ij} , are by definition frame independent and reflect the frictional interaction between components i and j irrespective of the number of components present. The same diffusion coefficients can be used to establish the diffusive fluxes, $(J_i)_R$, in any chosen frame of reference R by writing (5.1) as:

$$\begin{aligned}
 d_i &= - \sum_{j=1}^p \frac{x_i x_j [(u_i - u^R) - (u_j - u^R)]}{\bar{D}_{ij}} \\
 &= \sum_{j=1}^p \frac{x_i (J_j)_R - x_j (J_i)_R}{C_i \bar{D}_{ij}}
 \end{aligned}
 \tag{5.7}$$

The definition of the diffusive fluxes must of course be completed by adopting a particular reference velocity u^R for the mixture. The most convenient choice for diffusion in a nonporous membrane is the polymer-fixed frame of reference obtained by setting $u^R = u_P$ so that,

$$(J_P)_P = 0 \quad \text{polymer fixed frame} \tag{5.8}$$

by definition. The flux relative to stationary co-ordinates, N_i , is related to diffusive flux in the polymer-fixed frame of reference by:

$$N_i = (J_i)_P + u_P C_i \tag{5.9}$$

Writing this equation for the polymer and noting (5.8) shows that:

$$u_P = \frac{N_P}{C_P} \tag{5.10}$$

Under the assumption of negligible swelling, $N_P = u_P C_P = 0$, which implies that $u_P = 0$ and the fluxes N_i and $(J_i)_P$ are equal.

5.2.2 Irreversible Thermodynamic Formulation of Generalised Driving Forces

The driving force in multicomponent membrane transport may be partly due to internal forces represented by the local chemical potential gradients and partly due to external body forces such as those caused by an electrical field or a pressure gradient imposed across the membrane. An expression for a generalised driving force accounting for the various contributions may be derived through the postulates of irreversible thermodynamics [Degroot and Mazur, 1962]. The purpose of irreversible thermodynamics is to extend classical thermodynamics to systems undergoing irreversible processes such as heat transfer or diffusion. This is made possible by the central postulate of "local equilibrium" which assumes that all the thermodynamic

state properties of a system "*not too far from equilibrium*" may be defined locally using the same relationships used for a system at equilibrium [Degroot and Mazur, 1962, Slattery, 1981].

Using the postulates of irreversible thermodynamics allows the derivation of an explicit expression for the rate of entropy production per unit volume caused by the various irreversible processes taking place. The rate of entropy production due to isothermal diffusion, σ_{dif} , is given by [Slattery, 1981]:

$$T\sigma_{\text{dif}} = -\sum_{i=1}^p [(\nabla\tilde{\mu}_i)_T - \tilde{F}_i]j_i \geq 0 \quad (5.11)$$

Here, $j_i = \rho_i(u_i - u^M)$ is the diffusive mass flux of i relative to the mass average velocity u^M ; T is the absolute temperature; $\tilde{\mu}_i = \mu_i / M_i$ is the specific chemical potential of component i and $(\nabla\tilde{\mu}_i)_T$ represents its gradient under isothermal conditions, $\tilde{F} = F_i / M_i$ represents the external body force per unit mass of species i . The requirement $\sigma_{\text{dif}} \geq 0$ is dictated by the second law of thermodynamics.

It is convenient to separate out the contribution of pressure to the chemical potential by expanding $(\nabla\tilde{\mu}_i)_T$ to give:

$$(\nabla\tilde{\mu}_i)_T = \frac{1}{M_i}(\nabla\mu_i)_{T,P} + \frac{\bar{v}_i}{M_i}\nabla P \quad (5.12)$$

where $\bar{v}_i$ is partial molar volume of component i and ∇P is the pressure gradient. Equation (5.11) can now be written as:

$$T\sigma_{\text{dif}} = -\sum_{i=1}^p \left[\frac{1}{M_i}(\nabla\mu_i)_{T,P} + \frac{\bar{v}_i}{M_i}\nabla P - \tilde{F}_i \right] j_i \geq 0 \quad (5.13)$$

Further simplification of (5.13) is made possible by noting that for most chemical engineering processes mechanical equilibrium is achieved much faster than thermodynamic equilibrium. For a system at mechanical equilibrium, the pressure gradient is balanced by the external body forces:

$$-\frac{1}{\rho_t} \nabla P + \sum_{i=1}^p \omega_i \tilde{F}_i = 0 \quad \text{mechanical equilibrium} \quad (5.14)$$

We may therefore add (5.14) to each term of (5.13) without affecting the overall result:

$$T\sigma_{\text{dif}} = -\sum_{i=1}^p \left[\frac{1}{M_i} (\nabla \mu_i)_{T,P} + \frac{\bar{v}_i}{M_i} \nabla P - \tilde{F}_i + \left(-\frac{1}{\rho_t} \nabla P + \sum_{j=1}^p \omega_j \tilde{F}_j \right) \right] \cdot j_i \geq 0 \quad (5.15)$$

Substituting for $j_i = \rho_i(u_i - u^M)$ and noting that $C_i = \rho_i / M_i$ and $\phi_i = \bar{v}_i C_i$ enables us to express (5.15) as:

$$T\sigma_{\text{dif}} = -C_i R \sum_{i=1}^p d_i (u_i - u^M) \geq 0 \quad (5.16)$$

where, d_i , represents the generalised driving force for component i and is defined by:

$$C_i R T d_i = C_i (\nabla \mu_i)_{T,P} + (\phi_i - \omega_i) \nabla P - (C_i F_i - \sum_{j=1}^p C_j F_j) \quad (5.17)$$

The expression for $C_i R T d_i$ includes both the internal and the external forces which act on a molecule of component i and cause it to move relative to the mixture. We note here that a pressure gradient can affect a separation provided there is a difference between mass and volume fractions and this contribution becomes important in reverse osmosis. The last term on the right hand side of (5.17) represents other body forces that may be employed, for example an electrical force due to an external voltage gradient that is important in electrodialysis. The first term in (5.17) represents the internal forces caused by local departure from equilibrium and has the major contribution in processes such as dialysis, pervaporation and vapour permeation.

The chemical potential gradient, $(\nabla \mu_i)_{T,P}$, appearing in (5.17) is not an easy quantity to deal with and it is convenient to develop an expression in terms of 'measurable' composition gradients. This is achieved by noting that $\mu_i = \mu_i(x_1, x_2, \dots, x_{p-1})$ and:

$$(\nabla \mu_i)_{T,P} = \sum_{j=1}^{p-1} \left(\frac{\partial \mu_i}{\partial x_j} \right)_{T,P,\Sigma} (\nabla x_j) \quad (5.18)$$

The symbol Σ is used to indicate that differentiation of μ_i is carried out while keeping all mole fractions except that of j and p constant. Evaluation of the partial derivatives in (5.18) requires a thermodynamic model expressing the dependence of the chemical potential on composition component. Substituting (5.18) into (5.17) leads to:

$$C_i RT d_i = C_i \sum_{j=1}^{p-1} \left(\frac{\partial \mu_i}{\partial x_j} \right)_{T,P,\Sigma} (\nabla x_j) + (\phi_i - \omega_i) \nabla P - (C_i F_i - \omega_i \sum_{j=1}^{p-1} C_j F_j) \quad (5.19)$$

The flux equations (5.6) coupled with the generalised driving force (5.19) and a suitable thermodynamic model constitute a "generic" set of equations which may be applied to any process employing a nonporous polymer as the selective selection barrier. The chief advantage of this approach, over the phenomenological approach of chapter 4, is that the diffusive parameters are well defined and retain their physical significance in various processes such as reverse osmosis, electrodialysis, dialysis, pervaporation or vapour permeation. The major difference between these processes lies in the forces that drive the separation.

5.3 Transient Models of Dialysis and Pervaporation

We are now in a position to present the transient model equations for the dialysis and pervaporation cells shown in Figure 5.1. The continuity equations for the bulk phases are identical to those presented in Section 4.2 but the transport equations within the membrane are based on the Stefan-Maxwell formulation. For a ternary system containing components 1 and 2 and the polymer, p , equation (5.2) can be written as:

$$\begin{aligned} C_1 d_1 &= \frac{x_1 N_2 - x_2 N_1}{\bar{D}_{12}} - \frac{x_1 N_p - x_p N_1}{\bar{D}_{1p}} \\ C_1 d_2 &= \frac{x_2 N_1 - x_1 N_2}{\bar{D}_{12}} - \frac{x_2 N_p - x_p N_2}{\bar{D}_{2p}} \end{aligned} \quad (5.20)$$

Figure 5.1 Schematic of the dialysis and pervaporation cells

Assuming the polymer is stationary, $N_p = 0$, reduces (5.20) to:

$$\begin{aligned}
 C_t d_1 &= \frac{x_1 N_2 - x_2 N_1}{\bar{D}_{12}} - \frac{x_p N_1}{\bar{D}_{1p}} \\
 C_t d_2 &= \frac{x_2 N_1 - x_1 N_2}{\bar{D}_{12}} - \frac{x_p N_2}{\bar{D}_{2p}}
 \end{aligned}
 \tag{5.21}$$

It is convenient to express (5.21) in matrix form:

$$\begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} = -C_t \begin{bmatrix} d_1 \\ d_2 \end{bmatrix}
 \tag{5.22}$$

with the matrix elements B_{ij} defined by:

$$\begin{aligned}
 B_{11} &= \frac{x_2}{\bar{D}_{12}} + \frac{x_p}{\bar{D}_{1p}} & B_{12} &= -\frac{x_1}{\bar{D}_{12}} \\
 B_{21} &= -\frac{x_2}{\bar{D}_{12}} & B_{22} &= \frac{x_1}{\bar{D}_{12}} + \frac{x_p}{\bar{D}_{2p}}
 \end{aligned}
 \tag{5.23}$$

Equation (5.22) can be inverted to give the molar fluxes in terms of the two independent driving forces:

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -C_t \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix}^{-1} \begin{pmatrix} d_1 \\ d_2 \end{pmatrix} \quad (5.24)$$

The coupling of fluxes is inherent in (5.24) because the flux of each diffusing component is related to the driving forces of both components.

External driving forces have a minor influence in dialysis and pervaporation and the generalised force expression (5.19) reduces to:

$$d_i = \frac{x_i}{RT} \left\{ \left(\frac{\partial \mu_i}{\partial x_1} \right) \left(\frac{\partial x_1}{\partial z} \right) + \left(\frac{\partial \mu_i}{\partial x_2} \right) \left(\frac{\partial x_2}{\partial z} \right) \right\}; i = 1, 2 \quad (5.25)$$

Noting that $d\mu_i = RT d \ln(a_i)$ and introducing the equilibrium interaction matrix Γ with elements $\Gamma_{ij} = x_i \partial \ln(a_i) / \partial x_j$ we may combine (5.24) and (5.25) to arrive at,

$$\begin{pmatrix} -N_1 \\ -N_2 \end{pmatrix} = C_t \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix}^{-1} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{pmatrix} \frac{\partial x_1}{\partial z} \\ \frac{\partial x_2}{\partial z} \end{pmatrix} \quad (5.26)$$

Kinetic Equilibrium
coupling coupling

Equation (5.26) is the working transport equation for the membrane in either dialysis or pervaporation.

