LBNL-48572
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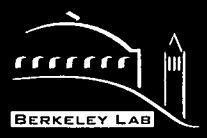

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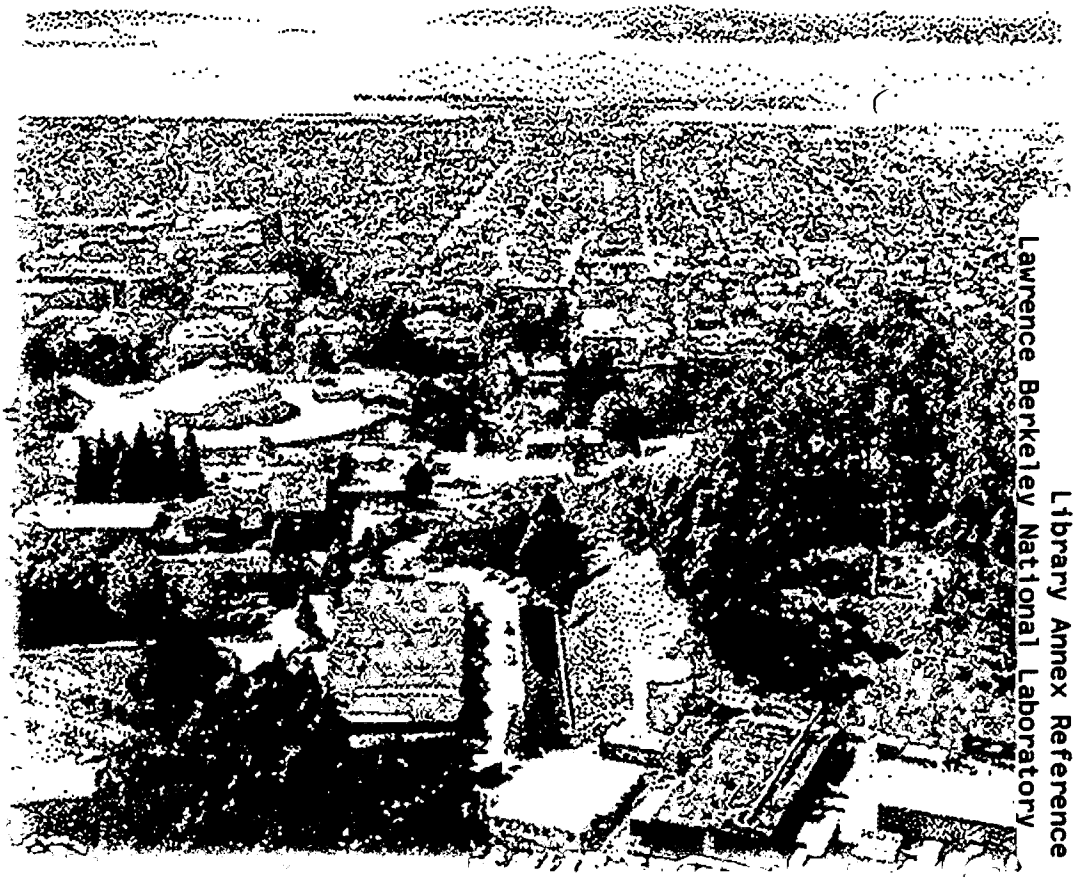
Chemical Sciences Division

June 2001

Submitted to
J. AIChE



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LBNL-48572

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June 2001

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This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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ABSTRACT

Because there is no simple method for measuring the solubilities of nonvolatile solutes in a polymer, this work presents a thermodynamic framework for estimating such solubilities from infinite-dilution distribution-coefficient data for aqueous solutions of the solute in equilibrium with the polymer.

The experimental infinite-dilution distribution-coefficient is related to that calculated from a molecular-thermodynamic model (Flory–Huggins). The three binary Flory parameters are obtained from water-solute and water-polymer data, and from the solute's distribution coefficient.

Solubilities of nineteen nonvolatile aromatic solutes were estimated in three polymers: ethyl-vinyl acetate copolymer (EVAc) with 33 (EVAc33), 45 (EVAc45) vinyl acetate content and poly(vinyl acetate) (PVAc) at 25 °C where most of the solutes are solids.

The data reported here may be useful for a variety of applications including design of membrane processes or drug-delivery systems, and for packaging technology for foods, chemicals and pharmaceuticals.

Keywords: solubility, nonvolatile solutes, Flory-Huggins, ethylene-vinyl acetate copolymers, poly(vinyl acetate).

INTRODUCTION

The literature is rich in both experimental and theoretical studies concerning the solubilities of volatile substances in polymeric materials (for example, Wolfarth, 1994; Hao *et al.*, 1992; Bonner, 1975). However, little is known about solubilities of non-volatile liquid and solid solutes in polymers, despite a need for this information in a variety of applications including controlled-release systems where the drug solubility in the supporting polymer plays an essential role for determining load capacity and diffusion rate into the physiological environment (Langer and Peppas, 1983). In packaging technology for foods and pharmaceuticals, sorption from the contained product may alter essential properties of both the product and the polymeric container; or release of oligomers or processing additives from the polymer may contaminate the stored product (Vergnaud, 1998; Jenke *et al.*, 1991; Hayward *et al.*, 1990; Hayward and Jenke, 1990b).

