Solubility of Binary Liquid Mixtures in Polymeric Materials

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SYNOPSIS

Experimental data on the permeation of binary mixtures through polymeric materials show that liquid mixtures can exhibit large, positive synergistic rates. As the permeation rate depends on both solubility and the diffusion coefficient, the existence of a maximum in the steady-state permeation rate vs. the composition curve could be due to an increase in solubility and/or diffusion coefficient. In this study, a theoretical model based on the Flory–Huggins equation was developed to predict the solubility of binary liquid mixtures in polymers. The equation has four adjustable parameters that can be determined from solubilities of pure liquids in the polymer and the vapor–liquid equilibrium data for the binary liquid mixture. The model was tested for two binary liquid mixture/polymer systems. The predicted values of solubilities are close to the experimental data. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The permeation process occurs in three steps: First, the permeating species enters the material (this is known as the solution), next it passes through the solid (diffusion), and, finally, it emerges from the downstream surface (evaporation). The permeation rate of chemicals through the polymeric membrane therefore depends on the solubility and diffusion coefficient of the permeating species in the material. The diffusion coefficient itself depends upon the concentration of the chemical in the membrane. The rate of mass transfer through the barrier is, therefore, a strong function of solubility. In the case of permeation of liquid mixtures, the rate of permeation of each species depends upon the concentration of all the species in the polymer.[1] The solubility, therefore, plays an important role in the effectiveness of the polymeric membranes.

A program was initiated in our laboratories to study the permeation of binary liquid mixtures through elastomeric materials. The goal of this project was to develop a method for predicting the rate of permeation of liquid mixtures through elastomers from the permeation data of pure compounds. In the first phase of this investigation, permeation experiments were performed for four binary liquid mixture/protective clothing material pairs.[1] Permeation curves for several mixture compositions were prepared for each system. The experimental data showed that for the systems in which the solubility of one chemical is much larger than the other the chemical with low solubility was affected synergetically by the other. In the systems in which the solubilities of pure liquids in the polymer are of the same order of magnitude, the liquid can show permeation enhancement or depression. In the second phase of the project, theoretical studies were done to develop a method for predicting the solubility of binary liquid mixtures in polymeric materials.

DEVELOPMENT OF THE METHOD

If a solid polymer film is exposed to a liquid, the fluid molecules enter and the result is a swollen membrane. Cross-linking is an important factor in solubility. The polymers with no cross-linking can disintegrate and completely dissolve in the liquid. The polymers with highly cross-linked structure, on the other hand, are swollen much less by the liquid. The activity of a pure liquid (solute) in a polymer is usually described by Flory–Huggins thermodynamics[2-4]:

$$\ln a_1 = \ln(1 - \phi_2) + \left(1 - \frac{V_1}{V_2}\right)\phi_2 + \chi\phi_2^2 \quad (1)$$

where V_1 and V_2 are the molar volumes of the liquid and polymer, respectively; ϕ_1 and ϕ_2, the volume fractions of the liquid and polymer, respectively; and χ, the Flory–Huggins interaction parameter.

Equation (1) represents the activity of a low molecular weight compound in a polymer. If the polymer is exposed to a binary liquid mixture, the equation may be extended for the ternary system (two liquids and one polymer), as follows[5]:

$$\ln a_1 = \ln \phi_1 + \phi_2 + \phi_3$$
$$- \phi_2 \frac{V_1}{V_2} - \phi_3 \frac{V_1}{V_3} + \chi_{12}\phi_2(\phi_2 + \phi_3)$$
$$+ \chi_{13}\phi_3(\phi_2 + \phi_3) - \chi_{23}\Phi_2\Phi_3 \frac{V_1}{V_2} \quad (2)$$

$$\ln a_2 = \ln \phi_2 + \phi_1 + \phi_3$$
$$- \phi_1 \frac{V_2}{V_1} - \phi_3 \frac{V_2}{V_3} + \chi_{12}\phi_1 \frac{V_2}{V_1}(\phi_1 + \phi_3)$$
$$+ \chi_{23}(\phi_1 + \phi_3) - \chi_{13}\phi_1\phi_3 \frac{V_2}{V_1} \quad (3)$$

where subscripts 1 and 2 denote components in the liquid mixture, and 3, in the polymer. The volume fraction Φ_i is defined as

$$\phi_i = \frac{N_i V_i}{\sum N_i V_i} \quad (4)$$

and χ_{ij} is the interaction parameter between components i and j.