The elements of the Stefan-Maxwell diffusivity matrix $[B]$ are given by (5.23). Explicit expressions for the elements of the inverse matrix $[B]^{-1}$, which represent the extent of the kinetic coupling of fluxes, is easily obtained for a ternary system:

$$[B]^{-1} = \begin{bmatrix} \frac{D_{1P}(x_1 D_{2P} + x_P D_{12})}{x_P(x_2 D_{1P} + x_1 D_{2P} + x_P D_{12})} & \frac{x_1 D_{1P} D_{2P}}{x_P(x_2 D_{1P} + x_1 D_{2P} + x_P D_{12})} \\ \frac{x_2 D_{1P} D_{2P}}{x_P(x_2 D_{1P} + x_1 D_{2P} + x_P D_{12})} & \frac{D_{2P}(x_2 D_{1P} + x_P D_{12})}{x_P(x_2 D_{1P} + x_1 D_{2P} + x_P D_{12})} \end{bmatrix} \quad (5.27)$$

The evaluation of the equilibrium interaction matrix $[\Gamma]$,

$$[\Gamma] = \begin{bmatrix} \frac{\partial \ln(a_1)}{\partial \ln(x_1)} & \frac{\partial \ln(a_1)}{\partial \ln(x_2)} \\ \frac{\partial \ln(a_2)}{\partial \ln(x_1)} & \frac{\partial \ln(a_2)}{\partial \ln(x_2)} \end{bmatrix} \quad (5.28)$$

requires a suitable thermodynamic model capable of describing the non-ideality of the polymer solution. The classical Flory-Huggins model discussed in chapter 2 provides a suitable starting point. In the case of polar solutes and non-polar polymers, however, the classical model with constant interaction parameters proves inadequate. In this chapter we shall consider a modified Flory-Huggins model with activity dependent interaction parameters, which complicates the evaluation of the equilibrium interaction terms substantially and deserves particular attention.

The activities a_1 and a_2 in the membrane can be viewed as either a function of two independent mole fractions x_1 and x_2 or two independent volume fractions ϕ_1 and ϕ_2 . We may therefore write:

$$\begin{aligned} \begin{pmatrix} d \ln(a_1) \\ d \ln(a_2) \end{pmatrix} &= \begin{bmatrix} \left(\frac{\partial \ln(a_1)}{\partial x_1} \right)_{x_2} & \left(\frac{\partial \ln(a_1)}{\partial x_2} \right)_{x_1} \\ \left(\frac{\partial \ln(a_2)}{\partial x_1} \right)_{x_2} & \left(\frac{\partial \ln(a_2)}{\partial x_2} \right)_{x_1} \end{bmatrix} \begin{pmatrix} dx_1 \\ dx_2 \end{pmatrix} \\ &= \begin{bmatrix} \left(\frac{\partial \ln(a_1)}{\partial \phi_1} \right)_{\phi_2} & \left(\frac{\partial \ln(a_1)}{\partial \phi_2} \right)_{\phi_1} \\ \left(\frac{\partial \ln(a_2)}{\partial \phi_1} \right)_{\phi_2} & \left(\frac{\partial \ln(a_2)}{\partial \phi_2} \right)_{\phi_1} \end{bmatrix} \begin{pmatrix} d\phi_1 \\ d\phi_2 \end{pmatrix} \end{aligned} \quad (5.29)$$

It is easy to show from (5.29) that:

$$\begin{bmatrix} \frac{\partial \ln(a_1)}{\partial \ln(x_1)} & \frac{\partial \ln(a_1)}{\partial \ln(x_2)} \\ \frac{\partial \ln(a_2)}{\partial \ln(x_1)} & \frac{\partial \ln(a_2)}{\partial \ln(x_2)} \end{bmatrix} = \begin{bmatrix} x_1 & 0 \\ \phi_1 & x_2 \\ 0 & \phi_2 \end{bmatrix} \begin{bmatrix} \frac{\partial \ln(a_1)}{\partial \ln(\phi_1)} & \frac{\partial \ln(a_1)}{\partial \ln(\phi_2)} \\ \frac{\partial \ln(a_2)}{\partial \ln(\phi_1)} & \frac{\partial \ln(a_2)}{\partial \ln(\phi_2)} \end{bmatrix} \begin{bmatrix} \frac{\partial \phi_1}{\partial x_1} & \frac{\partial \phi_1}{\partial x_2} \\ \frac{\partial \phi_2}{\partial x_1} & \frac{\partial \phi_2}{\partial x_2} \end{bmatrix} \quad (5.30)$$

The first and last matrices on the right hand side of (5.30) are readily obtained from the definition of volume fraction:

$$\phi_i = \frac{x_i \bar{V}_i}{x_1 \bar{V}_1 + x_2 \bar{V}_2 + x_p \bar{V}_p} ; i = 1, 2 \quad (5.31)$$

To evaluate the second matrix on the right hand side of (5.30) we start by viewing the Flory-Huggins model as:

$$\begin{aligned} a_1 &= \phi_1 \exp\{q_1\} \\ a_2 &= \phi_2 \exp\{q_2\} \end{aligned} \quad (5.32)$$

with

$$\begin{aligned} q_1(\chi_{1P}, \chi_{2P}, \phi_1, \phi_2) &= (1 - \phi_1) - (\bar{V}_1 / \bar{V}_2) \phi_2 + \phi_2 (1 - \phi_1) \chi_{12} \\ &\quad + (1 - \phi_1)(1 - \phi_1 - \phi_2) \chi_{1p}(a_1, a_2) \\ &\quad - (\bar{V}_1 / \bar{V}_2) \phi_2 (1 - \phi_1 - \phi_2) \chi_{2p}(a_1, a_2) \\ q_2(\chi_{1P}, \chi_{2P}, \phi_1, \phi_2) &= (1 - \phi_2) - (\bar{V}_2 / \bar{V}_1) \phi_1 + (\bar{V}_2 / \bar{V}_1) \phi_1 (1 - \phi_2) \chi_{12} \\ &\quad + (1 - \phi_2)(1 - \phi_1 - \phi_2) \chi_{2p}(a_1, a_2) \\ &\quad - (\bar{V}_2 / \bar{V}_1) \phi_1 (1 - \phi_1 - \phi_2) \chi_{1p}(a_1, a_2) \end{aligned} \quad (5.33)$$

We note here that (5.33) allows for the fact that in a ternary system the polymer-permeant interaction parameters may depend on the activities of both permeating species. Taking the total derivative of (5.32) yields,

$$\begin{pmatrix} e^{-q_1} da_1 \\ e^{-q_2} da_2 \end{pmatrix} = \begin{pmatrix} d\phi_1 \\ d\phi_2 \end{pmatrix} + \begin{pmatrix} \phi_1 dq_1 \\ \phi_2 dq_2 \end{pmatrix} \quad (5.34)$$

The total derivative dq_i is given by,

$$dq_i = \left(\frac{\partial q_i}{\partial \phi_1} \right)_{\substack{\phi_2 \\ \chi_{1P} \\ \chi_{2P}}} d\phi_1 + \left(\frac{\partial q_i}{\partial \phi_2} \right)_{\substack{\phi_1 \\ \chi_{1P} \\ \chi_{2P}}} d\phi_2 + \left(\frac{\partial q_i}{\partial \chi_{1P}} \right)_{\substack{\phi_1 \\ \phi_2}} d\chi_{1P} + \left(\frac{\partial q_i}{\partial \chi_{2P}} \right)_{\substack{\phi_1 \\ \phi_2}} d\chi_{2P} \quad (5.35)$$

and all the partial derivatives appearing in (5.35) can be obtained by formal differentiation of (5.33). Substituting for dq_1 and dq_2 from (5.35) into (5.34) and

noting that in general $d\chi_{iP} = \sum_{j=1}^2 (\partial \chi_{iP} / \partial a_j) da_j$ enables us to relate the changes in

activity to the changes in the volume fraction:

$$\begin{bmatrix} \frac{\partial \ln(a_1)}{\partial \ln(\phi_1)} & \frac{\partial \ln(a_1)}{\partial \ln(\phi_2)} \\ \frac{\partial \ln(a_2)}{\partial \ln(\phi_1)} & \frac{\partial \ln(a_2)}{\partial \ln(\phi_2)} \end{bmatrix} = \begin{bmatrix} 1 - e^{q_1} \sum_{j=1}^2 \left(\frac{\partial q_1}{\partial \chi_{jP}} \right) \left(\frac{\partial \chi_{jP}}{\partial a_1} \right) & -e^{q_2} \sum_{j=1}^2 \left(\frac{\partial q_1}{\partial \chi_{jP}} \right) \left(\frac{\partial \chi_{jP}}{\partial a_2} \right) \\ -e^{q_1} \sum_{j=1}^2 \left(\frac{\partial q_2}{\partial \chi_{jP}} \right) \left(\frac{\partial \chi_{jP}}{\partial a_1} \right) & 1 - e^{q_2} \sum_{j=1}^2 \left(\frac{\partial q_2}{\partial \chi_{jP}} \right) \left(\frac{\partial \chi_{jP}}{\partial a_2} \right) \end{bmatrix} \begin{bmatrix} 1 + \frac{\partial q_1}{\partial \phi_1} & \frac{\partial q_1}{\partial \phi_2} \\ \frac{\partial q_2}{\partial \phi_1} & 1 + \frac{\partial q_2}{\partial \phi_2} \end{bmatrix} \quad (5.36)$$

Given a specific form for the functional dependence of the interaction parameters $\chi_{iP} = \chi_{iP}(a_1, a_2)$ we may calculate the equilibrium interaction matrix through (5.30), (5.31) and (5.36). In the case of constant interaction parameters, the first matrix on the right hand side of (5.36) reduces to the unity matrix and the calculations are simplified substantially.

Figures 5.2 and 5.3 summarise the model equations and the boundary conditions for transient dialysis and pervaporation respectively. The numerical solution of these equations by the method of lines and the parameter estimation procedures remain as described in Chapter 4. A stable numerical solution was obtained by first using the equilibrium boundary conditions to calculate the interfacial concentrations in the membrane from those in the bulk liquid. The flux boundary conditions were then used to relate the interfacial concentration gradient in the bulk liquid to those in the membrane. A series of runs over a wide range of equilibrium and diffusive parameters was conducted to confirm the stability and accuracy of the numerical solution. Accurate and stable results were obtained in all cases when the 143 μm membrane and the first 2-cm of the upper and lower liquids were each divided into 30 or more equal increments. Parameter estimation was carried out using the constrained sequential quadratic programming procedure of Chen and Macchietto [1991] described in chapter 4.