Heavy organic solutes tend to be solids near room temperature. Because the rate of diffusion of a solid into a polymer is extremely slow, there is no simple, inexpensive way to measure a solid solute's solubility in a polymer. However, when the solute is dissolved in a solvent that does not dissolve the polymer, infinite-dilution distribution coefficient data can be obtained more easily. Coupled with a molecular-thermodynamic model and other experimental data, it is then possible to estimate the desired solubility.

In this work, we use the Flory-Huggins model (Flory, 1953) to estimate the solubilities of nineteen nonvolatile organic solutes in three polymers: two ethyl-vinyl acetate copolymers with 33 and 45 weight percent vinyl acetate (VAc) and poly(vinyl acetate) at 25 °C. We have recently measured infinite-dilution distribution coefficients for these solutes between water and polymer (Fornasiero *et al.*, 2001).

Table 1 presents the most relevant solute properties: molecular weights, densities and melting points. For solutes that are solid at 25 °C, the densities in Table 1 are those of the liquid at a temperature just above the melting point. In addition, Table 1 gives molar enthalpies of fusion and differences in the liquid and solid molar heat capacity.

For each of the three polymers, Table 2 shows the average molecular weight, density at 25 °C, VAc content and glass-transition temperature.

ESSENTIALS OF THE ESTIMATION METHOD

Solubility is an equilibrium property. When a solid solute is brought into contact with a polymer film, diffusion of molecules from the solid into the polymer is prohibitively slow. To attain equilibrium in a long (but reasonable) time, it is helpful to dissolve the solute in a liquid that is nearly immiscible with the polymer. In this work, the solvent is water. If the polymer absorbs a non-negligible amount of solvent, the polymer phase is a ternary system. Therefore, in addition to pure-component properties, the molecular-thermodynamic model contains three unknown binary Flory parameters: one for the water-solute binary χ_{ws}, one for the water-polymer binary χ_{wp} and one for the solute-polymer binary χ_{sp}. We need experimental information to evaluate each binary coefficient. We seek χ_{sp} because that enables us to calculate the solubility of the solute in the dry polymer.

The desired solubility of a solute in a dry polymer is obtained in two steps. First, we measure the distribution coefficient K_s for the solute between the polymer and the solute's aqueous solution; we also measure the (small) solubility of solute-free water in the polymer, as explained elsewhere (Fornasiero *et al.*, 2001). We also require the

solubility of the organic solute in water. (If the solute is completely miscible in water, we use vapor-liquid equilibrium data for the binary solute-water mixture.) Water-solute data are often available in the literature yielding Flory parameter χ_{ws}. Flory parameter χ_{wp} (water-polymer) is obtained from water-polymer data. After these have been determined, the remaining (and desired) Flory parameter χ_{sp} is obtained from the measured distribution coefficient K_s.

Second, knowing solute-polymer Flory parameter χ_{sp}, we calculate the desired solubility of the solute in the dry polymer using the Flory-Huggins model.

Calculation of χ_{ws} and χ_{wp}

For a binary solution of solute i (the larger molecule) in solvent j (the smaller molecule), the activities of components i and j are

$$\ln a_i = \ln\left(1-\Phi_j\right)+\left(1-\frac{r_i}{r_j}\right)\cdot\Phi_j+\chi_{ji}\cdot\frac{r_i}{r_j}\cdot\Phi_j^2 \qquad (1a)$$

$$\ln a_j = \ln\left(\Phi_j\right)+\left(1-\frac{r_j}{r_i}\right)\cdot\left(1-\Phi_j\right)+\chi_{ji}\cdot\left(1-\Phi_j\right)^2 \qquad (1b)$$

where χ_{ji} is the Flory interaction parameter and Φ_j represents the volume fraction of j defined by

$$\Phi_j = \frac{n_j r_j}{n_i r_i + n_j r_j} \qquad (2)$$

where n_j is the number of molecules of type j and r_j is the number of segments in molecule j. In the Flory-Huggins model, the number of segments per molecule appears only as a ratio set equal to the ratio of (liquid) molar volumes of the two components:

$$\frac{r_i}{r_j} = \frac{v_i}{v_j} \tag{3}$$

For solid solutes at 25 °C, molar volumes are those of the hypothetical liquid at 25 °C. We approximate these densities with the densities of the liquids slightly above the melting point.

First, consider the binary water(w)-solute(s) system. If s is a solid, the solubility of s in water is given by

$$f_{pure\,s}^{S} = \Gamma_{s,w}\Phi_{s,w}f_{pure\,s}^{L} \tag{4}$$

where $f_{pure\,s}^{L}$ is the fugacity of pure liquid s; $f_{pure\,s}^{S}$ is the fugacity of the pure solid; $\Phi_{s,w}$ is the measured aqueous solubility and $\Gamma_{s,w} = a_{s,w}/\Phi_{s,w}$ is the volume-fraction activity coefficient of the solute in water. Equation (4) assumes that there is negligible solubility of w in s. Equation (4) is rewritten

$$\left(\frac{f^{S}}{f^{L}}\right)_{pure\,s} = \Gamma_{s,w}\Phi_{s,w} \tag{5}$$

where superscript S stands for solid and superscript L for (subcooled) liquid. The ratio of the two pure-component fugacities is found from the melting temperature, the enthalpy of fusion and the heat capacities of the pure solid and pure liquid, as discussed in standard textbooks (for example, Prausnitz *et al.*, 1999).