For the polymer phase to be in equilibrium with the binary liquid phase, the following conditions should hold:

$$a_1^L = a_1^P \quad (5)$$

$$a_2^L = a_2^P \quad (6)$$

where a_1^L and a_2^L are the activities of components 1 and 2 in the liquid phase, respectively, and a_1^P and a_2^P, the activities of components 1 and 2 in the polymer, respectively.

a_1^P and a_2^P are given by eqs. (2) and (3), respectively. a_1^L and a_2^L are found from vapor liquid equilibrium data as follows: Several correlations have been proposed for activity coefficients in a liquid phase.[6] One of these correlations is the three-suffix Margules equation:

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})X_1]X_2^2 \quad (7)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})X_2]X_1^2 \quad (8)$$

where γ_1 and γ_2 are activity coefficients of components 1 and 2 in the liquid phase; A_{12} and A_{21}, activity coefficient parameters, calculated from equilibrium data; and

$$a_1^L = \gamma_1 X_1 \quad (9)$$

$$a_2^L = \gamma_2 X_2 \quad (10)$$

Substitution of eqs. (2), (3), and (7)–(10) in eqs. (5) and (6) yields

$$\ln X_1 + [A_{12} + 2(A_{21} - A_{12})X_1]X_2^2$$
$$= \ln \phi_1 + \phi_2 + \phi_3 - \phi_2 \frac{V_1}{V_2} - \phi_3 \frac{V_1}{V_3}$$
$$+ \chi_{12}\phi_2(\phi_2 + \phi_3) + \chi_{13}\phi_3(\phi_2 + \phi_3)$$
$$- \chi_{23}\phi_2\phi_3 \frac{V_1}{V_2} \quad (11)$$

$$\ln X_2 + [A_{21} + (A_{12} - A_{21})X_2]X_1^2$$
$$= \ln \phi_2 + \phi_1 + \phi_3 - \phi_1 \frac{V_2}{V_1} - \phi_3 \frac{V_2}{V_3}$$
$$+ \chi_{12}\phi_1 \frac{V_2}{V_1}(\phi_1 + \phi_3) + \chi_{23}(\phi_1 + \phi_3)$$
$$- \chi_{13}\phi_1\phi_3 \frac{V_2}{V_1} \quad (12)$$

Once the constants χ_{12}, χ_{13}, and χ_{23} are known, eqs. (11) and (12) can be solved to find the volume fractions of components 1 and 2 in the polymer Φ_1 and Φ_2. (Note that $\Phi_3 = 1 - \Phi_1 - \Phi_2$).

Evaluation of Parameters

Interaction Parameters χ_{13} and χ_{23}

These two parameters can be determined from solubility of pure liquids in the polymer.[7] The activity of a pure liquid (component 1) in a polymer (component 3) is given by eq. (1):

$$\ln a_1^P = \ln(1 - \phi_3) + (1 - V_1/V_3)\phi_3 + \chi_{13}\Phi_3^2 \quad (13)$$

For a pure liquid in equilibrium with a polymer phase

$$a_1^L = a_1^P = 1 \quad (14)$$

Substitution of eq. (14) into (13) yields

$$\ln(1 - \phi_3) + \left(1 - \frac{V_1}{V_3}\right)\phi_3 + \chi_{13}\phi_3^2 = 0 \quad (15)$$