Top half

$$z = L_{\text{Top}} \quad \frac{\partial C_i^L}{\partial z}(t, L_{\text{Top}}) = 0 \quad \text{closed to diffusion}$$

$$\frac{dL_{\text{Top}}}{dt} = \bar{v}_1^L N_i^L(t, L_{\text{mem}}) + \bar{v}_2^L N_2^L(t, L_{\text{mem}}) \quad \text{open to convection}$$

$$\frac{\partial C_i^L}{\partial t} = -\frac{\partial}{\partial z} \left[D_V^L \frac{\partial C_i^L}{\partial z} + \frac{dL_{\text{Top}}}{dt} C_i^L \right]$$

Membrane

$$z = L_{\text{mem}} \quad a_i(t, L_{\text{mem}}) = a_i^L(t, L_{\text{mem}}) \quad \text{instantaneous equilibrium}$$

$$N_i^L(t, L_{\text{mem}}) = N_i(t, L_{\text{mem}}) \quad \text{no accumulation}$$

Kinetic Coupling

$$\left(\frac{\partial C_i}{\partial z} \right) = \frac{\partial}{\partial z} \left\{ C_i \left[\begin{array}{cc} \frac{\bar{D}_{1P}(x_1 \bar{D}_{2P} + x_P \bar{D}_{12})}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} & \frac{x_1 \bar{D}_{1P} \bar{D}_{2P}}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} \\ \frac{x_2 \bar{D}_{1P} \bar{D}_{2P}}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} & \frac{\bar{D}_{2P}(x_2 \bar{D}_{1P} + x_P \bar{D}_{12})}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} \end{array} \right] \right. \\ \left. \left[\begin{array}{cc} x_1 \frac{\partial \ln(a_1)}{\partial x_1} & x_1 \frac{\partial \ln(a_1)}{\partial x_2} \\ x_2 \frac{\partial \ln(a_2)}{\partial x_1} & x_2 \frac{\partial \ln(a_2)}{\partial x_2} \end{array} \right] \left(\frac{\partial x_i}{\partial z} \right) \right\} \quad \text{Equilibrium coupling}$$

$$z=0 \quad a_i(t, 0) = a_i^L(t, 0) \quad \text{instantaneous equilibrium}$$

$$N_i^L(t, 0) = N_i(t, 0) \quad \text{no accumulation}$$

Bottom half

$$\frac{\partial C_i^L}{\partial t} = -\frac{\partial}{\partial z} \left[D_V^L \frac{\partial C_i^L}{\partial z} \right]$$

$$z = L_{\text{bot}} \quad \frac{dL_{\text{bot}}}{dt} = 0 \quad \text{closed to convection}$$

$$\frac{\partial C_i^L}{\partial z}(t, L_{\text{bot}}) = 0 \quad \text{closed to diffusion}$$

Figure 5.2 Continuity equations and boundary conditions for the dialysis cell.

(Negligible swelling)

Top half

$$z = L_{\text{Top}} \quad \frac{\partial C_i^L}{\partial z}(t, L_{\text{Top}}) = 0 \quad \text{closed to diffusion}$$

$$\frac{dL_{\text{Top}}}{dt} = \bar{v}_1^L N_1^L(t, L_{\text{mem}}) + \bar{v}_2^L N_2^L(t, L_{\text{mem}}) \quad \text{open to convection}$$

$$\frac{\partial C_i^L}{\partial t} = -\frac{\partial}{\partial z} \left[D_v^L \frac{\partial C_i^L}{\partial z} + \frac{dL_{\text{Top}}}{dt} C_i^L \right]$$

Membrane

$$z = L_{\text{mem}} \quad a_i(t, L_{\text{mem}}) = a_i^L(t, L_{\text{mem}}) \quad \text{instantaneous equilibrium}$$

$$N_i^L(t, L_{\text{mem}}) = N_i(t, L_{\text{mem}}) \quad \text{no accumulation}$$

Kinetic Coupling

$$\left(\frac{\partial C_i}{\partial z} \right) = \frac{\partial}{\partial z} \left\{ C_i \left[\begin{array}{cc} \frac{\bar{D}_{1P}(x_1 \bar{D}_{2P} + x_P \bar{D}_{12})}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} & \frac{x_1 \bar{D}_{1P} \bar{D}_{2P}}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} \\ \frac{x_2 \bar{D}_{1P} \bar{D}_{2P}}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} & \frac{\bar{D}_{2P}(x_2 \bar{D}_{1P} + x_P \bar{D}_{12})}{x_3(x_2 \bar{D}_{1P} + x_1 \bar{D}_{2P} + x_P \bar{D}_{12})} \end{array} \right] \right. \\ \left. \left[\begin{array}{cc} x_1 \frac{\partial \ln(a_1)}{\partial x_1} & x_1 \frac{\partial \ln(a_1)}{\partial x_2} \\ x_2 \frac{\partial \ln(a_2)}{\partial x_1} & x_2 \frac{\partial \ln(a_2)}{\partial x_2} \end{array} \right] \left(\frac{\partial x_i}{\partial z} \right) \right\} \\ \text{Equilibrium coupling}$$

$$z=0 \quad a_i(t, 0) = a_i^V(t, 0) \quad \text{instantaneous equilibrium}$$

$$N_i^V(t, 0) = N_i(t, 0) \quad \text{no accumulation}$$

Bottom half

$$\frac{dC_1^V}{dt} = \frac{1}{L_v} N_1^V(t, 0) - \frac{1}{\tau_v} C_1^V ; p_1 = \frac{C_1^V}{RT} \quad \text{well mixed ideal vapour}$$

$$\frac{dC_2^V}{dt} = \frac{1}{L_v} N_2^V(t, 0) - \frac{1}{\tau_v} C_2^V ; p_2 = \frac{C_2^V}{RT} \quad \text{well mixed ideal vapour}$$

Figure 5.3 Continuity equations and boundary conditions for the pervaporation cell.
(Negligible swelling)

5.4 Results and Discussion

The equilibrium and diffusive parameters appearing in the transient models of dialysis and pervaporation are in general highly concentration dependent. The detailed experimental information necessary for the direct evaluation of such concentration dependence is not normally available. In the rest of this chapter we present a progressive development of suitable procedures for extracting the model parameters from limited data available to us for the {ethanol-water}/silicon rubber system. The results obtained indicate that the generic model of membrane transport is capable of describing the dialysis and pervaporation processes with an identical set of parameters. Furthermore, the analysis below identifies the type of experimental work required to allow the confident evaluation of the model parameters.

5.4.1 Phase Equilibria: Modification of the Flory-Huggins Model

The separate evaluation of the kinetic and equilibrium contributions to the multicomponent transport processes requires a thermodynamic model for the non-ideality of the polymer solution. This thermodynamic model should be capable of describing both the liquid/polymer and the vapour/polymer equilibria using an identical set of parameters. This is because in pervaporation the membrane is in contact with a liquid at the feed side and an unsaturated low-pressure vapour at the permeate side. The classical Flory-Huggins model with constant interaction parameters is incapable of producing the characteristic shape observed for the uptake of small polar solutes such as water and ethanol by the "hydrophobic" silicone rubber, see Figure 4.13. Furthermore, the enthalpic and/or entropic modification of the Flory-Huggins model [Koningsveld and Kleingtjens, 1971; Lichtenthaler *et al*, 1974] suggested in the literature are of little help in this respect [Favre *et al*, 1993 and 1994]. An alternative is to retain the basic form of the Flory-Huggins model and allow the interaction parameters to be a simple function of activity.

In a ternary mixture the interaction parameters may be affected to varying degree by the activities of both permeating components. As a first attempt, however, we may assume that the interaction parameter of each component with the polymer is a function of its own activity. This is done in the hope that the mixing effects may be

properly accounted for by the Flory-Huggins model. For the uptake of a pure vapour, we may assume:

$$\chi_{ip}(a_i) = \alpha_{i0} + \alpha_{i1}a_i + \alpha_{i2}a_i^2 + \alpha_{i3}a_i^3 \quad (5.37)$$

where $a_i = p_i / p_i^0$ is the activity of the pure vapour and the α_{ij} 's are a set of constants. The choice of a cubic polynomial is motivated by the experimentally observed shape for the sorption of water and ethanol in silicone rubber (see Figure 2.16). One coefficient can be fixed from a single measurement for the uptake of the pure liquid (with $a_i = 1$) and (5.37) can be written as:

$$\chi_{ip}(a_i) = \alpha_{i0} + \alpha_{i1}a_i + \alpha_{i2}a_i^2 + [\chi_{ip}^0 - (\alpha_{i0} + \alpha_{i1} + \alpha_{i2})]a_i^3 \quad (5.38)$$

where χ_{ip}^0 is the interaction parameter for the uptake of the pure liquid.

The remaining constants α_{i0} , α_{i1} and α_{i2} should ideally be found from a match with the experimental pure vapour sorption isotherm. Unfortunately, reliable vapour sorption data for the system under study at 25 °C is not available. In absence of such information, we shall use the relative sorption data for {ethanol-water} liquid mixtures in silicone rubber. The relative sorption isotherm at 25 °C was measured by Bansal (1988) *without removing* the membrane from the free liquid and is shown on Figure 5.3. Adopting (5.38) for activity dependence of each interaction parameter introduces six coefficients which must be recovered from the 17 noisy relative sorption data points reported by Bansal[1988]. This is clearly a difficult task and it is essential to introduce sufficient constraints to ensure the parameters recovered lead to physically acceptable behaviour.

As a first physical constraint we know that silicon rubber is selective towards ethanol and the {ethanol-water}/silicon rubber system does not exhibit an azeotrope. The experimental relative sorption isotherm can exhibit a variety of shapes and those observed most frequently are shown in Figure 5.2. The limiting slopes at either end of the composition range establish the general shape of the relative isotherm. If the product of the two limiting slopes is negative, it is most likely that one component is preferentially adsorbed over the entire range of composition and an azeotrope is not formed. If the product of the two limiting slopes is positive, it is most likely that the

adsorbed phase shows a single azeotrope. In the case of {ethanol(1)-water(2)}/silicon rubber system, the interaction parameters recovered must therefore be such that the predicted limiting slopes of the relative sorption isotherm satisfy the following constraints:

$$\frac{d\eta_1}{dx_1^L} \Big|_{x_1^L \rightarrow 0} > 0 \quad \text{and} \quad \frac{d\eta_1}{dx_1^L} \Big|_{x_1^L \rightarrow 1} < 0 \quad (5.39)$$

The above constraints limit the space of the unknown parameters substantially and help ensure that the thermodynamic model conforms to the general behaviour observed experimentally.

Figure 5.2 Typical shape of relative sorption isotherms commonly observed

The calculation of the limiting slopes proceeds by recalling the relationship between the relative and individual sorption from chapter 2,

$$\eta_1 = (1 - x_1^L) N_1^s - x_1^L N_2^s \quad (5.40)$$

where N_1^s and N_2^s denote the individual uptake of components 1 and 2 expressed in moles/g of dry membrane. Differentiating (5.40) with respect to the liquid mole fraction, x_1^L , gives,

$$\frac{d\eta_1}{dx_1^L} = (1 - x_1^L) \frac{dN_1^s}{dx_1^L} - x_1^L \frac{dN_2^s}{dx_1^L} - (N_1^s + N_2^s) \quad (5.41)$$

Now, under the assumption of negligible swelling the volume of the membrane does not change as a result of sorption, so that

$$N_i^s = \frac{n_i}{M_d} = \frac{n_i}{\rho_d V_d} = \frac{n_i \bar{v}_i}{\rho_d \bar{v}_i V_d} = \frac{\phi_i}{\rho_d \bar{v}_i} \quad (5.42)$$

where M_d , V_d and ρ_d are the mass, volume and mass density of the dry membrane respectively. Differentiating (5.42) using the chain rule and noting that at equilibrium $a_i = a_i^{\text{mem}} = a_i^{\text{liq}}$ leads to:

$$\frac{dN_i^s}{dx_1^L} = \frac{dN_i^s}{d\phi_i^s} \left(\frac{\partial \phi_i^s}{\partial a_i} \right)_{a_{j \neq i}} \frac{da_i}{dx_1^L} = \frac{1}{\rho_d \bar{v}_i} \left(\frac{\partial \phi_i^s}{\partial a_i} \right)_{a_{j \neq i}} \frac{da_i}{dx_1^L} \quad (5.43)$$

The derivative da_i / dx_1^L can be found from the liquid phase activity model presented in chapter 4 and the partial derivative $\partial \phi_i / \partial a_i$ is obtained from the Flory-Huggins model using the procedures described in section 5.3.