If solute s is a liquid, the solubility of s in water is given by

$$f_{s}^{L} = \Gamma_{s,w}\Phi_{s,w}f_{pure\,s}^{L} \tag{6a}$$

where f_s^L is the fugacity of s in the liquid phase that is in equilibrium with the aqueous phase. If the solubility of water in that phase is negligible, $f_s^L \rightarrow f_{pure\,s}^L$ and the solubility of s in water becomes:

$$\Phi_{s,w} = \frac{1}{\Gamma_{s,w}} \tag{6b}$$

Equation (6b) is a reasonable approximation for liquid solutes that are sparingly soluble in water; therefore, we used Equation (6b) for benzonitrile, nitrobenzene, and 2- and 3-nitrotoluene (Benes and Dohnal, 1999).

Benzyl alcohol and benzonitrile show appreciable mutual solubility with water at 25 °C. For these solutes, we calculated the Flory solute-water parameter χ_{ws} from

$$\Gamma_{s,w}\Phi_{s,w} = \Gamma_{s,s}\Phi_{s,s} \tag{6c}$$

where $\Phi_{s,w}$ and $\Phi_{s,s}$ are the experimental volume fractions of solutes s in the water-rich phase and in the solute-rich phase, respectively. Activity coefficients $\Gamma_{s,w}$ and $\Gamma_{s,s}$ are given by Flory-Huggins equation. Experimental data are from Sorensen and Arlt (1979) and Solimo and Gramajo de Doz (1995).

Pyridine and nicotine are liquids at 25 °C; they are completely miscible in water. The equation of equilibrium for component j now is

$$\varphi_j y_j P = \Gamma_j \Phi_j f_{pure\,j}^L \tag{7}$$

where y_j is the vapor-phase mole fraction, P is the total pressure and φ_j is the vapor-phase fugacity coefficient. Vapor-liquid equilibrium data (Gmehling *et al.*, 1988) and gas-liquid chromatography data (Gmehling *et al.*, 1994) for the binary solute-water mixture are used to find Flory parameter χ_{ws} for pyridine and nicotine in water.

Table 3 gives aqueous solubilities at 25 °C for all solutes, infinite-dilution activity coefficients and Flory solute-water parameters together with sources of experimental data. For benzyl alcohol and acetophenone, Table 3 also gives mutual solubility data with water at 25 °C. For nitrobenzene and the three isomers of nitrotoluene and nitrophenol, the aqueous solubility at 25 °C has been calculated by linear interpolation of the experimental data (Benes and Dohnal, 1999) using van't Hoff coordinates ($\ln(x_1)$ versus $1/T$, where x_1 is the solubility in mole fraction).

In a similar manner, we obtain χ_{wp} from the measured solubility of solute-free water in the polymer, assuming negligible solubility of the polymer in water. Table 4 shows measured water solubilities in the three polymers and calculated Flory water-polymer parameters.

In general, Flory parameters vary with the solution composition. However, because the solubility of water in the polymer is small, final results (Table 7) are not sensitive to the coefficient χ_{ws} for EVAc copolymers, and they vary little for PVAc.

Calculation of Flory Parameter χ_{sp} from Distribution-Coefficient Data

For the ternary mixture containing water, solute and polymer, the distribution coefficient for the solute at infinite dilution, K_s^∞ is defined by

$$K_s^\infty = \lim_{\Phi_{s,p}\to 0} \frac{\Phi_{s,p}}{\Phi_{s,w}} = \frac{\Gamma_{s,w}^\infty}{\Gamma_{s,p}^\infty} \tag{8}$$

where $\Phi_{s,p}$ and $\Gamma_{s,p}^\infty$ refer to the wet polymer. Subscripts p and w stand, respectively, for the polymer phase and for the aqueous phase; Γ^∞ stands for the volume-fraction-based activity coefficient at infinite dilution. $\Gamma_{s,w}^\infty$ is obtained from experimental data for the

solute-water binary as discussed above. For 19 solutes, Table 5 shows the distribution coefficients and the corresponding infinite-dilution activity coefficients in three polymers, as calculated from Equation (8).

