

## Measurement and Analysis of Sorption Equilibria for Systems with Small Uptake: {Ethanol (1)-Water(2)}/Silicone Rubber

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### ABSTRACT

The difficulties inherent in the measurement of the total uptake for membrane systems with small uptake severely limit the reliability of the equilibrium data. The measurement of the relative (excess) adsorption isotherm, which does not require the removal of the membrane from the free liquid provides a powerful and general test of the consistency of the equilibrium data. Furthermore, for cases where the measurement of total uptake is unreliable, the extent and composition of the sorbed phase can be obtained by a thermodynamic analysis of the excess sorption isotherm alone. In this study, the relative sorption for the system of {ethanol (1)-water (2)}/silicon rubber was measured at different compositions of liquid mixture without removing the membrane from the bulk liquid. It was shown the total uptake measured by the conventional technique is in serious error due to unavoidable evaporative losses during the handling stages. In the absence of reliable total uptake data, the extent and composition of the sorbed liquid can be established from a thermodynamic analysis based on the relative sorption isotherm alone. This procedure was demonstrated for the {ethanol- (1)-water (2)}/silicone rubber system using the Flory-Huggins thermodynamic model. The relative sorption data is well fitted with constant polymer/solvent interaction parameters which is a prerequisite for the validity of the Flory model.

#### Key Words:

sorption;  
equilibria;  
membrane;  
silicone rubber;  
Flory-Huggins.

### INTRODUCTION

Independent measurement of sorption equilibria for a gas or vapour is usually done with vacuum microbalance [1-2] or pressure decay method [3-4]. The measurement of uptake from liquids proves to be more difficult. Such measurements are tradi-

tionally made by gravimetric methods [5-6]. This procedure suffers from the difficulty of obtaining a clean separation of the membrane from the free liquid and it is also prone to evaporative losses during handling. In the case of systems with

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small uptake such losses can lead to substantial error and limit the reliability and thermodynamic consistency of the data obtained.

A practical alternative for systems with small uptake is to determine the relative (excess) sorption isotherm, which can be measured without separating the membrane from the free liquid. The experimental relative isotherm provides direct check on the reliability of the total uptake measurements without recourse to any priori theoretical assumption. Furthermore, in cases where the total sorption isotherm is not available or is unreliable, the relative sorption isotherm can be analyzed in terms of a suitable thermodynamically consistent model to establish the individual amount of the various species adsorbed. The results obtained by this procedure for {ethanol (1)-water (2)}/silicone rubber (3) are presented in this article and analyzed in terms of the classical Flory-Huggins thermodynamic model.

To show the relationship between relative and total sorption isotherms, 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  $x_i$  as the free liquid mole fraction at equilibrium. The easily accessible experimental quantity is the relative sorption  $\Gamma_i$  defined as [7]:

$$\Gamma_i = \frac{N_0}{M} (x_{i0} - x_i) \quad (1)$$

with  $\Gamma_i$  expressed in mol/g of dry membrane. The relative sorption  $\Gamma_i$  can be determined without removing the membrane from the free liquid. The total amount  $N^S$  and composition of the sorbed phase  $x_i^S$  are related to the relative sorption,  $\Gamma_i$ , by a simple material balance:

$$\Gamma_i = N^S (x_i^S - x_i) \quad (2)$$

Consequently, an extra independent relationship is required to establish the total amount and composition of the sorbed phase. Ideally this extra relationship should be obtained by direct experimental measurement of the total uptake  $N^S$ . However, for volatile solutes with low uptake, such as the system considered here, 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 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 is obtained by noting that for any liquid/membrane system.