Another physical constraint is obtained by noting that at low vapour pressures silicon rubber has a greater affinity for ethanol compared to water. The Henry's constant derived from the Flory-Huggins model is given by:

$$\begin{aligned} H_i &= \lim_{P_i \rightarrow 0} \left(\frac{dN_i^s}{dP_i} \right) = \lim_{a_i \rightarrow 0} \left(\frac{1}{P_i^o \bar{v}_i \rho_d} \frac{d\phi_i^s}{da_i} \right) = \frac{1}{P_i^o \bar{v}_i \rho_d} \lim_{a_i \rightarrow 0} \left(\frac{\phi_i^s}{a_i} \right) \\ &= \frac{1}{P_i^o \bar{v}_i \rho_d} \exp \left\{ - \left[1 + \chi_{ip} (a_i = 0) \right] \right\} \end{aligned} \quad (5.44)$$

Evidently, the Henry's constant for ethanol must be greater than that for water, which implies that,

$$\frac{1}{P_1^o \bar{v}_1} \exp \left\{ - (1 + \alpha_{10}) \right\} > \frac{1}{P_2^o \bar{v}_2} \exp \left\{ - (1 + \alpha_{20}) \right\} \quad (5.45)$$

Finally, we also know that in order to reproduce the characteristic vapour isotherm shape of water and ethanol the cubic polynomial (5.38) must exhibit a single maximum in the activity range $0 < a_i < 1$. This in turn enables us to impose a number of constraints on the parameters to restrict the variation of χ_{ip} to the desired general form.

The constrained quadratic programming procedure [Chen and Machieto 1991] was used to extract the six parameters for ethanol and water from a match with the relative sorption data of Bansal [1988] while satisfying the constraints mentioned in previous paragraphs. The parameters recovered are shown in Table 5.1 and the solid line in Figure 5.3 shows the fit to the relative sorption data.

Table 5.1 Activity dependent Flory-Huggins interaction parameters recovered from the relative sorption data of Bansal [1988]

$$\dagger \chi_{IP}(a_i) = \alpha_{i0} + \alpha_{i1}a_i + \alpha_{i2}a_i^2 + [\chi_{IP}^0 - (\alpha_{i0} + \alpha_{i1} + \alpha_{i2})]a_i^3$$

Parameter	α_{i0}	α_{i1}	α_{i2}
Ethanol(1)	1.886	-0.230	3.730
Water(2)	4.240	5.000	-2.635

$$\dagger \chi_{1P}^0 = 2.19 \text{ and } \chi_{2P}^0 = 4.89$$

Figure5.3 Relative sorption isotherm for {ethanol(1)-water(2)}/silicon rubber at 25 °C predicted using the Flory-Huggins model with
 _____ activity dependent interaction parameters of Table 5.1
 ----- constant interaction parameters $\chi_{IP} = 2.19$ and $\chi_{2p} = 4.89$
 {• data of Bansal, 1988}

It is clear from Figure 5.3 that the activity dependent parameters recovered give a good fit of the experimental relative sorption data. In particular, the system exhibits no azeotrope for uptake from liquid mixtures and similar calculations confirm that no azeotropes are predicted for uptake from mixed vapours. The dashed line in Figure 5.3 shows the fit to the relative sorption isotherm obtained with constant interaction parameters $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$. In view of the measurement errors reported by Bansal [1988], the relative sorption data is more or less equally well fitted by either model. However, comparing the predicted pure vapour isotherms shown in Figure 5.4 brings out the significant advantage of the activity dependent interaction parameters. It is clear that the activity dependent parameters of Table 5.1 capture the characteristic shape observed experimentally whereas constant interaction parameters fail in this respect. We note here that experimental vapour isotherms at 25 °C are not available to us so a direct comparison with data is not possible. The data shown on Figure 5.4 was measured at 40 °C for a different silicon rubber membrane [Nguyen, *etal*, 1996] and is only included for qualitative comparison.

Figure 5.4 Predicted pure vapour sorption isotherms of ethanol and water by silicon rubber at 25 °C predicted by the Flory-Huggins model with:
 — activity dependent interaction parameters of Table 5.1
 - - - constant interaction parameters $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$
 { • data of Nguyen *etal* [1996] at 40 °C shown for comparison }

5.4.2 Estimation of “Average” Stefan-Maxwell Diffusivities

We now turn to the estimation of the Stefan-Maxwell diffusivities from the interference fringes measured by Bansal [1988] for the {ethanol(1)-water(2)}/silicon rubber system under transient dialysis conditions. The recovered diffusivities can then be used to assess the utility and reliability of the generic model by *predicting* the transient pervaporation fluxes reported by Abdel-Ghani [1992] for the same silicon rubber membrane. For a ternary system, the generic model of membrane transport contains three Stefan-Maxwell diffusivities $\bar{D}_{12}$, $\bar{D}_{1p}$ and $\bar{D}_{2p}$ with $\bar{D}_{ij}$ representing the extent of friction between the i-j pair in the ternary mixture. We shall assume that the friction between ethanol and water within the polymer solution is similar to that observed in the binary bulk liquid. This enables us to fix $\bar{D}_{12}$ at the geometric mean of the infinite dilution binary diffusivities in the liquid phase, $\bar{D}_{12} = 1.124 \times 10^{-5} \text{ cm}^2 / \text{s}$.

The two remaining Stefan-Maxwell diffusivities $\bar{D}_{1p}$ and $\bar{D}_{2p}$ representing the friction between the permeating species and the polymer must be recovered by matching the experimental and theoretical fringes. In general, the diffusivities $\bar{D}_{1p}$ and $\bar{D}_{2p}$ may be a function of composition and we shall have more to say on their concentration dependence later. For the present time, however, we shall analyse the transient dialysis process on the basis of constant “average” Stefan-Maxwell diffusivities. This is motivated by the fact that in the dialysis experiments of Bansal [1988] the concentration difference between the two halves of the dialysis cell was kept deliberately small (less than 5%). Evidently, the average Stefan-Maxwell diffusivities recovered should be considered as “integral” diffusion coefficients and will be denoted by $\hat{D}_{ij}$ to distinguish them from the “differential” coefficients $\bar{D}_{ij}$.

The numerical solution and parameter estimation procedures employed remain essentially the same as that described in section 4.4. The transient model of dialysis shown on Figure 5.2 was set up using the Flory-Huggins model with activity dependent parameters of Table 5.1 and average Stefan-Maxwell diffusivities. The resultant non-linear partial differential equations were solved by the method of lines to produce the liquid phase concentration profile for assumed values of $\hat{D}_{1p}$ and $\hat{D}_{2p}$.

The computed concentration profile was then used to generate the corresponding theoretical fringe taking full account of light deflection. The diffusivities $\hat{D}_{1p}$ and $\hat{D}_{2p}$ were adjusted using the constrained sequential quadratic programming procedure of Chen and Macchietto [1991] to match the theoretical and experimental fringes. Table 5.2 summarises the average Stefan-Maxwell diffusivities of ethanol and water in silicon rubber obtained through two-parameter searches conducted at different fringe times.

Table5.2 Average Stefan-Maxwell diffusivity of ethanol in silicon rubber at 25 °C

Fringe time (s)	Ethanol $10^7 \hat{D}_{1p}$ (cm ² / s)			
	0-3wt%	0-6wt%	15-20wt%	25-30wt%
600	0.632	0.333	0.120	0.110
900	0.605	0.315	0.123	0.109
1200	0.614	0.320	0.121	0.111
1500	0.607	0.288	0.117	0.106
1800	0.616	0.293	0.119	0.109
Mean	0.615	0.310	0.120	0.109
STD	0.01	0.02	0.02	0.02

Fringe time(s)	Water $10^7 \hat{D}_{2p}$ (cm ² / s)			
	0-3wt%	0-6wt%	15-20wt%	25-30wt%
600	1.42	0.821	0.452	0.375
900	1.37	0.863	0.485	0.390
1200	1.35	0.807	0.468	0.380
1500	1.32	0.745	0.440	0.395
1800	0.38	0.762	0.407	0.385
Mean	1.37	0.800	0.450	0.385
STD	0.03	0.04	0.03	0.02

Comparison of the entries in Table 5.2 confirms that the average Stefan-Maxwell diffusivities recovered from each of the four separate experiments reported by Bansal [1988] are independent of fringe time. However, different average values are required for different experiments, which is an indication of the concentration dependence of the Stefan-Maxwell diffusivities.

The basic transport processes occurring within the membrane are the same in pervaporation and dialysis and the generic model with the same set of parameters should describe either process. Figure 5.5 shows the transient pervaporation fluxes *predicted* by the generic membrane transport model using the equilibrium parameters given in Table 5.1 and the average Stefan-Maxwell diffusivities recovered from the 0-3 wt% dialysis experiments. The experimental pervaporation fluxes measured by Abdel-Ghani[1992] for the same silicon rubber membrane are also shown for comparison. We should emphasise of course that the experimental pervaporation data was not used in any way to extract or fit the model parameters.

Figure 5.5 Pervaporation of {ethanol(1)-water(2)}/silicone rubber at 25 °C predicted with the average Stefan-Maxwell diffusivities from 0-3wt% dialysis experiment{ $\hat{D}_{12} = 1.124 \times 10^{-5}$, $\hat{D}_{1p} = 6.15 \times 10^{-8}$, $\hat{D}_{2p} = 1.37 \times 10^{-7} \text{ cm}^2/\text{s}$; data from Abdel-Ghani, 1992 }

The average Stefan-Maxwell diffusivities recovered from 0-3wt% dialysis experiment give a surprisingly good *prediction* of the pervaporation performance. The flux of ethanol is well predicted over a wide range of feed composition but is in error close to pure ethanol or pure water feeds. The flux of water is, however, under estimated particularly at low ethanol feed concentrations. Figure 5.6 shows the pervaporation performance *predicted* using the average Stefan-Maxwell diffusivities recovered from the 0-6wt% dialysis experiment. It is evident that these coefficients grossly underestimate the pervaporation fluxes of both ethanol and water.

Figure 5.6 Pervaporation of {ethanol(1)-water(2)}/silicone rubber at 25 °C predicted with the average Stefan-Maxwell diffusivities from 0-6 wt% dialysis experiment { $\hat{D}_{12} = 1.124 \times 10^{-5}$, $\hat{D}_{1p} = 3.10 \times 10^{-8}$, $\hat{D}_{2p} = 0.80 \times 10^{-7} \text{ cm}^2 / \text{s}$; data from Abdel-Ghani, 1992 }

We take encouragement from the results in Figure 5.5 that the generic membrane transport model has the potential to describe both the dialysis and pervaporation processes using an identical set of parameters. The failure of the generic model to provide a quantitative prediction of pervaporation performance is clearly a consequence of the concentration dependence of the Stefan-Maxwell diffusivities, which must be accounted for explicitly. In the case of the transient dialysis experiments the change in composition is small and the concentration profiles

in the membrane are almost linear. Figure 5.7 shows the predicted concentration profiles of ethanol and water within the membrane for pervaporation of three different feed mixtures. In contrast to dialysis, in pervaporation the composition profiles within the membrane are highly non-linear and vary over a much wider range. Such strong variation in concentration will have a major impact on the diffusion coefficients within the polymer matrix and invalidate the use of composition independent average Stefan-Maxwell diffusivities. Evidently, the successful application of the generic model demands an explicit treatment of the concentration dependence of both the diffusive and equilibrium parameters which is considered next.