The molar volume of polymer V_3 is much larger than the molar volume of liquid V_1; therefore, $V_1/V_3 \approx 0$ and eq. (13) reduces to

$$\chi_{13} = -\frac{\ln(1 - \phi_3) + \Phi_3}{\phi_3^2} \quad (16)$$

where Φ_3 is the volume fraction of the polymer. Φ_3 is related to the solubility of pure liquid in the polymer as follows:

$$\phi_3 = \frac{1}{S_1/\rho_1 + 1} \quad (17)$$

where S_1 is the solubility of pure component 1 in the polymer (g of liquid/cm^3 of polymer) and ρ_1 is the density of liquid 1, g/cm^3.
Substitution of eq. (17) into (16) yields

$$\chi_{13} = -(S_1/\rho_1 + 1)$$
$$\times \left[1 + (S_1/\rho_1 + 1)\ln\frac{S_1/\rho_1}{S_1/\rho_1 + 1} \right] \quad (18)$$

and, similarly, for component 2:

$$\chi_{23} = -\left(\frac{S_2}{\rho_2} + 1\right)$$
$$\times \left[1 + \left(\frac{S_2}{\rho_2} + 1\right)\ln\frac{S_2/\rho_2}{S_2/\rho_2 + 1} \right] \quad (19)$$

Interaction Parameter χ_{12}

χ_{12} is the interaction parameter between the two liquids. The nonideality in liquids is usually expressed by excess functions. The relation between Gibbs energy of mixing and excess Gibbs energy for a binary mixture is given by[8]

$$\Delta G_{mix}/RT = X_1\ln X_1 + X_2\ln X_2 + G^E/RT \quad (20)$$

where G^E is the excess Gibbs energy and X_1 and X_2 is the liquid mole fractions of components 1 and 2, respectively.
  One can write the Flory–Huggins equation for a binary liquid mixture as follows:

$$\Delta G_{mix}/RT = X_1\ln \Psi_1 + X_2\ln \Psi_2$$
$$+ \chi_{12}\Psi_1\Psi_2(X_1 + X_2 V_2/V_1) \quad (21)$$

Substitution of eq. (20) into eq. (21) yields the fol-

lowing equation for χ_{12}:

$$\chi_{12} = \frac{1}{X_1\Psi_2}[X_1\ln(X_1/\Psi_1)$$
$$+ X_2\ln(X_2/\Psi_2) + G^E/RT] \quad (22)$$

where Ψ_1 and Ψ_2 are volume fractions in the liquid phase:

$$\Psi_1 = \frac{V_1X_1}{V_1X_1 + V_2X_2}, \quad \Psi_2 = \frac{V_2X_2}{V_1X_1 + V_2X_2} \quad (23)$$

and V_1 and V_2 are molar volumes of components 1 and 2, respectively. The excess Gibbs energy can be calculated from vapor–liquid equilibria data:

$$G^E/RT = \sum X_i\ln \gamma_i \quad (24)$$

If one uses the Margules relations to represent the activity coefficients [eqs. (7) and (8)], eq. (22) can be written in the following form [substitution of eqs. (7), (8), and (24) into eq. (22)]:

$$\chi_{12} = \frac{1}{X_1\Psi_2}\left[X_1\ln\left(\frac{X_1}{\Psi_1}\right) + X_2\ln\left(\frac{X_2}{\Psi_2}\right) \right.$$
$$\left. + X_1X_2(A_{12}X_2 + A_{21}X_1) \right] \quad (25)$$

Equation (25) indicates that χ_{12} is a function of liquid mole fractions, molar volume of pure compounds, and activity coefficient parameters. Several authors have used similar methods for determining the interaction parameter.[7,9,10]