$$|\Gamma_i| \leq N^S \quad \text{at all compositions} \quad (3)$$

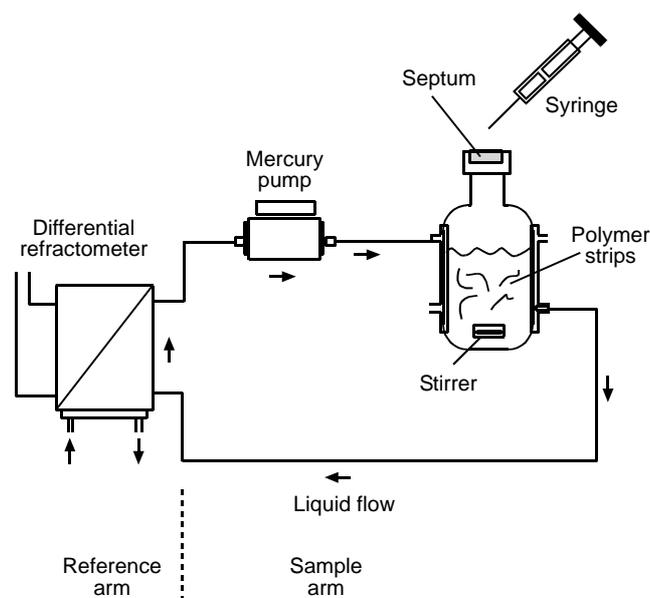
This is simply because  $N^S \geq 0$  and by definition,

$|x_i^S - x_i| \leq 1$ . It is important to recognize that eqn (3) is a very general constraint applicable to all types of non-porous membrane irrespective of the extent of swelling.

## EXPERIMENTAL

The silicone rubber (PDMS) used in this study was a commercial unsupported specimen (Silastic 500-1) supplied by Dow Corning and with a measured bulk density of  $1.03 \text{ g/cm}^3$ . All solutions were made up by weight using Anal-grade ethanol (>99.7%) and double distilled de-ionized water. Independent experiments were conducted to measure the relative and total sorption isotherms.

The relative sorption isotherm was measured using the apparatus shown schematically in Figure 1. A



**Figure 1.** Schematic diagram of the sorption measurement apparatus.

known mass of the dry membrane,  $M$  (in gram unit), was placed in a closed thermostated sorption vessel and a known mass of pure water,  $N_{20}$  moles, was added with a gas tight syringe through the septum. The liquid was circulated through the sample arm of the differential refractometer (Waters R400) using a reciprocating mercury pump and the instrument was zeroed against pure water in the reference arm. The reference liquid then was replaced with a solution of known composition  $x_1^{\text{ref}}$  to produce an offset reading on the refractometer. Incremental amounts of pure ethanol,  $\delta N_{10}$ , moles, were then injected through the septum to bring the refractometer, reading back to zero or null position.

At equilibrium, the free liquid has the same composition as the liquid in the reference arm:

$$x_1 = x_1^{\text{ref}} \quad (4)$$

The starting composition of the free liquid (before any sorption) was calculated from the known initial amount of pure water  $N_{20}$  and the cumulative amount of pure ethanol,  $\sum \delta N_{10}$  moles, required to bring the system back to the null position:

$$x_{10} = \frac{\sum \delta N_{10}}{N_{20} + \sum \delta N_{10}} \quad (5)$$

A single point on the relative isotherm at composition  $x_1^{\text{ref}}$  is, therefore, obtained by eqns (1) and (5),

$$\Gamma_1 = \frac{N_{20} + \sum \delta N_{10}}{M} (x_{10} - x_1^{\text{ref}}) \quad (6)$$

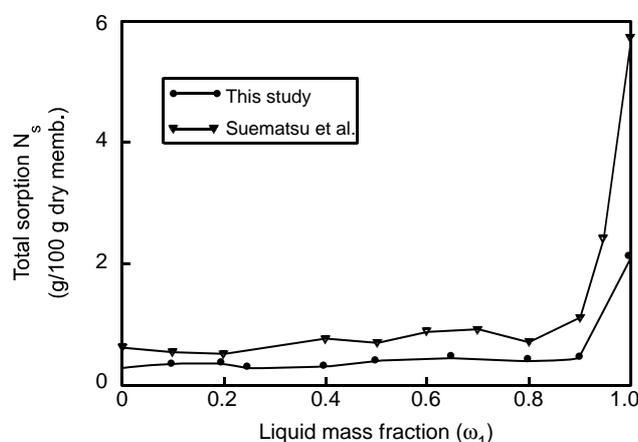
To determine another point, the reference arm solution was changed and further pure ethanol injected to bring the system back to the null position. The relative sorption for the system {ethanol-water}/silicone rubber at 25 C is shown in Table 1 and is positive over the entire concentration range which indicates that ethanol is preferentially adsorbed by silicone rubber and an azeotrope is not formed.