The activity coefficient of the solute in the wet-polymer phase ($\Gamma_{s,p}$) is given by the Flory-Huggins equation for a ternary system:

$$\ln\Gamma_{s,p} = (1-\Phi_s) - \Phi_w\frac{r_s}{r_w} - \Phi_p\frac{r_s}{r_p} + \left(\chi_{ws}\cdot\frac{r_s}{r_w}\cdot\Phi_w + \chi_{sp}\Phi_p\right)(\Phi_w+\Phi_p) - \chi_{wp}\frac{r_s}{r_w}\Phi_w\Phi_p \qquad (9a)$$

where all volume fractions are in the wet-polymer phase (subscript p has been omitted). At infinite dilution, $\Phi_s \to 0$, Equation (9a) becomes

$$\ln\Gamma^{\infty}_{s,p} = 1 - \Phi_w\frac{r_s}{r_w} - \Phi_p\frac{r_s}{r_p} + \chi_{ws}\cdot\frac{r_s}{r_w}\cdot\Phi_w + \chi_{sp}\Phi_p - \chi_{wp}\frac{r_s}{r_w}\Phi_w\Phi_p \qquad (9b)$$

Because Flory parameters χ_{ws} (for EVAc45 and PVAc) and χ_{wp} have been previously determined, Equation (9b) gives the desired Flory parameter χ_{sp}. In Equation (9b), Φ_w is set equal to the experimental solubility of solute-free water in the polymer. Because water solubility in EVAc33 is negligible, the terms containing Φ_w vanish. Because the unknown Flory parameter for water-EVAc33 binary multiplies Φ_w in Equation (9b), it does not affect our calculation of χ_{sp}. Table 6 shows calculated solute-polymer Flory parameters.

Solubilities in the dry polymers

For solute s in the dry polymer p, activity coefficient $\Gamma_{s,p}$ is related to the desired solubility $\Phi_{s,p}$ and to χ_{sp} by Equation (1b) for the binary system solute-(dry) polymer.

For solutes that are solids, once χ_{sp} is known, and assuming that polymer solubility in the solid solute is negligible, the desired solubility $\Phi_{s,p}$ is calculated from the equilibrium equation

$$\Gamma_{s,p}\Phi_{s,p} = \left(\frac{f^S}{f^L}\right)_{pure\,s} \tag{10}$$

Assuming negligible solubility of polymer in the solute is reasonable only for solid solutes. If pure s is a solid at 25 °C, the ratio $\left(\frac{f^S}{f^L}\right)_{pure\,s}$ is obtained from pure-component properties as indicated earlier. However, if pure s is a liquid at 25 °C, both components (solute and polymer) exhibit some mutual solubility. The solute chemical potential $\mu_{s,\alpha}$ and the polymer chemical potential $\mu_{p,\alpha}$ in phase α are, respectively:

$$\begin{aligned}\frac{\mu_{s,\alpha}}{RT} &= \ln\left(\Phi_{s,\alpha}\right) + \left(1-\Phi_{s,\alpha}\right)\cdot\left(1-\frac{r_s}{r_p}\right) + \chi_{s,p}\left(1-\Phi_{s,\alpha}\right)^2 + \frac{\mu^0_{s,\alpha}}{RT} \\ \frac{\mu_{p,\alpha}}{RT} &= \ln\left(1-\Phi_{s,\alpha}\right) + \Phi_{s,\alpha}\left(1-\frac{r_p}{r_s}\right) + \chi_{s,p}\cdot\frac{r_p}{r_s}\cdot\Phi^2_{s,\alpha} + \frac{\mu^0_{p,\alpha}}{RT}\end{aligned} \tag{11}$$

where superscript 0 indicates standard state. Similar relations hold for the chemical potentials in phase β. The equations of equilibrium are now $\mu_{s,\alpha} = \mu_{s,\beta}$ and $\mu_{p,\alpha} = \mu_{p,\beta}$. With $\mu^0_{s,\alpha} = \mu^0_{s,\beta}$ and $\mu^0_{p,\alpha} = \mu^0_{p,\beta}$, the equilibrium compositions of both phases can be calculated. However, it is well known (Flory, 1953) that polymer and solute are completely miscible if the solute-polymer Flory parameter is less than $\frac{1}{2}\cdot\left(1+\frac{1}{\sqrt{r_p/r_s}}\right)^2$. Because $r_p >> r_s$, the critical Flory parameter is 0.5. Therefore, we apply the phase-

equilibrium equations only if $\chi_{sp} > 0.5$. In this calculation, χ_{sp} is assumed independent of composition and equal to its infinite-dilution value.

RESULTS AND DISCUSSION

Table 4 shows calculated water-polymer interaction parameters. Because water solubility in EVAc33 is negligible, χ_{wp} is large. While we cannot precisely determine χ_{wp}, calculated solubilities in dry EVAc33 are not affected by this uncertainty because the volume fraction of water in the polymer phase is essentially zero. For EVAc45, we obtained $\chi_{wp} = 4.61$, very close to 4.91 reported by Chuang *et al.* (2000) for EVAc copolymer with 37% VAc at 32 °C. For PVAc, we determined a Flory parameter equal to 1.88 at 25 °C, while Immergut *et al.* (1999) give $\chi_{wp} = 2.5$ at 40 °C.

Table 6 reports solute-polymer interaction parameters and Table 7 shows calculated solubilities in the dry polymer[1]. Solubilities range from a minimum of 1% volume fraction for 4-nitroaniline in EVAc33 to complete miscibility for nicotine and pyridine in all three polymers.