Procedure for Calculating Solubility of Mixtures in Polymers

1. Determine the solubility of pure compounds in the polymer (immersion experiment).
2. Calculate interaction parameters χ_{12} and χ_{21} from eqs. (18) and (19), respectively.
3. Determine activity coefficient parameters A_{12} and A_{21} from vapor–liquid equilibrium data.
4. Calculate interaction parameters χ_{12} from eq. (25).
5. Solve eqs. (11) and (12) simultaneously to find Φ_1 and Φ_2. (These equations are nonlinear and should be solved by the numerical method.)
6. Convert the volume fractions into solubilities

in g/cm^3:

$$S_1^{mix} = \frac{\rho_1\phi_1}{1 - \Phi_1 - \Phi_2} , S_2^{mix}$$

$$= \frac{\rho_2\phi_2}{1 - \phi_1 - \phi_2} \quad (26)$$

where S_1^{mix} and S_2^{mix} are the solubilities of components 1 and 2 in the polymer from the binary liquid mixture. A computer program was developed to solve the equations and to compute the solubilities in terms of the composition of the liquid.

RESULTS AND DISCUSSION

Benzene-Cyclohexane-Poly(γ-methyl-L-glutamate) (PMLG)

Suzki and Onozata[11] measured the solubility of benzene-cyclohexane mixtures in PMLG. The solubilities of pure benzene (1) and pure cyclohexane (2) in PMLG along with densities and vapor-pressure constants used in the calculations area given in Table I.[12] The interaction parameters X_{13} and X_{23} were calculated from eqs. (16) and (17), respectively, and are given in Table II. Vapor-liquid equilibrium (VLE) data for the benzene-cyclohexane mixture at 25°C[13] were used to compute the activity coefficient parameters A_{12} and A_{21}. Combining eqs. (5) and (6), one gets

$$\ln \frac{\gamma_1}{\gamma_2} = A_{12}[3X_1^2 - 4X_1 + 1]$$

$$+ A_{21}[2X_1 - 3X_1^2] \quad (27)$$

The activity coefficient of a component in the liquid phase is given by

$$\gamma_i = \frac{(Y_iP)}{(p_i^* X_i)} \quad (28)$$

where P is the pressure; p_i^*, the vapor pressure of component i; and Y_i, the vapor-phase mol fraction in equilibrium with x_i.

Substitution of eqs. (28) into (27) yields

$$\ln \frac{Y_1X_2P_2^*}{X_1P_1^*Y_2} = A_{12}[3X_1^2 - 4X_1 + 1]$$

$$+ A_{21}[2X_1 - 3X_1^2] \quad (29)$$

The least-square method was used to find parameters A_{12} and A_{21} in eq. (29) from vapor-liquid equilibrium data. The calculated parameters are given in Table III. In a book,[14] Hala et al. compiled the activity coefficient parameters A_{12} and A_{21} for many binary liquid mixtures. These parameters may therefore be found directly from this reference.

The interaction parameters and the activity coefficient parameters were used as input to the computer program, and the solubilities of benzene and cyclohexane in PMLG were determined for the entire range of composition. The results of calculation along with Suzki and Onozata's[11] experimental data are given in Figure 1. This system is an extreme case in which one component is highly soluble in the polymer (0.75 g/cm^3) and the other component is almost insoluble in it (0.025 g/cm^3). It would be difficult to predict the solubility curve for such a system. Despite this, the predicted values of solubilities are fairly close to the experimental data. The model shows a maximum in the solubility of cyclohexane at a composition of about 0.4 mol fraction. This is consistent with the experimental data.

Table I   Data Used for the Prediction of Solubilities of Benzene-Cyclohexane and Methanol-Water Mixtures in PMLG

Substance	Density at 20°C (g/cm^3)	Solubility in PMG (g/cm^3)	Vapor pressure (mmHg) $\log p^* = A - B/(t + c)$		
			A	B	C
Benzene	0.879	0.75	6.90565	1211.033	220.790
Cyclohexane	0.799	0.02	6.84498	1203.526	222.863
Methanol	0.792	0.22	8.07246	1574.990	238.860
Water	0.998	0.05	7.96681	1668.210	228.000

Table II   Binary Interaction Parameters for Benzene–Cyclohexane/PMLG and Methanol–Water/PMLG Systems

