Polymer Miscibility in Mixed Organic Liquids. An Extension of the Two-Dimensional Approach

SHOW-AN CHEN, *Converted Plastics Group, W. R. Grace & Co., Duncan, South Carolina 29334*

Synopsis

Previous work on the two-dimensional approach to polymer miscibility in organic liquids is extended to polymer–mixed liquid systems. From thermodynamic considerations methods for calculating δ_h of the mixed liquid and χ_H of the polymer–mixed liquid system from properties of pure components are proposed, where δ_h is the hydrogen-bonding solubility parameter of the liquid, and χ_H is a term which takes account of the dispersion and polar interactions between the liquid and the polymer and of effects due to temperature and molecular size of the liquid. Using these two calculated parameters, the solvent power of the mixed liquid can be determined from its location on the χ_H–δ_h plane.

INTRODUCTION

In the previous article[1] it was proposed that the solvent power of an organic liquid for a given polymer can be characterized by two parameters, δ_h and χ_H. Here, δ_h is the hydrogen bonding solubility parameter of the liquid, and χ_H is a term which takes account of the dispersion and polar interactions between the liquid and the polymer and of effects due to temperature and molecular size of the liquid. Using these two parameters, a two-dimensional (2-D) solubility diagram can be constructed in which a given liquid or polymer is represented by a point. Thus, a given polymer will be represented in the diagram by a point $(0,\delta_{h,P})$. Around the point $(0,\delta_{h,P})$, a circle can be constructed of a radius such that any liquid characterized by a point $(\chi_H,\delta_{h,L})$ lying within the circle is a solvent for the polymer, while a liquid represented by a point outside the circle is a nonsolvent for the polymer. In the diagrams, the unit length on the axis reprsented by χ_H is twice the unit length used for δ_h. The radius of the circle must be determined experimentally and was found to be equal to that of Hansen's[2,3] solubility sphere.

In this article, the 2-D approach is extended to polymer–mixed liquid systems. A mixed liquid is treated as a "single liquid"; thermodynamic principles are then applied to derive equations for calculating δ_h of the mixed liquid and χ_H of the polymer–mixed liquid system from the properties of the pure components. Using these two calculated parameters, the solvent power of the mixed liquid can be determined from its location on the χ_H–δ_h plane. Sometimes, it is desired to mix two nonsolvents (or poor plasti-

cizers) to form a good mixed solvent (or plasticizer) for a given polymer. Three examples involving poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) are given to demonstrate the applicability of the 2-D approach for this problem. A method for selecting a pair of liquids to form a good mixed solvent for the polymer is proposed. The proposed approach is also applicable for systems containing three or more liquids.

THERMODYNAMIC CONSIDERATIONS

In the previous article[1] it has been proposed that the Gibbs free energy of mixing, ΔG^M, for any given polymer–solvent system can be expressed as

$$\frac{\Delta G^M}{RT} = f_b(\phi_S, \delta_{h,S}, \delta_{h,P}) + \chi_{PS} x_S \phi_P \tag{1}$$

$$\chi_{PS} = \chi_S + \chi_H \tag{2}$$

$$\chi_S = 1/z \tag{3}$$

$$\chi_H = \frac{V_S A_{PS}}{RT} \tag{4}$$

$$A_{PS} = (\delta_{d,S} - \delta_{d,P})^2 + (\delta_{p,S} - \delta_{p,P})^2 \tag{5}$$

where δ, x, and ϕ are solubility parameter, mole fraction, and volume fraction, respectively; the subscripts b, S, and P refer to binary system, solvent, and polymer, respectively; δ_d and δ_p are dispersion and polar solubility parameters; f_b is a function of ϕ_S, $\delta_{h,S}$, and $\delta_{h,P}$; and z is the number of nearest neighbors.

In eq. (1), the parameters χ_{PS} and δ_h's, which characterize the polymer–solvent interactions, were considered to be concentration independent.[1] χ_{PS} was further separated into two concentration-independent terms as in eq. (2), the entropy term χ_S ($=1/z$) derived by Huggins[4,5] and the enthalpy term χ_H of the Scatchard-Hildebrand type of expression[5] for taking account of the physical interactions (the dispersion and polar interactions). The consideration of the concentration independence of the parameters was based on the fact that, in the associated solution theories from which eq. (1) was derived,[1] the association constant K and the physical interaction parameter χ_H (or A_{12}) are concentration independent.[1,6−9]

It should be noted that χ_{PS} in eq. (1) has a different meaning from the Flory interaction parameter in the Flory-Huggins equation. Despite the fact that the Flory-Huggins equation was derived for nonpolar polymer solutions, it was used for all types of polymer solution; and, consequently, the Flory interaction parameter and its two components, the entropy term and the enthalpy term, were found to be concentration dependent.[10,11] For systems in which mutual association occurs, such as poly(ethylene oxide)–chloroform solution[12] at 25°C, the Flory interaction parameter can even be negative. However, in the associated solution theories, and therefore in eq. (1), the association effect due to hydrogen bonding forma-

tion was taken into account by the association constant K, and therefore the physical interaction parameter χ_H is always positive.