Figure 5.7 Predicted composition profiles inside the membrane at 3600 s for pervaporation of different feed mixtures at a permeate pressure of 0.5 mbar. $\{\hat{D}_{12} = 1.124 \times 10^{-5}, \hat{D}_{1P} = 6.15 \times 10^{-8}, \hat{D}_{2P} = 1.37 \times 10^{-7} \text{ cm}^2/\text{s}\}$

5.4.3 Concentration Dependence of Diffusive and Equilibrium Parameters

The concentration dependence of polymer phase diffusion coefficients was discussed in chapter 2. In the case of small polar solutes and hydrophobic polymers we are forced to consider an empirical relationship and in selecting an empirical expression we must negotiate two conflicting criteria. First, the expression adopted must be sufficiently flexible to capture the variation of diffusivity with concentration accurately. Second, the form used must be as simple as possible and contain few easily determined adjustable parameters. We shall use the Vignes relationship [1966] originally developed for diffusion in binary liquids since it can be logically extended to multicomponent systems. This enables us to take full advantage of the fact that the Stefan-Maxwell diffusivities retain their physical significance irrespective of the number of components presents.

Vignes [1966] proposed that the composition dependence of the diffusivity in a binary ij -mixture is expressed by the relationship,

$$D_{ij} = (D_{ij}^0)^{x_j} (D_{ji}^0)^{x_i} \quad \text{binary } ij\text{-mixture} \quad (5.46)$$

where D_{ij}^0 represents the binary diffusion coefficient in an infinitely diluted mixture of i in j . Wesselingh and Krishna [1990] and Kooijman and Taylor [1991] suggested that the Vignes relationship is extended to a multicomponent mixture by,

$$D_{ij} = \prod_{k=1}^P (D_{ij, x_k \rightarrow 1})^{x_k} \quad \text{multicomponent mixture} \quad (5.47)$$

where $D_{ij, x_k \rightarrow 1}$ represents the limiting value of the Stefan-Maxwell diffusion coefficient measured in a mixture where component k is present in a very large excess. The terms $D_{ij, x_j \rightarrow 1}$ and $D_{ij, x_i \rightarrow 1}$ can be identified as the infinite dilution binary diffusion coefficients D_{ij}^0 and D_{ji}^0 respectively, which reduces (5.47) to:

$$D_{ij} = (D_{ij}^0)^{x_j} (D_{ji}^0)^{x_i} \prod_{\substack{k=1 \\ k \neq i, j}}^P (D_{ij, x_k \rightarrow 1})^{x_k} \quad \text{multicomponent mixture} \quad (5.48)$$

Using (5.48) we can express the multicomponent Stefan-Maxwell diffusion coefficients in a ternary system composed of components 1 and 2 and the polymer p by,

$$\begin{aligned} \mathfrak{D}_{12} &= (\mathfrak{D}_{12}^0)^{x_2} (\mathfrak{D}_{21}^0)^{x_1} (\mathfrak{D}_{12,x_p \rightarrow 1})^{x_p} \\ \mathfrak{D}_{1p} &= (\mathfrak{D}_{1p}^0)^{x_p} (\mathfrak{D}_{p1}^0)^{x_1} (\mathfrak{D}_{1p,x_2 \rightarrow 1})^{x_2} \\ \mathfrak{D}_{2p} &= (\mathfrak{D}_{2p}^0)^{x_p} (\mathfrak{D}_{p2}^0)^{x_2} (\mathfrak{D}_{2p,x_1 \rightarrow 1})^{x_1} \end{aligned} \quad (5.49)$$

We note here that the above equations reduce to the binary form (5.46) naturally. Furthermore, the binary infinite dilution diffusion coefficients $\mathfrak{D}_{ij}^0$ appearing in (5.49) are in principle open to direct measurement. For example, $\mathfrak{D}_{1p}^0$ can be measured from diffusion of pure component 1 in the polymer at very low vapour pressure.

Development of suitable expressions for the limiting diffusivities $\mathfrak{D}_{ij,x_k \rightarrow 1}$ in multicomponent liquid mixtures has also received some attention [Wesselingh and Krishna 1990, Kooijman and Taylor 1991]. Any model used for this purpose must obey certain restrictions inherent in the definition of the Stefan-Maxwell diffusion coefficients. For example, the multicomponent Stefan-Maxwell diffusivities are by definition symmetric $\mathfrak{D}_{ij} = \mathfrak{D}_{ji}$ and the final expression must secure this restriction automatically. Furthermore, in order to avoid discontinuities in the diffusion coefficients we must have,

$$\lim_{x_i \rightarrow 0} (\mathfrak{D}_{ij,x_j=0}) = \lim_{x_j \rightarrow 0} (\mathfrak{D}_{ij,x_i=0})$$

Kooijman and Talyor [1991] and Wesselingh and Krishna [1990] have considered a variety of models that satisfy the above restrictions for diffusion in multicomponent liquid mixtures.

In order to reduce the number of adjustable parameters we shall assume that the frictional interaction between ethanol and water within the polymer is similar to that in the bulk liquid and employ the simple expression suggested by Wesselingh and Krishna [1990],

$$\mathfrak{D}_{12,x_p \rightarrow 1} = (\mathfrak{D}_{12}^0 \mathfrak{D}_{21}^0)^{1/2} \quad (5.50)$$

Combining (5.49) and (5.50) we arrive at,

$$\mathfrak{D}_{12} = (\mathfrak{D}_{12}^0)^{(1+x_2-x_1)/2} (\mathfrak{D}_{21}^0)^{(1+x_1-x_2)/2} \quad (5.51)$$

which enables us to estimate the composition dependence of the multicomponent diffusivity $\mathfrak{D}_{12}$ from a knowledge of the binary infinite dilution diffusivities in the liquid phase $\mathfrak{D}_{12}^0 = 1.240 \times 10^{-5}$ and $\mathfrak{D}_{21}^0 = 1.143 \times 10^{-5} \text{ cm}^2/\text{s}$. This leaves 6 adjustable diffusive parameters to be determined,

$$\begin{aligned} \mathfrak{D}_{1P} &= (\mathfrak{D}_{1P}^0)^{x_P} (\mathfrak{D}_{P1}^0)^{x_1} (\mathfrak{D}_{1P, x_2 \rightarrow 1})^{x_2} \\ \mathfrak{D}_{2P} &= (\mathfrak{D}_{2P}^0)^{x_P} (\mathfrak{D}_{P2}^0)^{x_2} (\mathfrak{D}_{2P, x_1 \rightarrow 1})^{x_1} \end{aligned} \quad (5.52)$$

Four of these parameters $\mathfrak{D}_{1P}^0, \mathfrak{D}_{P1}^0, \mathfrak{D}_{2P}^0$ and $\mathfrak{D}_{P2}^0$ can be determined from relatively simple binary experiments but the remaining two require multicomponent data.

We must also consider the possibility that the Flory-Huggins interaction parameters in a ternary system may depend on the activities of both sorbed species $\chi_{iP} = \chi_{iP}(a_1, a_2)$. To accommodate this we shall assume that,

$$\begin{aligned} \chi_{1P} &= \{\alpha_{10} + \alpha_{11}a_1 + \alpha_{12}a_1^2 + (\chi_{1P}^0 - (\alpha_{10} + \alpha_{11} + \alpha_{12}))a_1^3\} \\ &\quad \{1 + \beta_{10}a_2 + \beta_{11}a_2^2 + \beta_{12}a_2^3\} \\ \chi_{2P} &= \{\alpha_{20} + \alpha_{21}a_2 + \alpha_{22}a_2^2 + (\chi_{2P}^0 - (\alpha_{20} + \alpha_{21} + \alpha_{22}))a_2^3\} \\ &\quad \{1 + \beta_{20}a_1 + \beta_{21}a_1^2 + \beta_{22}a_1^3\} \end{aligned} \quad (5.53)$$

We note here that all the parameters appearing in the first braces in (5.53) can be obtained from binary experiments. In particular, χ_{iP}^0 can be determined from the uptake of the pure liquid, for our system $\chi_{1P}^0 = 2.19$ and $\chi_{2P}^0 = 4.89$. The coefficients α_{i0}, α_{i1} and α_{i2} can be obtained from a match with the pure vapour sorption isotherm. The determination of the cross parameters β_{i0}, β_{i1} and β_{i2} would of course require multicomponent sorption data.

5.4.4 Estimation of Binary Parameters from Pervaporation of Pure Liquids

From the previous section it is clear that allowing for the concentration dependence of the diffusive and equilibrium parameters of the generic transport

model introduces a large number of adjustable parameters. The determination of these parameters is facilitated by the fact that many of them can be obtained from binary rather than multicomponent experimental data. For instance, the pervaporation of a pure liquid through a polymeric membrane does not constitute a separation process but such measurements can provide very useful information on the concentration dependence of diffusivity within the membrane. Furthermore, the pervaporation process is sensitive to the pure vapour/ polymer phase equilibria and, in the absence of direct information on the pure vapour isotherm, may be used to evaluate the combined effect of phase equilibria and diffusivity. In this section we use the data measured by Abdel-Ghani [1992] for the variation of the pure pervaporation flux with the permeate pressure to extract the binary model parameters.

For the pervaporation of a pure liquid i across a polymer p we have,

$$\chi_{ip} = \{\alpha_{i0} + \alpha_{i1}a_i + \alpha_{i2}a_i^2 + (\chi_{ip}^0 - (\alpha_{i0} + \alpha_{i1} + \alpha_{i2}))a_i^3\} \quad (5.54)$$

$$D_{ip} = (D_{ip}^0)^{x_p} (D_{pi}^0)^{x_i} \quad (5.55)$$

The value of χ_{ip}^0 can be found from the uptake of the pure liquid, this leaves three equilibrium and two diffusivity parameters that must be found from a fit to the pure component pervaporation flux data. Tables 5.3 and 5.4 summarise the parameters recovered by a five-parameter search minimising the sum of the squared errors between the calculated and measured pure component fluxes. Figure 5.8 compares the calculated and experimental fluxes and it is evident that the parameters obtained provide an excellent fit of the measured data for both ethanol and water.