The total sorption isotherm was measured by contacting a weighed strip of the dry membrane (about 1 g) with a large volume of ethanol (1)-water (2) mixture of known composition in a closed vessel. The vessel was placed in a thermostated shaker bath controlled at 25 C over prolonged periods of up to one week. After equilibrium was attained, the membrane strip was removed and its external surface quickly dried between two sheets of filler paper and its weight was determined in

**Table 1.** The experimental relative sorption data for the system {ethanol-water}/silicone rubber at 25 C.

| Mole fraction ( $x_i$ ) | $\Gamma_1$ Relative sorption (mmol/g dry memb.) |
|-------------------------|---|
| 0.000000                | 0.000000  |
| 0.004358                | 0.027799  |
| 0.021139                | 0.058816  |
| 0.022167                | 0.051200  |
| 0.041630                | 0.107250  |
| 0.043813                | 0.098700  |
| 0.053449                | 0.148357  |
| 0.065413                | 0.223486  |
| 0.085750                | 0.219037  |
| 0.085750                | 0.228420  |
| 0.108647                | 0.221088  |
| 0.132933                | 0.231003  |
| 0.242760                | 0.214026  |
| 0.348374                | 0.214026  |
| 0.452959                | 0.167086  |
| 0.866571                | 0.085834  |
| 1.000000                | 0.000000  |

a stoppered bottle. Figure 2 shows the apparent total uptake of the liquid against the free liquid weight fraction associated with the data reported by Suematsu et al. [8] which shows a similar trend but it is consistently larger than that of this study, particularly at high



**Figure 2.** The experimental total sorption for the system {ethanol- water}/silicone rubber at 25°C.

ethanol concentration.

In theory, the combination of the total uptake and the relative sorption is sufficient to determine the composition of the sorbed phase, as given in eqn (2). For the {ethanol (1)-water (2)}/silicone rubber system, however, the data presented in Table 1 and Figure 2 lead to values of adsorbed phase mole fraction much greater than unity. A brief examination of the measured data reveals that the measured relative sorption is consistently greater than the total uptake. The constraint  $|\Gamma_i| \leq N^S$  is, therefore, violated and the experimental data although reproducible is not consistent. The inconsistency in data can be traced to the difficulty inherent in the measurement of total uptake, which requires the removal of the membrane sample from the free liquid. This causes a systematic error due to evaporative losses.

## RESULTS AND DISCUSSION

In the face of the inherent difficulties associated with the removal of the membrane sample from the free liquid we can resort to a thermodynamic analysis based on the relative sorption isotherm alone. Such analysis can be undertaken under various levels of detail. As a more realistic model of sorption by elastomeric polymers we may resort to the thermodynamic model of Flory [9] which accounts for a large difference in the size of the polymer and the sorbed molecules. This model is often used in practical terms on polymeric membranes while its inherent assumption is quite frequently ignored. It is prudent at this point to briefly review the basic assumptions made in the development of the Flory-Huggins model.

For the molecules of widely differing size the configurational entropy of mixing is better represented in terms of volume rather than mole fraction. Flory derived the configurational entropy of mixing using a lattice model in which each cell contained either a solvent molecule or a polymer segment with the polymer chains restricted to occupy adjacent cells. For a binary system the configurational entropy is then:

$$\Delta S_{cf} = -R \left[ x_1^S \ln(\phi_1^S) + x_P \ln(\phi_P^S) \right] \quad (7)$$

where,  $x_1$  and  $x_P$  are the mole fraction of the solvent and polymer, respectively, and the corresponding vol-

ume fractions are given by:

$$\phi_1^S = \frac{n_1^S v_1}{n_1^S v_1 + n_P^S v_P} \quad \phi_P^S = \frac{n_P^S v_P}{n_1^S v_1 + n_P^S v_P}$$

with  $v_1$  and  $v_P$  representing the partial molar volumes. Eqn (7) is reduced to a usual expression for configurational entropy of an ideal fluid only when the partial molar volumes are equal.