Applying the same considerations[1] as in the formulation of eq. (1), ΔG^M for a ternary solution of polymer–solvent 1–solvent 2 can be expressed as

$$\frac{\Delta G^M}{RT} = f_i(\phi_1, \phi_2, \delta_{h,1}, \delta_{h,2}, \delta_{h,P}) + \chi_{P1} x_1 \phi_P + \chi_{P2} x_2 \phi_P + \frac{V_m}{RT} \phi_1 \phi_2 A_{12} \quad (6)$$

where the subscripts 1, 2, and t refer to solvent 1, 2, and ternary, respectively; A_{12} is defined as in eq. (5), with the subscripts P and S replaced by 1 and 2. Also A_{12} is considered as a concentration-independent term based on the associated solution theories.[6-9] V_m is the molar volume of the polymer solution.

Let us consider solvents 1 and 2 in the ternary polymer solution as a "single solvent" and that the polymer solution is formed by mixing the polymer and the mixed solvent. The ternary polymer solution can then be considered as a pseudobinary polymer solution for which its ΔG^M can be expressed as in eq. (1), with the subscript S refering to the mixed solvent. Thus, by appropriate differentiations of eqs. (1) and (6), the chemical potential of the polymer μ_P in the ternary polymer solution can be expressed in two ways as follows:
For polymer–solvent 1–solvent 2 tenary solution:

$$\mu_P - \mu_P{}^* = \left(\frac{\partial f_t}{\partial x_P}\right)_{x_1, x_2, T, P} + \chi_{P1} \phi_1 \frac{V_P}{V_1} (1 - \phi_P)$$

$$+ \chi_{P2} \phi_2 \frac{V_P}{V_2} (1 - \phi_P) - \frac{A_{12}}{RT} \phi_1 \phi_2 V_P \quad (7)$$

For polymer-mixed solvent pseudo-binary solution:

$$\mu_P - \mu_P{}^* = \left(\frac{\partial f_b}{\partial x_P}\right)_{x_S, T, P} + \frac{V_P}{V_S} \chi_{PS} \phi_S{}^2 \quad (8)$$

with

$$V_S = x_1{}^0 V_1 + x_2{}^0 V_2$$

where $\mu_P{}^*$ is the chemical potential of the pure polymer in a random state; $x_1{}^0$ and $x_2{}^0$ are mole fractions of solvents 1 and 2 in the mixed solvent, respectively; and the superscript 0 refers to polymer-free basis, i.e., $x_1{}^0 + x_2{}^0 = 1$.

Since the ternary polymer solution formed by mixing the polymer, solvent 1, and solvent 2 is identical to that formed by mixing the polymer and the mixed solvent at the same temperature and pressure, thus we must have

$$\mu_P \text{ of ternary solution} = \mu_P \text{ of pseudobinary solution.} \quad (9)$$

Combining eqs. (7), (8), and (9) and using the consideration that there is no coupling effect between combinatory and noncombinatory contributions[1] in the formulation of ΔG^M, we obtain

$$\left(\frac{\partial f_t}{\partial x_P}\right)_{x_1, x_2, T, P} = \left(\frac{\partial f_b}{\partial x_P}\right)_{x_S, T, P} \quad (10)$$

and

$$\frac{V_P}{V_S} \chi_{PS} \phi_S{}^2 = \chi_{P1} \phi_1 \frac{V_P}{V_1} (1 - \phi_P) + \chi_{P2} \phi_2 \frac{V_P}{V_2} (1 - \phi_P) - \frac{A_{12}}{RT} \phi_1 \phi_2 V_P$$

(11)

$\chi_{PS,H}$ of Polymer–Mixed Solvent System

Since eq. (11) is valid for any ϕ_P, by letting ϕ_P in the equation equal zero we obtain an expression for χ_{PS} of polymer–mixed solvent solutions as

$$\chi_{PS} = x_1{}^0 \chi_{P1} + x_2{}^0 \chi_{P2} - \frac{A_{12} V_s}{RT} \phi_1{}^0 \phi_2{}^0$$