Table 5.3 Infinite dilution diffusivities of ethanol and water in silicon rubber at 25 °C recovered from the pure component pervaporation data of Abdel-Ghani[1992]

Infinite Dilution Binary Diffusivity (cm ² /s)	Ethanol (1)	Water (2)
D_{ip}^0	2.211×10^{-6}	27.56×10^{-6}
D_{pi}^0	7.783×10^{-8}	14.13×10^{-8}

Table 5.4 Binary Flory-Huggins interaction parameters for {ethanol(1) and water 2)}/silicone rubber at 25 °C recovered from the pure component pervaporation data of Abdel-Ghani [1992].

$$\chi_{iP} = \{\alpha_{i0} + \alpha_{i1}a_i + \alpha_{i2}a_i^2 + (\chi_{iP}^0 - (\alpha_{i0} + \alpha_{i1} + \alpha_{i2}))a_i^3\}$$

	χ_{iP}^0	α_{i0}	α_{i1}	α_{i2}
Ethanol (1)	2.19	1.647	4.524	-5.000
Water (2)	4.89	4.032	5.000	-4.200

Figure 5.8 Variation of pure ethanol and pure water pervaporation flux with permeate pressure predicted using parameters of Tables 5.3 and 5.4.

We must recognise of course that the above procedure is essentially a data fitting exercise and the excellent fit shown on Figure 5.8 cannot be used to justify the validity or reliability of the model parameters. We are, however, strongly encouraged by the fact that both the diffusive and the equilibrium parameters obtained are physically reasonable for the following reasons. First, we note from Table 5.3 that $\mathfrak{D}_{ip}^0 \gg \mathfrak{D}_{pi}^0$ for both ethanol and water. This is to be expected since $\mathfrak{D}_{ip}^0$ represents the diffusion of a small molecule in a large excess of polymer whereas $\mathfrak{D}_{pi}^0$ represents the diffusion of the much larger polymer "molecule" in a large excess of component i. Second, $\mathfrak{D}_{2p}^0 > \mathfrak{D}_{1p}^0$ which is again expected since the water molecule is smaller than the ethanol molecule and also has a smaller affinity for the silicone rubber polymer.

The variation of the binary Flory-Huggins interaction parameters with activity calculated using the parameters of Table 5.4 are shown in Figure 5.9 and have the shape expected for the uptake of small polar solutes by hydrophobic polymers. Finally, the pure vapour sorption isotherm predicted by the Flory-Huggins model with the parameters of Table 5.4 are shown in Figure 5.10 and exhibit the characteristic shape observed for the uptake of ethanol and water by silicon rubber

Figure 5.9 Variation of Flory-Huggins interaction parameter with activity based on the parameters of Table 5.4.

Figure 5.10 Predicted pure vapour sorption isotherms of ethanol and water by silicon rubber at 25 °C predicted by the Flory-Huggins model with:
 — activity dependent interaction parameters of Table 5.4
 - - - - - constant interaction parameters $\chi_{1P} = 2.19$ and $\chi_{2P} = 4.89$
 {• data of Nguyen *et al* [1996] at 40 °C shown for comparison}

5.4.5 Equilibria Revisited: activity dependent ternary interaction parameters

With the binary equilibrium interaction parameters, $\chi_{iP}^0, \alpha_{i0}, \alpha_{i1}$ and α_{i2} , determined in the previous section, we now turn to the estimation of the six cross parameters β_{i0}, β_{i1} and β_{i2} appearing in,

$$\begin{aligned} \chi_{1P} &= \{\alpha_{10} + \alpha_{11}a_1 + \alpha_{12}a_1^2 + (\chi_{1P}^0 - (\alpha_{10} + \alpha_{11} + \alpha_{12}))a_1^3\} \\ &\quad \{1 + \beta_{10}a_2 + \beta_{11}a_2^2 + \beta_{12}a_2^3\} \\ \chi_{2P} &= \{\alpha_{20} + \alpha_{21}a_2 + \alpha_{22}a_2^2 + (\chi_{2P}^0 - (\alpha_{20} + \alpha_{21} + \alpha_{22}))a_2^3\} \\ &\quad \{1 + \beta_{20}a_1 + \beta_{21}a_1^2 + \beta_{22}a_1^3\} \end{aligned} \quad \text{cf(5.53)}$$

These parameters can be recovered from the relative sorption data points reported by Bansal[1988] using the constrained optimisation procedure detailed in section 5.4.1. The use of physical constraints is again essential to limit the search space and ensure

that the interaction parameters obtained lead to physically reasonable prediction of the multicomponent phase equilibria. Table 5.5 summarises the full set of parameters needed to describe the equilibria for the {ethanol(1)-water(2)}/silicon rubber system at 25 °C. Figure 5.11 shows the fit to the relative sorption data points using the activity dependent Flory-Huggins parameters based on Table 5.5.

Table 5.5 Activity Dependent Flory-Huggins Interaction Parameters for the {ethanol(1)-water(2)}/silicon rubber system at 25 °C.

Parameter	Ethanol (1)	Water (2)
χ_{iP}^0	2.190	4.890
α_{i0}	1.647	4.032
α_{i1}	4.524	5.000
α_{i2}	-5.000	-4.200
β_{i0}	0.245	0.746
β_{i1}	-1.000	-1.000
β_{i2}	0.578	0.837

Figure5.11 Relative sorption isotherm for {ethanol(1)-water(2)}/silicon rubber at 25 °C predicted using the Flory-Huggins modelwith activity dependent interaction parameters of Table 5.5
 {• data of Bansal, 1988}

In pervaporation the upstream membrane interface is in contact with an atmospheric liquid while the downstream interface is maintained at a low pressure. The multicomponent phase equilibria of the {ethanol(1)-water(2)}/silicon rubber system predicted by the Flory-Huggins model with activity dependent parameters is shown in Figure 5.12 for conditions ranging from an atmospheric liquid mixture to a mixed vapour at 1 mbar. It is evident that the system does not exhibit an azeotrope and the silicon rubber membrane is selective towards ethanol at all conditions. The individual uptakes of ethanol and water from a binary bulk mixture are, however, highly non-linear at high pressure but become progressively linear as the pressure is reduced.

Ethanol mole fraction

Figure 5.12 Prediction of phase equilibria for {ethanol(1)-water(2)}/silicon rubber at 25 °C using the Flory-Huggins model with activity dependent parameters of Table 5.5.

5.4.6 Estimation of Ternary Stefan-Maxwell Diffusivities

We are now in a position to complete the estimation of the ternary concentration dependent Stefan-Maxwell diffusivities:

$$\begin{aligned} \mathfrak{D}_{1P} &= (\mathfrak{D}_{1P}^0)^{x_P} (\mathfrak{D}_{P1}^0)^{x_1} (\mathfrak{D}_{1P,x_2 \rightarrow 1})^{x_2} \\ \mathfrak{D}_{2P} &= (\mathfrak{D}_{2P}^0)^{x_P} (\mathfrak{D}_{P2}^0)^{x_2} (\mathfrak{D}_{2P,x_1 \rightarrow 1})^{x_1} \end{aligned} \quad \text{cf(5.52)}$$

The infinite dilution binary diffusivities $\mathfrak{D}_{1P}^0$ and $\mathfrak{D}_{P1}^0$ are given in Table 5.3 and this leaves the two parameters $\mathfrak{D}_{1P,x_2 \rightarrow 1}$ and $\mathfrak{D}_{2P,x_1 \rightarrow 1}$, which may be estimated from the transient dialysis experiments reported by Bansal [1988]. The recovered parameters may then be used to *predict* the pervaporation flux of {ethanol-water} measured by Abdel-Ghani[1992] for the same silicon rubber membrane.

The transient dialysis model equations were set up using the Flory-Huggins model with the activity dependent interaction parameters of Table 5.5 and concentration dependent Stefan-Maxwell diffusivities given by (5.52). The model equations were solved by the method of lines for assumed values of $\mathfrak{D}_{1P,x_2 \rightarrow 1}$ and $\mathfrak{D}_{2P,x_1 \rightarrow 1}$ to establish the concentration profile in the liquid. The computed concentration profile was then used to generate the corresponding theoretical fringe taking full account of light deflection. The parameters $\mathfrak{D}_{1P,x_2 \rightarrow 1}$ and $\mathfrak{D}_{2P,x_1 \rightarrow 1}$ were adjusted using the constrained sequential quadratic programming procedure of Chen and Macchieto [1991] to match the theoretical and experimental fringes. Table 5.6 summarises the parameters obtained from separate two-parameter searches conducted at different fringe times for the 0-3 and the 0-6wt% transient dialysis experiments of Bansal [1988]. The recovered parameters are independent of fringe time for each experiment. However, different parameters are obtained for the 0-3 and the 0-6 wt% experiments, which is an indication of the concentration dependence of the limiting diffusivities $\mathfrak{D}_{1P,x_2 \rightarrow 1}$ and $\mathfrak{D}_{2P,x_1 \rightarrow 1}$.

Table 5.6 Limiting diffusivities recovered from a match with experimental fringes

measured by Bansal [1988] under dialysis conditions.

Fringe time (s)	$10^8 \bar{D}_{1P,x_2 \rightarrow 1} \text{ (cm}^2 \text{ / s)}$	
	0-3wt%	0-6wt%
600	3.95	1.82
900	3.83	1.80
1200	3.75	1.75
1500	3.91	1.76
1800	3.85	1.79
Mean	3.86	1.78
STD	0.05	0.05

Fringe time (s)	$10^8 \bar{D}_{2P,x_1 \rightarrow 1} \text{ (cm}^2 \text{ / s)}$	
	0-3wt%	0-6wt%
600	91.4	11.6
900	91.3	11.6
1200	90.0	10.8
1500	90.5	11.0
1800	90.8	11.1
Mean	90.8	11.2
STD	0.60	0.40

Figure 5.13 shows the pervaporation fluxes of the {ethanol(1)-water(2)}/silicone rubber system at 25 °C *predicted* by the generic model using the Flory-Huggins thermodynamic model with activity dependent interaction parameters and concentration dependent Stefan-Maxwell diffusivities. We note here that the mixture pervaporation flux data shown on Figure 5.13 was not used in any way to extract the model parameters. The activity dependence of the Flory-Huggins interaction parameters was recovered from the relative sorption data of Bansal [1988] and the variation of pure component fluxes with permeate pressure measured by Abdel-Ghani [1992]. The concentration dependence of the ternary Stefan-Maxwell diffusivities was described by the multicomponent extension of the Vignes [1966] relationship:

$$\begin{aligned} \bar{D}_{1P} &= (\bar{D}_{1P}^0)^{x_P} (\bar{D}_{P1}^0)^{x_1} (\bar{D}_{1P,x_2 \rightarrow 1})^{x_2} \\ \bar{D}_{2P} &= (\bar{D}_{2P}^0)^{x_P} (\bar{D}_{P2}^0)^{x_2} (\bar{D}_{2P,x_1 \rightarrow 1})^{x_1} \end{aligned} \quad \text{cf(5.52)}$$

The four binary infinite dilution diffusivities ($\mathfrak{D}_{\text{IP}}^0, \mathfrak{D}_{\text{Pi}}^0, i=1,2$) in the above expression were obtained from the variation of pure component pervaporation flux with permeate pressure and the two limiting diffusivities ($\mathfrak{D}_{1\text{P},x_2 \rightarrow 1}$ and $\mathfrak{D}_{2\text{P},x_1 \rightarrow 1}$) were obtained from the transient 0-3 and 0-6wt% transient dialysis experiments of Bansal [1988].