Flory initially assumed that interaction between the solvent and polymer molecules only contributes to the enthalpy of mixing and ignored any contributions to the entropy. The heat of mixing was approximated by an expression analogous to the Van Laar expression employed in vapour-liquid equilibria:

$$\Delta H_m = (RT\chi_{1P})x_1^S\phi_P^S \quad (8)$$

with  $\chi_{1P}$  an interaction parameter representing the strength of interactions. The Gibbs free energy,  $\Delta G_m$ , is obtained by combining eqns (7) and (8):

$$\Delta G_m = \Delta H_m - T\Delta S_{cf} = RT \left[ x_1^S \ln \phi_1^S + x_P^S \ln \phi_P^S + \chi_{1P} x_1^S \phi_P^S \right] \quad (9)$$

Multiplying the above equation by total number of moles ( $n$ ), the following expression is obtained:

$$\frac{n\Delta G_m}{RT} = [n_1^S \ln \phi_1^S + n_P^S \ln \phi_P^S + \chi_{1P} n_1^S \phi_P^S]$$

Now, differentiating eqn (10) with respect to  $n_1^S$ , it leads to:

$$\left[ \frac{\partial(n\Delta G_m)/RT}{\partial n_1^S} \right]_{T,P,n_{j \neq i}} = \ln(a_1^S) = \ln(1 - \phi_P^S) + \left(1 - \frac{\bar{v}_1}{\bar{v}_2}\right)\phi_P^S + \chi_{1P}(\phi_P^S)^2 \quad (10)$$

The extension of the above formulation to a ternary system composed of a binary liquid and a single polymer results in [9]:

$$\Delta G_m = RT \left[ x_1^S \ln \phi_1^S + x_2^S \ln \phi_2^S + x_P^S \ln \phi_P^S + \chi_{12} x_1^S \phi_2^S + \chi_{1P} x_1^S \phi_P^S + \chi_{2P} x_2^S \phi_P^S \right] \quad (11)$$

Similarly, multiplying eqn (11) by total number of

moles ( $n$ ) and partial differentiation of the resultant expression with respect to  $n_1^S$  and  $n_2^S$  at constant  $T$  and  $P$ , gives the activity of the imbibed species:

$$\begin{aligned} (\ln a_1^S) = & \ln(\phi_1^S) + (1 - \phi_1^S) - \phi_2^S \left(\frac{\bar{v}_1}{\bar{v}_2}\right) - \phi_P^S \left(\frac{\bar{v}_1}{\bar{v}_P}\right) + \\ & (\chi_{12}\phi_2^S + \chi_{1P}\phi_P^S)(\phi_2^S + \phi_P^S) - \chi_{2P} \left(\frac{\bar{v}_1}{\bar{v}_2}\right) \phi_2^S \phi_P^S \end{aligned} \quad (12a)$$

$$\begin{aligned} (\ln a_2^S) = & \ln(\phi_2^S) + (1 - \phi_2^S) - \phi_1^S \left(\frac{\bar{v}_2}{\bar{v}_1}\right) - \phi_P^S \left(\frac{\bar{v}_2}{\bar{v}_P}\right) + \\ & (\chi_{12}\phi_1^S \left(\frac{\bar{v}_2}{\bar{v}_1}\right) + \chi_{2P}\phi_P^S)(\phi_1^S + \phi_P^S) - \chi_{1P} \left(\frac{\bar{v}_2}{\bar{v}_1}\right) \phi_1^S \phi_P^S \end{aligned} \quad (12b)$$

Eqn (12) can be further simplified by noting that the partial molar volume of the polymer is much greater than that of the solvent, so that terms including  $\bar{v}_i/\bar{v}_P$  can be dropped.