For solid solutes, the solubility depends on the strength of polymer-solute interaction as well as on the melting properties of the pure solid. The solubilization process can be split into two steps: the first corresponds to melting the pure solute[2] and the second corresponds to mixing the (subcooled) liquid solute with the polymer[3]. Solubility increases upon lowering the melting point and the enthalpy of fusion because

[1] For PVAc, calculated solubilities at 25 °C are reliable if the saturated polymer-solute mixtures have glass-transition temperatures lower than 25 °C, as discussed in the Appendix.
[2] The enthalpy required to raise the temperature of the pure solute from the experimental temperature to the triple point and lowering it back to the experimental temperature after melting is usually negligible when compared with the enthalpy of fusion.
[3] For solid solutes at 25 °C, we use the density of the hypothetical liquid at 25 °C.

less energy is required for the melting transition. Solubility also increases with a decreasing Flory parameter that provides an inverse measure of solute-polymer affinity: the lower the parameter, the higher the affinity. Therefore, when we compare calculated solubilities for different solutes in the same polymer, there is no direct correlation between Flory parameter and solubility because the melting properties differ from solute to solute. On the other hand, if we compare the solubility for the same solute in our three different polymers, there is a clear trend with Flory parameter. For liquid solutes, the solute with the smallest Flory interaction parameter has the largest solubility since here the melting properties play no role; for $\chi_{sp} < 0.5$ we have complete miscibility.

Complete miscibility is predicted for pyridine and nicotine in all three polymers; for benzyl alcohol in EVAc45 and PVAc; for acetophenone in EVAc copolymers and for 2-nitrotoluene with EVAc45. For these systems, we tested the prediction by preparing solutions with ~50% polymer weight faction. Clear solutions were obtained at 25°C for PVAc in pyridine and nicotine. For EVAc45, clear solutions were obtained for pyridine, benzyl alcohol, acetophenone and 2-nitrotoluene, suggesting complete miscibility for these systems. For PVAc + benzyl alcohol and EVAc45 + nicotine mixtures, some cloudiness is observed for 50% polymer weight fraction, indicating possible partial solubility or, more likely, need for a long time to attain equilibrium. For EVAc33, results are inconclusive.

Solubility increases with VAc content in the polymer for most solutes (nitroanilines, nitrophenols, etc.). The solubility of 1-naphthol in EVAc33 is the same as that in EVAc45 within experimental error. Only acetophenone shows the reverse trend,

while nitrobenzene, 2- and 4-nitrotoluene, benzophenone and benzonitrile have the highest solubilities in EVAc45.

For a copolymer AB in a solvent *s*, Flory interaction parameter $\chi_{s(AB)}$, is given by:

$$\chi_{s(AB)} = \chi_{sA}\Phi_A + \chi_{sB}\Phi_B - \chi_{AB}\Phi_A\Phi_B \qquad (12)$$

where χ_{sA}, χ_{sB} and χ_{sB} are Flory interaction parameters for A-s, B-s and A-B, respectively (A = VAc, B = ethylene, *s* = solute); Φ_A and Φ_B represent the volume faction of monomer A and B in the copolymer, respectively (Stockmayer *et al.*, 1955). Therefore, the calculated Flory parameter $\chi_{sp}=\chi_{s(AB)}$ is, in general, a non-monotonic function of the copolymer composition and a minimum or maximum can be found for some copolymer composition depending on χ_{sA}, χ_{sB} and χ_{AB}. Equation (12) may explain the solubility maximum in EVAc45 for some of the solutes. For PVAc, all solutes with polar moieties give Flory parameters that are negative or much smaller than 0.5, probably because of attractive specific interactions between the vinyl acetate group in the polymer chain and polar groups in the solute molecules. The ortho-substituted phenol, 2-nitrophenol, is an exception because the nitro group in the ortho position may form attractive intramolecular interactions with the hydroxyl group, decreasing affinity with vinyl acetate. Nitrotoluenes, acetophenone, benzonitrile, benzophenone and nitrobenzene have positive Flory parameters. We notice also that the latter are the same solutes that do not show rising solubilities with increasing VAc content in the EVAc copolymers. When solute-polymer interactions are dominated by attractive specific interactions between polar moieties and the vinyl acetate group, solubility increases monotonically with VAc content; otherwise, it presents an inverse trend or a maximum in the range 33-100% VAc content.

Our calculations rest on the validity of Flory-Huggins theory for ternary systems. By comparing experimental equilibrium data for polymer-solvents ternary systems with the prediction of Flory-Huggins model, Favre *et. al.* (1996) showed that fairly good agreement can be achieved for sorption of apolar liquids in elastomers. However, the application of Flory-Huggins theory to ternary systems leads to large deviations for polar liquids in both homopolymers and copolymers, and for semi-crystalline polymers. The observed discrepancies are probably due to non-constancy of the polymer-solvent Flory parameter.

In our calculations the solute-polymer Flory parameter χ_{sp} is assumed independent of composition; this approximation is reasonable if the predicted solubility in the polymer is small. However, Table 7 show that for most solutes the solubility is quite large. This is not consistent with the approximation, reducing confidence in these calculations. We expect, therefore, that uncertainties in calculated solubilities may be significantly larger than those estimated from uncertainties in the experimental data shown in Table 7.