Figure 5.13 Pervaporation flux for {ethanol(1)-water(2)}/silicon rubber system at 25 °C *predicted* using activity dependent Flory-Huggins interaction parameters and concentration dependent Stefan-Maxell diffusivities.
 {Top Panel: $\mathfrak{D}_{1\text{P},x_2 \rightarrow 1} = 3.85 \times 10^{-8}$, $\mathfrak{D}_{2\text{P},x_1 \rightarrow 1} = 90.7 \times 10^{-8} \text{ cm}^2 / \text{s}$
 Bottom Panel: $\mathfrak{D}_{1\text{P},x_2 \rightarrow 1} = 1.78 \times 10^{-8}$, $\mathfrak{D}_{2\text{P},x_1 \rightarrow 1} = 11.2 \times 10^{-8} \text{ cm}^2 / \text{s}$
 Other parameters given in Tables 5.3 and 5.5}

It is evident from Figure 5.13 that the diffusive parameters recovered from either the 0-3wt% or the 0-6 wt% transient dialysis experiments provide a fairly good prediction of the pervaporation behaviour. The differences observed is due to the concentration dependence of the limiting diffusivities $\bar{D}_{1P,x_2 \rightarrow 1}$ and $\bar{D}_{2P,x_1 \rightarrow 1}$, which was not accounted for explicitly. By way of a final example, Figure 5.14 shows the almost perfect *prediction* of the pervaporation flux and selectivity obtained by setting the limiting diffusivities at the geometric mean of the values recovered from the 0-3 and the 0-6 wt% transient dialysis experiments.

Figure 5.14 Pervaporation flux and selectivity for {ethanol(1)-water(2)}/silicon rubber system at 25 °C *predicted* by the generic model of membrane transport at 1 hour. { $\bar{D}_{1P,x_2 \rightarrow 1} = 2.62 \times 10^{-8}$, $\bar{D}_{2P,x_1 \rightarrow 1} = 31.9 \times 10^{-8}$ cm² / s , other parameters given in Tables 5.3 and 5.5}

5.5 Conclusion

The Stefan-Maxwell formulation of multicomponent diffusion and the basic postulates of irreversible thermodynamics were used to develop a generic model of membrane transport. The generic model is, in principle, applicable to any separation process employing a homogeneous nonporous membrane as the selective separation barrier. Examples of such processes include dialysis, electrodialysis, reverse osmosis, vapour permeation and pervaporation. In particular, the model parameters are physically well defined so that the parameters recovered under one processing condition may be used in the description of a process employing the same membrane under different processing conditions. Furthermore, the kinetic and equilibrium contributions to the transport process are clearly separated which is essential for a proper understanding of the process performance for the purpose of design, scale-up and optimisation. The generic model and the parameter extraction procedures developed in this study provide a general framework for the description of a wide range of membrane separations employing nonporous membranes.

In common with all solution-diffusion based models of membrane transport, the generic model developed in this study contains a large number of equilibrium and diffusive parameters. Such parameters are often highly concentration dependent and their determination from experimental data presents a formidable challenge. A notable advantage of the generic model lies in the fact that the Stefan-Maxwell diffusivities retain their physical significance irrespective of the number of parameters present. This offers the opportunity of recovering many of the model parameters from relatively simple binary experiments. This is not possible with phenomenological models of membrane transport based on the generalisation of Fick's law to multicomponent systems. There is in fact no formal relationship between the binary and multicomponent phenomenological diffusion coefficients, which precludes the use of binary experiments.

The *predictive* capabilities of the generic model were tested for the {ethanol(1)-water(2)}/silicon rubber system. This system provides a stringent test of the generic model for two reasons. First, the multicomponent sorption of small polar molecules such as water and ethanol in the "hydrophobic" silicon rubber polymer is known to be very complex. Second, the diffusion coefficients of small polar solutes

in "hydrophobic" polymers do not conform to the available theories of diffusion and shows intricate concentration dependence. As a result, the fluxes of ethanol and water within the silicon rubber polymer are highly coupled by both equilibrium and kinetic interactions.

The results obtained indicate that the generic model is capable of describing the pervaporation and dialysis performance of the {ethanol(1)-water(2)}/silicon rubber system with an identical set of concentration dependent equilibrium and diffusive parameters. Suitable procedures were developed which enable the direct determination of the binary Flory-Huggins equilibrium interaction parameters from pure component vapour adsorption isotherms and the binary infinite dilution Stefan-Maxwell diffusivities from variation of pure component flux with permeate pressure. The ternary equilibrium parameters may be recovered from the relative sorption isotherm by imposing a number of general physical constraints in the parameter extraction procedure. The concentration dependence of the ternary Stefan-Maxwell diffusivities is well described by a natural extension of the binary Vignes relationship [1966] to multicomponent systems.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6. Conclusion and Recommendations

Selective transport of low molecular weight species across a nonporous polymer arises in diverse processes such as dialysis, pervaporation, vapour permeation, reverse osmosis and electrodialysis. Such processes may differ in the manner in which the driving force for separation is generated but the basic phenomena occurring within the nonporous polymer are essentially the same in all cases. The theoretical description of multicomponent transport across nonporous polymers is complicated by the coupling of fluxes and intricate polymer-permeant and permeant-permeant interactions. An adequate description of such interactions and their influence on the solubility and diffusivity of the various species within the polymer is essential for accurate design, scale-up and optimisation of membrane separations using a nonporous polymer as the selective separation barrier.

The primary objective of this study was the development of a theoretical model of multicomponent transport across nonporous polymers with physically well-defined parameters. Ideally, such a model would allow the description of various membrane separations using the same set of model parameters. Selective transport may arise as a result of differences in the solubility and/or diffusivity of the various species and may be described in terms of a variety of solution-diffusion models. Such models contain a large number of parameters, which may prove to be highly concentration dependent. In general, experimental data for multicomponent membrane transport are fairly scarce and highly system specific. An important task was therefore the identification of suitable simple experiments for model parameter estimation and the development of suitable procedures for obtaining the model parameters from limited experimental data. The validity and reliability of the theoretical model may be critically assessed by recovering its parameters from experiments conducted under one set of processing conditions and using these parameters to *predict* the performance under different processing conditions.

Three alternative approaches to multicomponent diffusion, the empirical generalisation of Fick's law, the phenomenological approach of irreversible thermodynamics and the mechanistic Stefan-Maxwell formulation, can be used to describe multicomponent membrane transport. The empirical generalisation of Fick's law proves inappropriate because the multicomponent Fick diffusivities incorporate

both equilibrium and kinetic effects and as a result exhibit very complex concentration dependence. In contrast, the phenomenological approach of irreversible thermodynamic and the Stefan-Maxwell formulation can separate the equilibrium and kinetic effects explicitly and offer a better basis for model development.

In one approach based on irreversible thermodynamics, the diffusive flux of each species is expressed as a linear sum of all the independent driving forces. The coefficients appearing in this linear sum may be expressed as "multicomponent diffusion coefficients". Such coefficients are, however, phenomenological in the sense that they are not based on a mechanistic model of the diffusion process itself. In the Stefan-Maxwell formulation, on the other hand, the driving force for each species is expressed as a linear sum of all the independent fluxes using a mechanistic model of the diffusion process. Postulates of irreversible thermodynamics are used in this approach to identify the various internal and external contributions to the individual driving forces. Either approach can be used to give a fairly comprehensive treatment of multicomponent membrane transport and were considered in this study. The phenomenological approach is easier to apply, since it gives the flux directly in terms of the driving forces, but the phenomenological diffusion coefficients are difficult to interpret. The Stefan-Maxwell formulation is more difficult to apply, since the driving force is for each species expressed in terms of all the independent fluxes. However, the multicomponent Stefan-Maxwell diffusivities have a well-defined physical basis and represent the frictional interactions between the various binary pairs in the multicomponent mixture. This facilitates the interpretation of the Stefan-Maxwell diffusion coefficients and eases the determination of their concentration dependence.

Irrespective of the approach used for the description of the multicomponent transport process, the model will inevitably contain a large number of parameters, which must be extracted from suitable experimental data. Conventional techniques for the experimental investigation of membrane transport involve the measurement of steady state fluxes. Such measurements do not, in general, carry sufficient information to allow the confident evaluation of model parameters. Transient measurements coupled with transient models of membrane transport offer an opportunity for a more critical evaluation of the validity and reliability of the model and its parameters. To our knowledge, transient techniques have so far been confined

to the application of the well known time lag method to transport of pure components across polymers. We were in fact unable to find a theoretical study of multicomponent membrane transport under transient conditions in the literature other than that reported by Bansal [1988]. Transient models of membrane transport constitute a highly coupled set of non-linear partial differential equations that do not admit an analytical solution. The computational effort associated with the numerical solution of such equations appears to have deterred the use of the more informative transient techniques for multicomponent membrane transport systems. The numerical solution procedure developed and tested in chapter 3 of this study can handle the transient model equations in their full complexity. It provides a highly convenient and easy to apply general procedure and should ease the reluctance for the development and application of transient measurement techniques to multicomponent systems.

The theoretical models developed in this study are tested using transient data measured for the {ethanol-water}/silicon rubber system by previous workers in our research group at the University of Surrey. Bansal [1988] measured transient transport across silicon rubber using a non-intrusive laser interferometer under dialysis conditions and also reports limited sorption measurements. Subsequently, Abdel-Ghani [1992] measured the transient flux across the same silicon rubber membrane for pure water, pure ethanol and {ethanol-water} mixtures under pervaporation conditions. This system provides an inherently difficult test of the theoretical model since the phase equilibria are highly non-ideal and the diffusion of the polar water and ethanol molecules through the hydrophobic silicon rubber is also highly concentration dependent. A unique feature of this study is an attempt to recover the model parameters from measurements made under transient dialysis conditions and predicting the performance of the transient pervaporation process using the same set of parameters. It is important to recognise that this procedure provides a highly critical test of both the model and its parameters which, to our knowledge, has not been previously attempted. Previously reported studies of multicomponent membrane transport are confined to steady state measurements and the proposed model is only checked for its ability to fit the same data used in extracting the model parameters.

The phenomenological approach to modelling of multicomponent transport across nonporous membranes was considered in detail in chapter 4. A phenomenological description of transport was presented which enabled the separate evaluation of equilibrium and kinetic coupling and made proper allowance for diffusion induced non-selective bulk flow. Transient models of dialysis and pervaporation were then developed which shared exactly the same description for the membrane and differed only in the description of transport through the bulk phases bathing the membrane. To keep the model as simple as possible, the thermodynamic non-ideality of the membrane solution was described in terms of the classical Flory-Huggins model with constant interaction parameters recovered from independent liquid phase sorption measurements.

The transient model of dialysis was used to extract average values for the phenomenological diffusion coefficients from the interference fringes recorded by Bansal [1988] for four separate transient dialysis experiments. This was achieved by predicting the transient concentration profiles in the liquid boundary layer and calculating the corresponding theoretical fringe taking full account of light deflection in a medium of varying refractive index, see chapter 3 for details. Average values of the phenomenological diffusion coefficients were recovered by matching the experimental and theoretical fringes. The average diffusivities obtained were then used to *predict* the transient pervaporation data of Abdel-Ghani [1992] measured for the same silicon rubber membrane.