Binary Pair	Interaction Parameter
Benzene/PMLG	0.82
Cyclohexane/PMLG	2.90
Methanol/PMLG	1.20
Water/PMLG	2.30

Methanol–Water–Poly(γ-methyl-L-glutamate) (PMLG)

Suzki and Onozata[15] measured the solubility of methanol–water mixtures in PMLG. The solubilities of pure liquids in PMLG and vapor–liquid equilibrium data for methanol–water were used to predict the solubilities of the binary mixture in the polymer and the results were compared with the experimental data. The data used in the calculations are given in Table I. The binary interaction parameters of methanol/PMLG (X_{13}) and water/PMLG (X_{23}) are given in Table II [from eqs. (16) and (17)].

The activity coefficient parameters A_{12} and A_{21} for the binary mixture of methanol–water were computed from VLE data at 35°C[16] using eq. (29) (least-square method). These parameters are given in Table III. The results of solubility calculations (from the computer program) along with Suzki and Onozata's experimental data are illustrated in Figure 2. The calculated values of solubilities are very close to the experimental data.

The Effect of Binary Interaction Parameters on Solubilities

Solubility of binary liquid mixtures in polymer depends on the binary interactions between liquids and polymer as well as between the two liquids. The interaction parameters of liquid/polymer pairs depend on the solubility of pure liquids in the polymer [eqs. (18) and (19)]. The liquid/liquid interaction parameter, on the other hand, depends on activity coefficients and molar volumes of liquids [eq. (25)].

Table III   Activity Coefficient Parameters

| Binary Mixture	A_{12}	A_{21}
Benzene (1)–cyclohexane (2)	0.469	0.4450
Methanol (1)–water (2)	0.596	0.3990
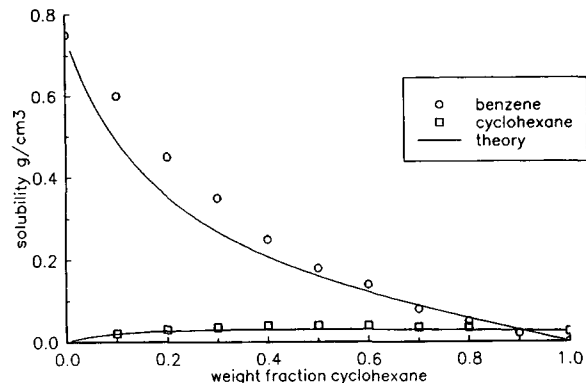
Figure 1   Solubilities of benzene and cyclohexane in PMLG against weight fraction of cyclohexane in liquid mixture.

If each liquid is dissolved in polymer independent of the other liquid (ideal system), one would expect to see a straight line for solubility vs. liquid composition:

$$S_1^{mix} = S_1(1 - X_2) \qquad (30)$$

$$S_2^{mix} = S_2 X_2 \qquad (31)$$

In the real systems, the solubility of each liquid in polymer depends on the solubility of both liquids, and the solubility curves are not linear. To determine the effect of interaction parameters on the shape of solubility curves of binary liquid/polymer systems, the model developed in the previous section was used to generate solubility curves for a wide range of parameters. The results of computation are illustrated in Figures 3–6. Figure 3 represents a system in which liquid 1 is highly soluble in polymer ($S_2/\rho_2 = 0.9$ cm³ of liquid/cm³ of polymer). Figure 4 is for a
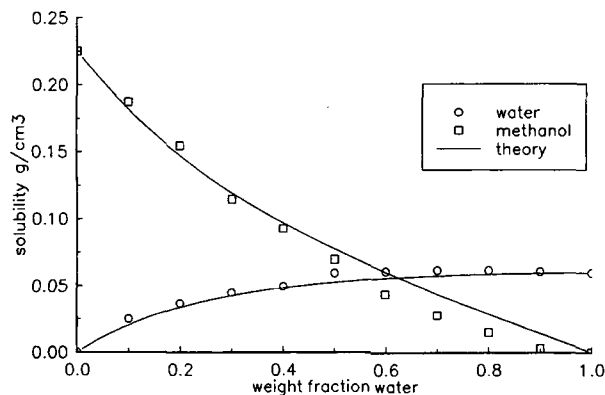
Figure 2   Solubilities of methanol and water in PMLG against weight fraction of water of liquid mixture.
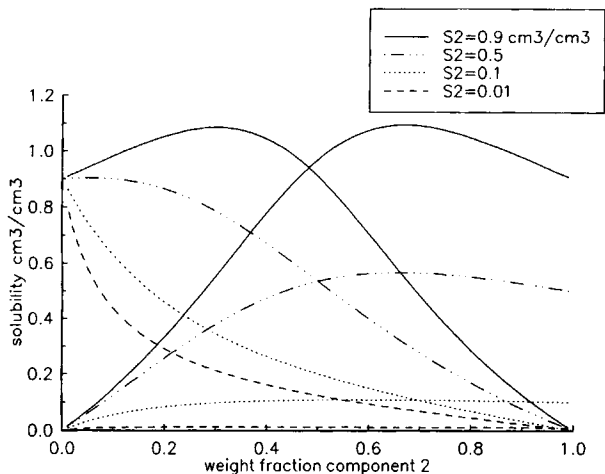
Figure 3 Solubility curves of binary liquid mixtures in polymers for the case of $S_1 = 0.9$ cm^3 of liquid/cm^3 of polymer, $V_1/V_2 = 1.5$, $A_{12} = 0.6$, and A_{21}, = 0.4.

Figure 5 Solubility curves of binary liquid mixtures in polymers for the case of $S_1 = 0.1$ cm^3 of liquid/cm^3 of polymer, $V_1/V_2 = 1.5$, $A_{12} = 0.6$, and $A_{21} = 0.4$.
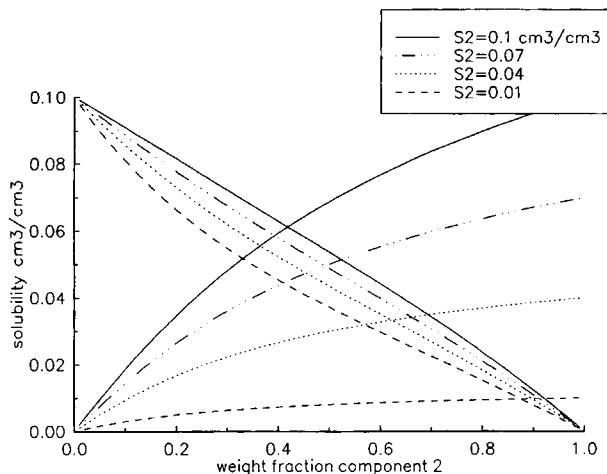
moderate solubility of liquid 1 (0.5 cm^3/cm^3) and Figure 5 is for a case in which component 1 is slightly soluble in the polymer (0.1 cm^3/cm^3). For the systems in which both liquids have large solubilities in the polymer, solubility curves pass through a maximum. This indicates that the presence of one liquid in the polymer helps to increase the solubility of the other one (plasticizing effect). The solubility of both liquids are higher than for an ideal system [eqs. (30) and (31)]. For the systems with one liquid highly soluble in polymer and the other one only slightly soluble, the solubility curve for the first liquid is concaved upward and the other curve shows a slight -