The above treatment is strictly applicable to a system where the polymer molecules are free to move. For polymers networks, an additional term is required to allow for the restricted motion of the polymer chains and the elastic deformation of the network. A first order approximation for this term was derived by Flory and leads to an additional contribution to the activity.

$$\begin{aligned} (\ln a_1^S) = & \ln(1 - \phi_P^S) + \left(1 - \frac{\bar{v}_1}{\bar{v}_2}\right) \phi_P^S + \chi_{1P}(\phi_P^S)^2 + \\ & \frac{\bar{v}_1}{M_c V_P} [(\phi_1^S)^{1/3} - 1/2\phi_P^S] \end{aligned} \quad (13)$$

where,  $M_c$  represents the average molecular weight between successive polymer cross-links and  $V_P$  the specific volume of the polymer. The contribution of the last terms depends in first instance on the molecular weight  $M_c$  and for large molecular polymers used in this study can be safely neglected.

The application of the Flory-Huggins model to a binary liquid/polymer system is straightforward. At equilibrium the activity of components 1 and 2 in the membrane must be equal to those in the bulk liquid. Thus, given the liquid phase activities and the interaction parameters  $\chi_{12}$ ,  $\chi_{1P}$  and  $\chi_{2P}$  the composition within the membrane can be calculated. Conversely, with the appropriate sorption data available, the values of the interaction parameters can be recovered through

eqn (12) which will be considered next.

According to the model, the interaction between the individual solvent molecules and the polymer are accounted for  $\chi_{1P}$  and  $\chi_{2P}$ . The interaction parameter,  $\chi_{12}$ , which characterizes the solvent-solvent interaction inside the membrane is within the formulation of Flory independent of the nature of the polymer. We shall discuss the validity of this assumption subsequently, for now we note that the value of  $\chi_{12}$  is usually recovered from the Gibbs free energy of the bulk liquid. For a binary mixture, eqn (11) reduces to,

$$\chi_{12} = \frac{1}{x_1^S \phi_1^S} [-x_1^S \ln \phi_1^S + x_2^S \ln \phi_2^S] + \frac{\Delta G_m}{RT} \quad (14)$$

Experimental data derived from vapour-liquid equilibria is normally expressed in terms of the excess Gibbs free energy,  $\Delta G_E$ . This can be related to the molar Gibbs free energy of mixing by adding the ideal contribution:

$$\frac{\Delta G_m}{RT} = \frac{\Delta G_E}{RT} + [x_1^S \ln x_1^S + x_2^S \ln x_2^S]$$

Substituting above equation into eqn (14) leads to:

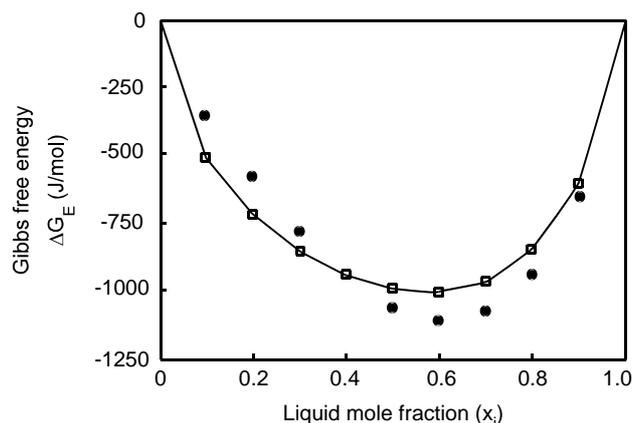
$$\begin{aligned} \chi_{12} = & \frac{1}{x_1^S \phi_1^S} [(x_1^S \ln(x_1^S / \phi_1^S) + x_2^S \ln(x_2^S / \phi_2^S)) + \\ & \frac{\Delta G_E}{RT}] \end{aligned} \quad (15)$$

A similar expression may result if the molar volume of the components are equal [10]:

$$\chi_{12} = \frac{1}{x_1^S \phi_1^S} \frac{\Delta G_E}{RT} \quad (16)$$

but this expression is not suited for ethanol and water whose molar volumes differ by a factor of about three. The best fit of the free energy data of Hanson and Miller [10] with eqn (15) was obtained for  $\chi_{1P} = 3.65$  and is shown in Figure 3. Although the fit is not particularly good we shall see later that its contribution to the activity in the polymer is very small.