For liquid solutes, the calculated polymer volume fractions in the solute-rich phase $\Phi_{p,s}$ are negligible when $\chi_{sp} > 0.6$. For EVAc45 in nitrobenzene, $\Phi_{p,s}$ reaches the maximum value $6.72 \cdot 10^{-4}$ with $\chi_{sp} = 0.53$ and decreases rapidly with rising χ_{sp}. The Flory-Huggins model predicts that the solute-rich phase is nearly pure solute. However, because we calculated the Flory parameters at infinite dilution of solute, calculated results in the solute-concentrated phase may be unreliable.

CONCLUSION

Because there is no simple method to determine experimentally the solubility of a solid or non-volatile liquid in a polymer, a simple method based on the Flory-Huggins model is proposed to calculate that solubility. This method requires infinite-dilution distribution-coefficient data for the solute's distribution between the polymer and a liquid solvent that does not dissolve the polymer. Additional required data include the solubility of the solute in the solvent and the solubility of the solvent in the polymer. From these data we determine the Flory parameter for the solute- (dry) polymer system; that parameter gives us the desired solubility of the solute in the (dry) polymer.

This thermodynamic framework is applied to nineteen aromatic non-volatile solutes in ethylene-vinyl acetate with 33% or 45% vinyl acetate content, and poly(vinyl acetate). For solid solutes, solubility depends on the strength of polymer-solute interaction as well as on the melting properties of the pure solute, while for liquid solutes it depends only on the former. Solubility increases monotonically with VAc content in the polymer for those solutes where attractive specific interactions between polar moieties in the solute molecules and the vinyl acetate group in the polymer dominate the solute-polymer interaction.

The procedure described here rests on the validity of the Flory-Huggins model for ternary (solute-solvent polymer) systems. Therefore, there is some uncertainty in the accuracy of the solubilities presented here. Nevertheless, they may be useful for process and product design whenever polymers are used as membranes, as matrices for drug-delivery systems or as packaging materials for foods, chemicals, or pharmaceuticals.

ACKNOWLEDGEMENT

For financial support, the authors are grateful to the Office of Basic Energy Sciences, US Department of Energy and to the Donors of the Petroleum Research Fund administrated by the American Chemical Society. For research grants, MO thanks the Ministerio de Educacion y Ciencia (Spain). For his significant contributions in the early phase of this research, the authors are grateful to Van Nguyen.

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APPENDIX: EFFECT OF GLASS-TRANSITION TEMPERATURE

The Flory-Huggins model applies only to mixtures where the polymer is rubbery. While ethylene-vinyl acetate copolymers EVAc33 and EVAc45 are rubbery at room temperature, pure poly(vinyl acetate) is glassy; its glass-transition temperature T_{g0} is 39.7 °C. However, sorption of a solute lowers the glass-transition temperature; this lowering is often called plasticization. The plasticization effect of a solute may be estimated using Chow's equation (1980):

$$\ln\left(\frac{T_g}{T_{g0}}\right) = \zeta\left[(1-\theta)\ln(1-\theta) + \theta\ln\theta\right] \tag{I.1}$$

where T_g is the glass-transition temperature of the polymer-solute mixture and T_{g0} is the glass-transition temperature of the solute-free polymer; ζ is a physically significant constant and θ is a measure of solute concentration defined by:

$$\zeta = \frac{zR}{M_{mon}\Delta C_p}$$
$$\theta = \frac{M_{mon}\rho_s}{zM_w\rho_p}\frac{\Phi_{s,p}}{1-\Phi_{s,p}} \tag{I.2}$$

where z is the lattice coordination number, R is the gas constant, ΔC_p is the variation of the isobaric specific heat at the glass transition, ρ_s and ρ_p are solute and polymer densities, and M_{mon} and M_w are monomer and solute molecular weights. We used z=2 as suggested by Chow, ΔC_p = 0.5 kJ/kg K (Brandrup *et al.*, 1999), and M_{mon} =86.1 gr/mol.

In our solubility calculations, we assume that the mixture solute-polymer is rubbery. We consider the calculated solubilities to be reliable, if they are larger than the solute volume fraction required to depress T_g to 25 °C (Φ_{25}). For all solutes studied here,

this condition is verified except 4-nitroaniline and 4-nitrotoluene, for which Φ_{25} is 8.9 and 8.3%, respectively. At saturation, the calculated glass-transition temperatures for their mixtures with PVAc are 28.6 and 27.6 °C respectively; therefore, the calculated solubilities at 25 °C should be viewed with caution. For water, Bair *et al.* (1981) showed that Φ_{25} required to lower T_g to 25 °C is approximately equal to 2.5%, lower than the measured water solubility in PVAc (7 weight percent). Therefore, we can determine with confidence the water-polymer Flory interaction parameter from water-solubility data.