maximum. The effect of the more soluble liquid is to enhance the solubility of the other component in the polymer. The effect of the less soluble liquid is to depress the solubility of the first liquid in the polymer. The result is one solubility curve that is below the ideal mixture line (for the more soluble liquid) and another curve that is above the straight line represented by eqs. (30) and (31) (for the less soluble liquid). Benzene–cyclohexane/PMLG and methanol–water/PMLG systems discussed previously are examples of this category. For the ternary systems in which both liquids dissolve slightly in the polymer, the solubility curves do not show any
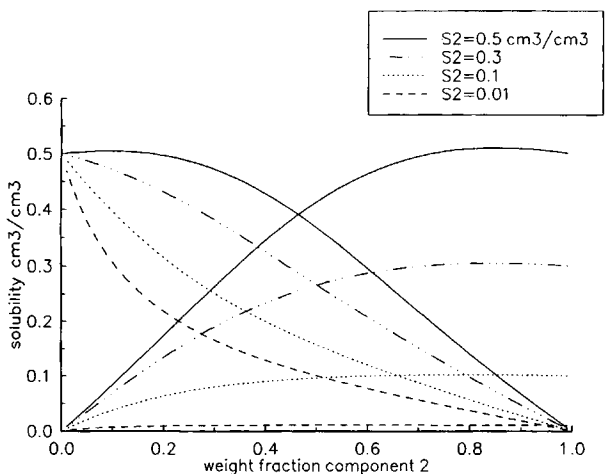

Figure 4 Solubility curves of binary liquid mixtures in polymers for the case of $S_1 = 0.5$ cm^3 of liquid/cm^3 of polymer, $V_1/V_2 = 1.5$, $A_{12} = 0.6$, and $A_{21} = 0.4$.

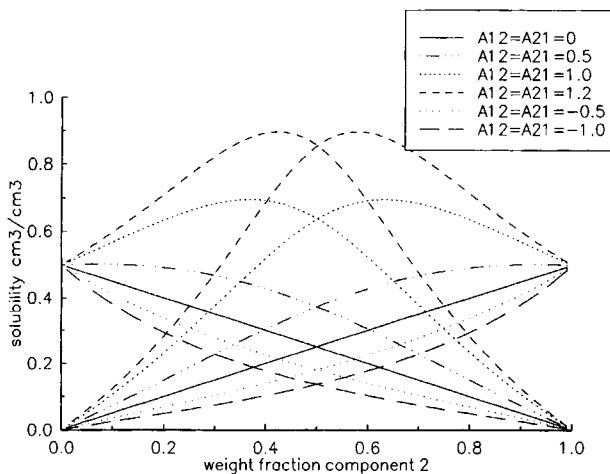**Figure 6** Solubility curves of binary liquid mixtures in polymers for the case of $S_1 = S_2 = 0.5$ cm^3 of liquid/cm^3 of polymer and $V_1/V_2 = 1.0$.

curvature. They are very close to the solubility lines for ideal systems. This is an indication that at low solubilities the mixture behave ideally.

The effect of liquid/liquid interaction parameter on the solubility curves is shown in Figure 6. For constant values of interaction parameters X_{13} and X_{23}, and the ratio of liquid molar volumes equal to unity ($V_1/V_2 = 1$), solubility curves are plotted for various values of activity coefficient parameters A_{12} and A_{21}. For an ideal liquid solution ($A_{12} = A_{21} = 0$), the solubility curves are straight lines. For the solutions that have positive deviations from Raoult's law (positive values of A_{12} and A_{21}), the curves are above the straight lines for the ideal system and solubility enhancement has occurred. If the binary liquid solution has negative deviations from Raoult's law (negative values of A_{12} and A_{21}), the solubility curves are below the ideal solution lines and solubility depression is experienced. It should be noted that Figure 6 is for a system in which both liquids have moderate solubilities in the polymer and the activity coefficient parameters are equal ($A_{12} = A_{21}$). Similar curves could be produced for other cases.

CONCLUSION

A theoretical model was developed to predict the solubility of binary liquid mixtures in polymeric materials. The model is based on the Flory–Huggins equation and uses solubility of pure liquids in polymer and vapor–liquid equilibria data for binary liquid mixtures to compute the solubility of liquid mixtures in polymers. The model was used to calculate the solubilities of benzene–cyclohexane and methanol–water mixtures in PMLG, and the results were compared with experimental data. The predicted values of solubilities are close to the experimental data. The model was also used to determine the effect of binary liquid/polymer and liquid/liquid interactions on the shape of solubility curves.

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