The simplest procedure for the determination of the interaction parameters is obtained by noting that for a pure liquid in contact with a membrane, eqn (10) can be rearranged to:

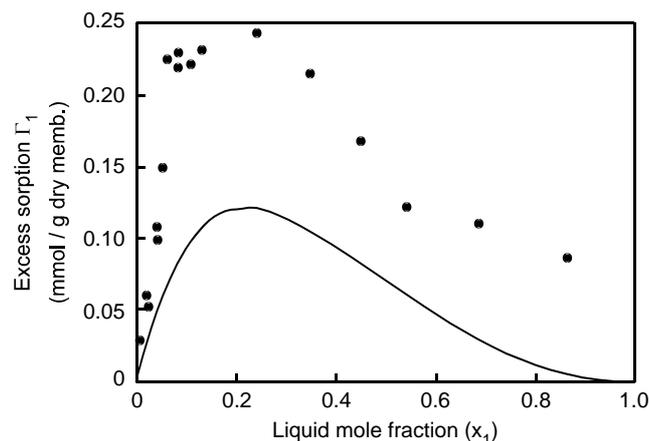


**Figure 3.** A fit to the free energy data of Hanson and Miller [10] for the binary {ethanol(1)-water(2)} liquid mixture.

$$\chi_{iP} = - \left[ \frac{\ln \phi_i^S + (1 - \phi_i^S)}{(1 - \phi_i^S)^2} \right] \quad (17)$$

Thus, given the uptake of the pure component  $i$  its interaction parameter  $\chi_{iP}$  can be calculated directly. Unfortunately, for system with small uptake the practical utility of this simple procedure is severely limited by the difficulties inherent in the accurate measurement of total uptake. For the silicone rubber membrane considered in this study, the measured uptake of pure ethanol, 0.021 g/g dry membrane, leads to  $\chi_{1P} = 2.8$  and that of water, 0.003 g/g dry membrane, results in  $\chi_{2P} = 4.8$ . The relative isotherm based on these values is shown in Figure 4 and seriously underestimates the measured data. To establish that the inconsistency observed for the ethanol-water/silicone rubber system is due to error in the total uptake data it is necessary to rule out other factors, which could also contribute to this mismatch.

One shortcoming in the application of the Flory model lies in the calculation of the solvent-solvent interaction parameter within the polymer  $\chi_{12}$ , from data on the bulk liquid. This is unsatisfactory since there is no theoretical or experimental justification that the interaction between ethanol and water molecules within the hydrophobic polymer matrix remains similar to that in the bulk liquid. This is in fact highly unlikely as the bulk liquid exhibits an azeotrope, which is not observed in the sorbed phase. A radically modified thermodynamic behaviour for ethanol-water mixtures adsorbed within a rigid hydrophobic matrix has been demonstrated by Farhadpour and Bono [12]. For-

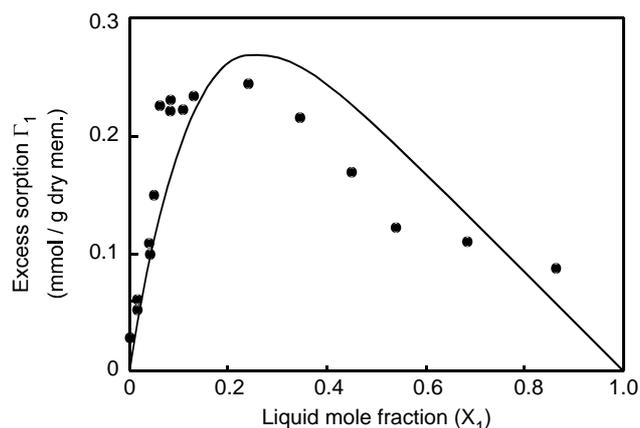


**Figure 4.** The relative sorption isotherm based on solvent-polymer interaction parameters recovered from total sorption data ( $\chi_{12} = 3.65$ ,  $\chi_{1P} = 2.80$  and  $\chi_{2P} = 4.80$ ).