(12)

where

$$\phi_1{}^0 = \frac{x_1{}^0 V_1}{x_1{}^0 V_1 + x_2{}^0 V_2}$$

and

$$\phi_2{}^0 = \frac{x_2{}^0 V_2}{x_1{}^0 V_1 + x_2{}^0 V_2}$$

Eliminating χ_S from eq. (12), we obtain

$$\chi_{PS,H} = x_1{}^0 \chi_{P1,H} + x_2{}^0 \chi_{P2,H} - \frac{A_{12} V_s}{RT} \phi_1{}^0 \phi_2{}^0.$$

(13)

Using eq. (13), $\chi_{PS,H}$ of a polymer–mixed solvent system can be calculated from properties of pure components or of binary solutions. Equation (13) also shows that a large value of A_{12}, an indication of great dissimilarities in polarity and structure between solvent 1 and 2, can make $\chi_{PS,H}$ small and therefore favors the miscibility between the polymer and mixed solvent.

By following the same procedure, equations for χ_{PS} and $\chi_{PS,H}$ of a polymer solution containing n solvents can be expressed as

$$\chi_{PS} = \sum_{i=1}^{n} x_i{}^0 \chi_{Pi} - \frac{1}{2} \frac{V_s}{RT} \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} \phi_i{}^0 \phi_j{}^0$$

(14)

with

$$A_{ii} = 0$$

and

$$\chi_{PS,H} = \sum_{i=1}^{n} x_i{}^0 \chi_{Pi,H} - \frac{1}{2} \frac{V_s}{RT} \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} \phi_i{}^0 \phi_j{}^0$$

(15)

with

$$A_{ii} = 0$$

where

$$V_S = \sum_{i=1}^{n} x_i^0 V_i$$

$$A_{ij} = (\delta_{d,i} - \delta_{d,j})^2 + (\delta_{p,i} - \delta_{p,j})^2$$

$$\phi_i^0 = \frac{x^0_i V_i}{V_S}.$$

Solubility Parameter and Three-Dimensional Solubility Parameter of Mixed Liquid

Since eq. (10) provides no explicit expression for calculating δ_h of mixed liquids, another method of calculation is considered below.

The molar cohesive energy, $-E_S$, of a binary liquid mixture can be written as

$$-E_S = -E_1 x_1^0 - E_2 x_2^0 - \Delta E^M \qquad (16)$$

where ΔE^M is the molar energy of mixing. Dividing eq. (16) by the molar volume of the mixture, V_S, multiplying the numerator and denominator of the first term of the right side of eq. (16) by V_1 and those of the second term by V_2, and applying the definition of solubility parameter, $\delta_i^2 = -E_i/V_i$, we obtain

$$\delta_S^2 = \phi_1^0 \delta_1^2 + \phi_2^0 \delta_2^2 - \frac{\Delta E^M}{V_S}. \qquad (17)$$

According to Hansen's concept of three-dimensional solubility parameter, in which cross effects among dispersion, polar, and hydrogen bonding interactions were neglected, the three-dimensional solubility parameter for a mixed liquid can be expressed as

$$\delta_{j,S}^2 = \phi_1^0 \delta_{j,1}^2 + \phi_2^0 \delta_{j,2}^2 - \frac{\Delta E_j^M}{V_S} \qquad j = d, p, h. \qquad (18)$$

By comparing experimental data[13] of $\Delta E^M/V_S$ with those of δ_S^2 for all types of liquid mixtures, it can be found that $\Delta E^M/V_S$ in eq. (17) is negligible in a calculation of δ_S. Since this conclusion is also valid for aliphatic hydrocarbon mixtures, in which only dispersion interaction is involved, $\Delta E_d^M/V_S$ in eq. (18) is also negligible in a calculation of $\delta_{d,S}$. As a method for calculating ΔE_p^M is not available, a comparison between $\Delta E_p^M/V_S$ and $\delta_{p,S}^2$ is difficult. But it is not unreasonable to assume that $\Delta E_p^M/V_S$ is also negligible in eq. (18), because the polar contribution possesses the same nature as the dispersion contribution.[1]