Table 1: Solute properties: molecular weight M (g/mol), density ρ_s (g/cm^3), melting point T_f (°C), molar enthalpy of fusion ΔH_f (J/mol) and molar heat-capacity difference between liquid and solid state Δc_p (J/mol K)

Solute	M	ρ_s	T_f	ΔH_f	Δc_p
1-Naphthol	114	1.113[a]	95.0[c]	23470[c]	-
2-Naphthol	114	1.078[a]	120.4[c]	18790[c]	-
2-Nitroaniline	138	1.280[a]	69.3[c]	16110[c]	-
3-Nitroaniline	138	1.210[a]	113.8[c]	23690[c]	-
4-Nitroaniline	138	1.050[a]	147.5[c]	21150[c]	-
2-Nitrophenol	139	1.294[a]	44.8[c]	17450[c]	-
3-Nitrophenol	139	1.280[a]	96.8[d]	19200[d]	86.1[d]
4-Nitrophenol	139	1.281[a]	113.8[c]	18250[c]	85.0[d]
2-Nitrotoluene	137	1.163[b]	-3.8[d]	-	-
3-Nitrotoluene	137	1.157[b]	16.0[d]	-	-
4-Nitrotoluene	137	1.123	51.6[c]	16810[c]	-
Acetophenone	120	1.055[b]	19.6[e]	-	-
Benzoic Acid	122	1.084[a]	112.3[c]	18060[c]	-
Benzonitrile	103	1.010[b]	-12.8[c]	-	-
Benzophenone	182	1.098[a]	47.8[c]	18190[c]	55.55[c]
Benzyl Alcohol	108	1.045[b]	-15.5[c]	-	-
Nicotine	162	1.010[b]	-80.0[f]	-	-
Nitrobenzene	123	1.196[b]	5.7[c]	-	-
Pyridine	79.1	0.978[b]	-41.6[c]	-	-

[a] Density of the liquid just above the melting point (Beilstein)
[b] All liquid solute densities are at 20 °C (Nguyen, 1999)
[c] Domalski and Hearing (1996)
[d] Domalski and Hearing (1990)
[e] Benes and Dohnal (1999)
[f] International Chemical Safety Card (1993)

Table 2: Polymer properties: average molecular weight M (g/mol), density ρ_s (g/cm^3), composition (comonomer weight percent), glass-transition temperatures T_{g0} (°C)

Polymer	*M*	ρ_s	VAc *wt.%*	T_{g0}
PVAc	500000	1.189	100	39.7 (±1.5)[a]
EVAc45	250000	0.952	45	-80[b]
EVAc33	150000	0.936	33	-95[b]

[a] Measured by modulated differential scanning calorimetry (DSC 2920, Modulated DSC *TA Instrument*) at a heating rate of 3 °C/min, with modulation amplitude of ±1 °C and period of 60 sec

[b] Estimated using Equation (1) and T_g (PVAc)=32 °C, T_g (PE)=-125 °C (Brandrup *et al.*, 1999).

Table 3: Properties of aqueous solutions for nineteen solutes: aqueous solubility $\Phi_{s,w}$ (10^4 volume fraction) at 25 °C, infinite-dilution activity coefficient and solute-water Flory parameter

Solute	$\Phi_{s,w}$	$\Gamma^{\infty}_{s,w}$	χ_{ws}
1-Naphthol	7.10[a]	236	1.62
2-Naphthol	5.91[a]	272	1.62
2-Nitroaniline	7.06[b]	619	1.91
3-Nitroaniline	5.16[b]	218	1.69
4-Nitroaniline	3.69[b]	227	1.61
2-Nitrophenol	11.0[c]	596	1.91
3-Nitrophenol	82.5[c]	38.7	1.44
4-Nitrophenol	98.0[c]	30.9	1.40
2-Nitrotoluene	5.59[c]	1810	2.00
3-Nitrotoluene	4.41[c]	2289	2.03
4-Nitrotoluene	2.01[c]	2867	2.03
Acetophenone	64.3[d]	156	1.64
Benzoic Acid	26.9[a]	74.2	1.53
Benzonitrile	19.8[a]	522	1.93
Benzophenone	1.23[a]	4933	1.82
Benzyl Alcohol	426[d]	22.7	1.37
Nicotine	c.m.	1.38[e]	0.92
Nitrobenzene	16.6[c]	619	1.95
Pyridine	c.m.	3.92[f]	1.08

[a] Howard and Meylan (1997)
[b] Beilstein
[c] Benes and Dohnal (1999)
[d] The corresponding equilibrium volume fractions of water in the solute-rich phase are $153 \cdot 10^{-4}$ (Sorensen and Arlt, 1979) for acetophenone and $969 \cdot 10^{-4}$ (Solimo and Gramajo de Doz, 1995) for benzyl alcohol.
[e] Gmehling *et al.* (1994)
[f] Gmehling *et al.* (1988)

Table 4: Water content in the saturated polymers (weight %) and polymer-water Flory parameter

	EVAc33	*EVAc45*	*PVAc*
Water content	~0	0.43 (±0.04)	7.0 (±0.3)
χ_{wp}	large	4.60	1.88

Table 5: Distribution coefficients K_s between water and polymers and infinite-dilution activity coefficients $\Gamma_{s,p}^{\infty}$ in three polymers for nineteen non-volatile solutes