unately, for systems with small uptake any errors in the description of the solvent-solvent interaction only has a minor effect. This is simply because the dominating contributions arise as a result of polymer-solvent rather than solvent-solvent interactions. Put another way, for systems with small uptake, the volume fraction of the sorbed species  $\phi_1^S$  and  $\phi_2^S$  are much smaller than that of the polymer  $\phi_P^S$  and solvent-solvent interaction play a secondary role. A numerical sensitivity analysis confirmed the predicted isotherm is not sensitive to the value of solvent-solvent interaction.

Another common difficulty in the application of the Flory-Huggins model concerns the choice of the numerical values for the partial molar volume of the sorbed species. The calculation presented above were performed using the procedure in which the partial molar volumes are equated to those in the bulk liquid ( $V_1^0 = 58.7$  and  $V_2^0 = 18.2$  mL/mol at 25 C). A sensitivity analysis based on values of  $V_1^0$  ranging between 50-70 mL/mol indicated that the predicted isotherm is marginally sensitive to the particular values adopted and cannot describe the large discrepancy observed. We, therefore, conclude that for the system considered in this study the observed mismatch is caused primarily by the error in the total uptake measurement which is reflected in incorrect polymer-solvent interaction parameters.

As an alternative to above procedure, the values of the interaction parameters  $\chi_{1P}$  and  $\chi_{2P}$  can be obtained from a match of the Flory model with the relative sorption data which can be measured without separating the



**Figure 5.** The relative sorption isotherm based on solvent-polymer interaction parameters recovered from the relative sorption data  $\{\chi_{12} = 3.65, \chi_{1P} = 2.19, \text{ and } \chi_{2P} = 4.89\}$ .

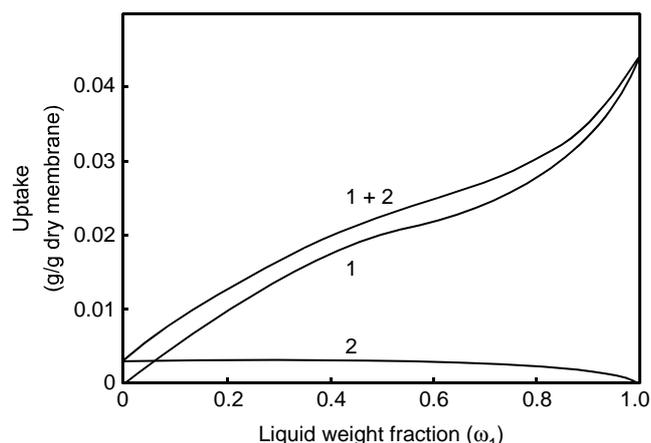
membrane from the free liquid. A non-linear regression fit of the model to the data presented in Table 1 gave the best values of  $\chi_{1P} = 2.19$  and  $\chi_{2P} = 4.89$ . The fit obtained with these parameter values is shown in Figure 5 and provides a good description of the relative sorption data.

Further confidence in the interaction parameters is obtained by considering the realistic values predicted for true uptake of the pure components (Table 2).

The above analysis indicates that the sorption equilibria for the system {ethanol (1)-water (2)}/silicone rubber is well represented by the Flory-Huggins thermodynamic model. In particular, constant interaction parameters are sufficient to fit the sorption data, which is a good indication of the validity of the basic model. Some caution is, however, required in accepting a thermodynamic model, which is only validated against the relative sorption data. This is best demonstrated by comparing the uptake of the individual components predicted on the basis of the Flory-Huggins model, which are demonstrated in Figure 6. The application of

**Table 2.** Pure component uptake of ethanol and water based on the parameters recovered from the relative sorption isotherm.

| Solvent | Interaction parameter | Predicted uptake g/g dry membrane | Measured uptake g/g dry membrane |
|---------|-----------------------|-----------------------------------|----------------------------------|
| Ethanol | $\chi_{1P} = 2.19$    | 0.045                             | 0.021 – 0.007                    |
| Water   | $\chi_{2P} = 4.89$    | 0.0027                            | 0.003 – 0.001                    |



**Figure 6.** The uptake of the individual components predicted based on the Flory-Huggins model with the interaction parameters  $\{\chi_{12} = 3.65, \chi_{1P} = 2.19, \text{ and } \chi_{2P} = 4.89\}$ .