The results obtained indicate that non-selective bulk flow has a minor effect for the {ethanol-water}/silicon rubber system. This is because both the sorption levels and the fluxes are small for this system and are in keeping with the general conclusions reached by Kamaruddin and Koros [1997]. A more striking conclusion is reached concerning the critical importance of the Onsager reciprocal relationships, which are an integral part of the development of the irreversible thermodynamic approach. The phenomenological coefficient matrix is symmetric so that for an n -component mixture there are only $n(n-1)/2$ independent multicomponent diffusion coefficients. The remaining elements of the phenomenological coefficient matrix are obtained by symmetry.

The formulation of the phenomenological model for a ternary system leads to the introduction of four multicomponent diffusion coefficients. However, only three of these parameters are truly independent and the fourth may be obtained from the Onsager reciprocal relationship. However, in the reported applications of this approach, all four diffusion coefficients are usually assumed as independent. For example, Bansal [1988] set the cross coefficients in the diffusivity matrix to zero and fitted his experimental fringes by adjusting the two diagonal terms in the diffusivity matrix. This is in effect equivalent to assuming that all four phenomenological diffusion coefficients are independent. The diffusivities obtained by Bansal [1988] fit the experimental fringe patterns very well but fail to even predict the qualitative trends observed by Abdel-Ghani [1992] under pervaporation conditions. Indeed, the diffusive parameters reported by Bansal [1988] predict that the hydrophobic silicon rubber membrane is selective towards water under pervaporation conditions. On the other hand, imposing the Onsager reciprocal relationship reduces the number of diffusive parameters to one, fits the experimental fringes equally well and provides a good qualitative *prediction* of the pervaporation performance.

An extremely important conclusion of this study is that the phenomenological approach to modelling of transport across polymeric membranes *must* include the restrictions posed by the Onsager reciprocal relationships explicitly. Failure to do so will result in phenomenological diffusion coefficients that may be seriously erroneous. The same conclusion applies to less detailed models based on the empirical generalisation of Fick's law. The multicomponent Fick diffusivities are not independent and are interrelated, this interrelationship is however difficult to express within a purely empirical approach.

The failure of the phenomenological approach to provide a quantitative *prediction* of transient pervaporation with the parameters recovered from data measured under dialysis conditions may be attributed to two major factors. First, the classical Flory-Huggins model with constant interaction parameters cannot provide an accurate description of the sorption equilibria for the {ethanol-water}/silicon rubber system. Second, the multicomponent phenomenological diffusion coefficients are highly concentration dependent and the use of average values is not warranted. Furthermore, setting the off diagonal diffusion coefficients to zero is arbitrary and

imposes a level of kinetic coupling of fluxes that may be erroneous. Explicit inclusion of the concentration dependence of the diffusivities is difficult within a phenomenological framework. The phenomenological diffusion coefficients do not have a mechanistic basis and this complicates the problem. The mechanistic Stefan-Maxwell formulation, although more difficult to apply, provides a better alternative in this respect.

The separate evaluation of the kinetic and equilibrium contributions to the multicomponent transport process requires a thermodynamic model for the non-ideality of the polymer solution. This thermodynamic model should be capable of describing both the liquid/polymer and the vapour/polymer equilibria using an identical set of parameters. This is because in pervaporation the membrane is in contact with a liquid at the feed side and an unsaturated low-pressure vapour at the permeate side. The classical Flory-Huggins model with constant interaction parameters is incapable of producing the characteristic shape observed for the uptake of small polar solutes such as water and ethanol by the "hydrophobic" silicone rubber. Furthermore, the reported enthalpic and/or entropic modifications of the Flory-Huggins model were found to be of little help for the {ethanol-water}/silicon rubber system.

An empirical modification of Flory-Huggins model was proposed in this study which retains the basic form of the Flory-Huggins model but allows the interaction parameters to be a simple function of activity. Many of the constants associated with the proposed empirical relationship can be obtained from pure vapour sorption isotherms. The remaining parameters can be obtained from a limited set of multicomponent sorption data, for example the liquid phase relative sorption isotherm that can be measured without removing the membrane from the liquid. Extracting a large number of parameters from limited data is by no means a simple task. To avoid over-fitting and ensure that the recovered parameters lead to physically reasonable behaviour it is essential to impose suitable general physical constraints within the parameter estimation procedure. Such physical constraints are easily introduced within the general formalism of constrained non-linear optimisation and help to limit the parameter search space substantially. In the case of {ethanol-water}/silicon rubber system constraints can be imposed to ensure that the system does not exhibit

an azeotrope within the sorbed phase, that it is selective towards ethanol at low vapour pressure and that the activity dependent interaction parameters have the desired form. Using such constraints enabled us to obtain a physically realistic description of the multicomponent sorption equilibria over conditions ranging from a low-pressure vapour to a saturated liquid. The constrained parameter extraction procedure demonstrated in this study is an important and versatile tool that should find ready application for other systems.

A notable advantage of the Stefan-Maxwell formulation is that the associated diffusivities retain their physical significance irrespective of the number of components present. This offers the opportunity of recovering many of the model parameters from relatively simple binary experiments. This is not possible with the phenomenological models of membrane transport or the empirical generalisation of Fick's law to multicomponent systems. There is in fact no formal relationship between the binary and multicomponent phenomenological diffusion coefficients, which precludes the use of binary experiments.

A generic model for transport of multicomponent mixtures across a nonporous polymer was developed in chapter 5. The multicomponent flux equations were first formulated using the mechanistic Stefan-Maxwell formulation. An expression for a generalised driving force, which includes the contributions from both the internal and the external driving forces, was derived from the postulates of irreversible thermodynamics. The combined flux equations and the generalised driving force expression constitute a generic model that may be applied to any separation process employing a nonporous polymer as the selective separation barrier. The influence of non-selective diffusion induced bulk flow is automatically included in this model and the kinetic coupling of fluxes is also an inherent feature of the generic model.

Transient models of dialysis and pervaporation were developed which used exactly the same generic model to describe the transport through the membrane and differed only in the description of transport through the bulk phases bathing the membrane. A systematic procedure was developed to extract the model parameters from the limited experimental data available to us for the {ethanol-water}/silicon rubber system. An accurate evaluation of the kinetic contribution requires the explicit inclusion of the concentration dependence of the Stefan-Maxwell diffusivities. A

notable advantage of the generic model lies in the fact that the Stefan-Maxwell diffusivities retain their physical significance irrespective of the number of components present. This offers the opportunity of recovering many of the model parameters from relatively simple binary experiments. For example, the pervaporation of a pure liquid through a polymeric membrane does not constitute a separation process but such measurements can provide very useful information on the concentration dependence of diffusivity within the membrane. Furthermore, the pervaporation process is sensitive to the vapour/ polymer phase equilibria and, in the absence of direct information on the pure vapour isotherm, may be used to evaluate the combined effect of phase equilibria and diffusivity.

The concentration dependence of the binary Stefan-Maxwell diffusivities was described through the Vignes relationship [1966]:

$$D_{ip} = (D_{ip}^0)^{x_p} (D_{pi}^0)^{x_i} \quad \text{binary system}$$

where D_{ij}^0 represents the infinite dilution binary diffusivity and are treated as constant parameters. The data measured by Abdel-Ghani [1992] for the variation of the pure component pervaporation flux with permeate pressure was used to extract the binary model parameters through constrained optimisation. The recovered binary diffusivity and equilibrium parameters were able to give a realistic description of the pure vapour sorption isotherm and a highly accurate fit to the variation of the pure component pervaporation flux with permeate pressure for both ethanol and water.

The ternary equilibrium interaction parameters were extracted from the limited data reported by Bansal [1988] for the liquid phase relative sorption isotherm of the {ethanol-water}/silicon rubber system using a constrained optimisation procedure with suitable physical constraints. The parameters obtained gave a physically realistic description of the multicomponent sorption equilibria over a wide range of conditions. The concentration dependence of the ternary Stefan-Maxwell diffusivities was described by a natural extension of the binary Vignes relationship to multicomponent systems:

$$\begin{aligned} D_{ip} &= (D_{ip}^0)^{x_p} (D_{p1}^0)^{x_1} (D_{1p,x_2 \rightarrow 1})^{x_2} \\ D_{2p} &= (D_{2p}^0)^{x_p} (D_{p2}^0)^{x_2} (D_{2p,x_1 \rightarrow 1})^{x_1} \end{aligned} \quad \text{ternary system}$$

Average values of the limiting diffusivities $\bar{D}_{iP, x_i \rightarrow 1}$ were obtained from the transient dialysis data of Bansal [1988] by matching the theoretical and experimental fringe patterns. The parameters obtained gave an excellent quantitative *prediction* of the transient pervaporation flux data of Abdel-Ghani [1992].

To conclude, the results obtained indicate that the generic model is capable of describing the transient pervaporation and dialysis performance of the {ethanol-water}/silicon rubber system with an identical set of concentration dependent equilibrium and diffusive parameters. Suitable procedures were developed which enable the direct determination of the binary Flory-Huggins equilibrium interaction parameters from pure component vapour sorption isotherms and the binary infinite dilution Stefan-Maxwell diffusivities from variation of pure component flux with permeate pressure. The ternary equilibrium parameters may be recovered from the relative sorption isotherm by imposing a number of general physical constraints in the parameter extraction procedure. The concentration dependence of the ternary Stefan-Maxwell diffusivities may be described by a natural extension of the binary Vignes relationship to multicomponent systems.

The generic model of multicomponent membrane transport developed and tested in this study has well-defined equilibrium and diffusive parameters, which retain their physical significance under different operating conditions. It provides a solid framework for the theoretical description of diverse processes employing a nonporous polymer as the selective separation barrier. Future work should concentrate on application of this model to a wider range of systems and the development of improved theories and experimental techniques for parameter estimation and model validation.

Future theoretical work should concentrate on the development of better thermodynamic models, which obviate the need for activity dependent interaction parameters. Lessons learnt in the theoretical development of thermodynamic models of multicomponent vapour/liquid and liquid/liquid equilibria provide a good starting point. A better understanding of the concentration dependence of polymer phase diffusivity may enable us to replace the empirical the Vignes relationship with a more fundamental description. Recent advances in the measurement of diffusion by the

pulsed field gradient NMR technique [Masaro and Zhu 1999] is beginning to provide data that can guide such developments.

From an experimental view point, the interferometric technique of Bansal [1988] can be enhanced by attaching a capillary to the diffusion cell to make a direct measurement of diffusion induced non-selective bulk flow. This effect was small for the {ethanol-water}/silicon rubber system but may be significant in other cases. A similar technique was used by Mackie and Mears [1956]. An independent check on the model can also be obtained by the simultaneous measurement of the refractive index profiles in the top and bottom halves of the diffusion cell. This enables the direct estimation of the extent of accumulation within the polymer, which can be checked against the theoretical predictions. Recent developments by Watson [1991 and 1995] and Yeom *et al* [1999] can also be combined with the techniques of Abdel-Ghani [1992] for improved transient pervaporation measurements.

The validity of a model for membrane transport is best checked against the measured concentration distribution *within* the membrane itself. This is, however, a difficult experimental task which to our knowledge has not been previously attempted. Korthauer *et al* [1985] describe a micro-interferometer capable of producing interference fringes generated by the diffusion of albumin within a single 110 μm transparent Sepharose bead. This device could possibly be used to investigate the concentration distribution within transparent polymers. However, a quantitative analysis would be difficult since little is known about the variation of the refractive index within a polymeric system. It is likely that the indirect verification of models of membrane transport will be the major experimental approach for some time.

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