Solute	K_s			$\Gamma_{s,p}^{\infty}$		
	EVAc33	*EVAc45*	*PVAc*	*EVAc33*	*EVAc45*	*PVAc*
1-Naphthol	599	623	2203	0.39	0.38	0.11
2-Naphthol	372	743	1693	0.73	0.37	0.16
2-Nitroaniline	66.3	140	350	9.33	4.42	1.77
3-Nitroaniline	36.5	80.1	264	5.97	2.72	0.83
4-Nitroaniline	25.2	65.9	322	9.02	3.45	0.71
2-Nitrophenol	93.7	122	185	6.36	4.88	3.22
3-Nitrophenol	44.1	94.2	313.6	0.88	0.41	0.12
4-Nitrophenol	33.9	87.3	374.2	0.91	0.35	0.08
2-Nitrotoluene	336	483	435	5.39	3.75	4.16
3-Nitrotoluene	105	249	386	21.80	9.19	5.93
4-Nitrotoluene	345	471	423	8.31	6.09	6.78
Acetophenone	38.7	41.5	55.7	4.04	3.76	2.80
Benzoic Acid	5.18	13.9	53.4	14.32	5.34	1.39
Benzonitrile	43.9	54.5	77.1	11.90	9.59	6.78
Benzophenone	1356	2231	1782	3.64	2.21	2.77
Benzyl Alcohol	2.79	10.8	23.4	8.13	2.10	0.97
Nicotine	1.42	22	46	0.97	0.06	0.03
Nitrobenzene	91.5	145	172	6.76	4.27	3.60
Pyridine	1.09	2.65	5.32	3.59	1.48	0.74

Table 6: Polymer-solute interaction parameters χ_{sp} and activities $\left(\frac{f^S}{f^L}\right)_{pure\ s}$ of pure solid solutes in three polymers

Solute	χ_{sp}			$\left(\frac{f^S}{f^L}\right)_{pure\ s}$
	EVAc33	*EVAc45*	*PVAc*	
1-Naphthol	-1.93	-1.89	-2.97	0.165
2-Naphthol	-1.31	-1.92	-2.50	0.159
2-Nitroaniline	1.23	0.57	-0.03	0.431
3-Nitroaniline	0.79	0.10	-0.71	0.112
4-Nitroaniline	1.20	0.35	-0.74	0.083
2-Nitrophenol	0.85	0.67	0.62	0.645
3-Nitrophenol	-1.13	-1.80	-2.68	0.288
4-Nitrophenol	-1.09	-1.95	-3.10	0.270
2-Nitrotoluene	0.68	0.41	0.89	-
3-Nitrotoluene	2.08	1.31	1.26	-
4-Nitrotoluene	1.12	0.90	1.42	0.574
Acetophenone	0.40	0.42	0.64	-
Benzoic Acid	1.66	0.77	-0.06	0.192
Benzonitrile	1.48	1.34	1.40	-
Benzophenone	0.29	-0.07	0.77	0.605
Benzyl Alcohol	1.10	-0.17	-0.43	-
Nicotine	-1.03	-3.66	-4.27	-
Nitrobenzene	0.91	0.53	0.70	-
Pyridine	0.28	-0.56	-1.47	-

Table 7: Calculated solubilities $\Phi_{s,p}$ (volume fraction) for nineteen nonvolatile solutes in three polymers

Solute	$\Phi_{s,p}$					
	EVAc33		*EVAc45*		*PVAc*	
1-Naphthol	0.237	(±0.001)	0.234	(±0.004)	0.325	(±0.002)
2-Naphthol	0.171	(±0.001)	0.230	(±0.001)	0.282	(±0.001)
2-Nitroaniline	0.056	(±0.003)	0.113	(±0.002)	0.198	(±0.001)
3-Nitroaniline	0.020	(±0.001)	0.039	(±0.001)	0.081	(±0.001)
4-Nitroaniline	0.010	(±0)	0.022	(±0)	0.063	(±0)
2-Nitrophenol	0.149	(±0.008)	0.181	(±0.003)	0.192	(±0.006)
3-Nitrophenol	0.256	(±0.002)	0.331	(±0.001)	0.408	(±0.001)
4-Nitrophenol	0.238	(±0.001)	0.331	(±0.003)	0.424	(±0.001)
2-Nitrotoluene	0.614	(±0.075)	c.m.	-	0.391	(±0.030)
3-Nitrotoluene	0.092	(±0.003)	0.185	(±0.002)	0.202	(±0.002)
4-Nitrotoluene	0.121	(±0.003)	0.118	(±0.003)	0.065	(±0.001)
Acetophenone	c.m.[a]	-	c.m.	-	0.675	(±0.024)
Benzoic Acid	0.014	(±0.001)	0.036	(±0.005)	0.081	(±0.001)
Benzonitrile	0.144	(±0.003)	0.176	(±0.007)	0.162	(±0.011)
Benzophenone	0.239	(±0.005)	0.316	(±0.001)	0.148	(±0.004)
Benzyl Alcohol	0.266	(±0.014)	c.m.	-	c.m.	-
Nicotine	c.m.	-	c.m.	-	c.m.	-
Nitrobenzene	0.375	(±0.006)	0.921[b]	(±0.045)	0.592	(±0.061)
Pyridine	c.m.	-	c.m.	-	c.m.	-

[a] c.m. = complete miscibility

[b] The calculated polymer volume fraction in the solute-rich phase is $6.72 \cdot 10^{-4}$ for nitrobenzene in EVAc45. For all the other polymer-solute systems, it is negligible.

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098