Flory-Huggins model leads to a realistic curve of the individual uptake, which shows the silicone rubber is selective toward ethanol at the entire range of composition

## CONCLUSION

The technique normally used to measure the amount and composition of a liquid mixture adsorbed in a non-porous homogeneous membrane requires the removal of the membrane sample from the free liquid. Such technique suffers from the inherent difficulties of obtaining a clean separation and it is also prone to evaporative losses during the handling stages. Such practical difficulties are less acute for non-volatile solutes with large uptake but severely limit the reliability of the measured data for volatile solutes with small uptake.

For systems with small uptake it is advantageous to determine the relative sorption isotherm which can be measured without separating the membrane from the free liquid. The experimental relative sorption isotherm provides a powerful and general check of the reliability and consistency of measured total uptake data. Quite simply, the relative sorption must be smaller than the total uptake,  $|\Gamma_i| \leq N^S$ , at all compositions irrespective of the nature of the polymer and the extent of swelling. The violation of this constraint for any of sorbed species points to experimental errors in the total uptake, which is more difficult to measure.

In the case of {ethanol- (1)-water (2)}/silicone rubber, the total uptake measured by the conventional technique is in serious error due to unavoidable evaporative losses during the handling stages and this is clearly reflected in the violation of the constraint  $|\Gamma_i| \leq N^S$ . Similar conclusion can also be drawn for the data of Suematsu et al. for {ethanol- (1)-water (2)}/silicone rubber. In the absence of reliable total uptake data, the extent and composition of the sorbed liquid can be established from a thermodynamic analysis based on the relative sorption isotherm alone. This procedure was demonstrated for the {ethanol- (1)-water (2)}/silicone rubber system using the Flory-Huggins thermodynamic model. The relative sorption data is well fitted with constant polymer/solvent interaction parameters which is a prerequisite for the validity of the Flory model.

The separate evaluation of the kinetic and equilibrium contributions to the multi-component 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 some membrane processes such as 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 are incapable of producing the characteristic shape observed for the uptake of small polar solutes such as water and ethanol vapour by elastomers. Any enthalpic and/or entropic modification of the Flory-Huggins model suggested in the literature are shown to be of little help in this respect [13,14].

An empirical modification of the Flory-Huggins model 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 new development will be considered in forthcoming article.

## NOMENCLATURE

$a_i^S$  activity of component i in sorbed phase  
 $\Delta G_m$  free energy of mixing  
 $\Delta G_E$  excess free energy change of mixing  
 $\Delta H_m$  enthalpy change of mixing

$N_0$  total number of moles  
 $N_{i0}$  number of moles of component i  
 $N^S$  total adsorption (mol/g dry membrane)  
 $M$  mass of membrane sample  
 $R$  universal gas constant  
 $\Delta S_{cf}$  configurational entropy change of mixing  
 $\bar{v}_i$  partial molar volume of component i in sorbed phase  
 $V_p$  special volume of polymer  
 $x_i$  mole fraction of component i in bulk liquid  
 $x_i^S$  mole fraction of component i in sorbed phase  
 $\Gamma_i$  relative sorption of component i (mol/g dry membrane)  
 $\gamma_i$  activity coefficient of component i in bulk liquid  
 $\gamma_i^S$  activity coefficient of component i in sorbed phase  
 $\phi_i^S$  volume fraction of component i sorbed phase  
 $\phi_p^S$  volume fraction of polymer in sorbed phase  
 $\chi_{ij}$  binary interaction parameter for component i and j  
 $\omega_i$  mass fraction of component i in bulk liquid

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