For liquid mixtures involving hydrogen bonding such as ethanol–n-hexane system at 30°C, $\Delta E_h^M/V_S$ at equal molar concentration calculated using associated solution theory[6,8] is 1.26 cal/cc, which is 4.1% of the $\delta_{h,S}^2$ value of 30.3 cal/cc. But the $\delta_{h,S}$ value calculated using eq. (18) with $\Delta E_h^M/V_S$ neglected, 5.4 (cal/cc)$^{1/2}$, deviates only 1.8% from the actual

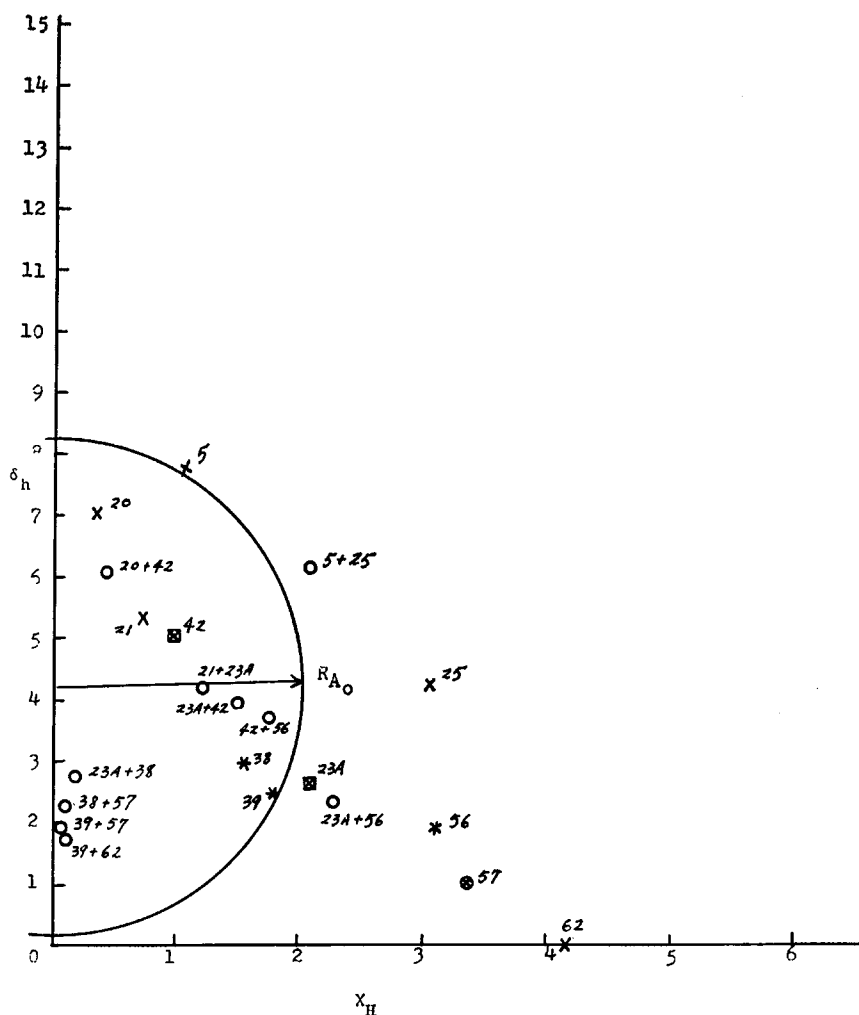Fig. 1. Solubility of poly(methyl methacrylate) in mixed liquids using Hansen's experimental δ_j and R_{A_0} values for the polymer obtained from the solvent placement method: (O) soluble, group 1; (⊗) nearly soluble, group 2; (⊡) strongly swollen, slightly soluble, group 3; (⊠) swollen, group 4; (×) slightly swollen, group 5; (*) no visible effect, group 6.

$\delta_{h,s}$ value of 5.5 $(cal/cc)^{1/2}$. For water–methanol mixture[14] at 19.68°C, $\Delta E^M/V_S$ at equal molar concentration is -6.65 cal/cc, which is 3% of the $\delta_{h,s}^2$ value of 219.8 cal/cc calculated using eq. (18) with $\Delta E_h{}^M/V_S$ neglected. Thus, for hydrogen-bonding mixtures, $\delta_{h,s}$ can be calculated using eq. (18) with $\Delta E_h{}^M/V_S$ neglected.

It should be noted that the term "hydrogen bonding" means a formation of hydrogen bond detectable from spectroscopy and that the term "hydrogen bonding solubility parameter," according to Hansen's concept,[2,3] represents a component of solubility parameter contributed from hydrogen-
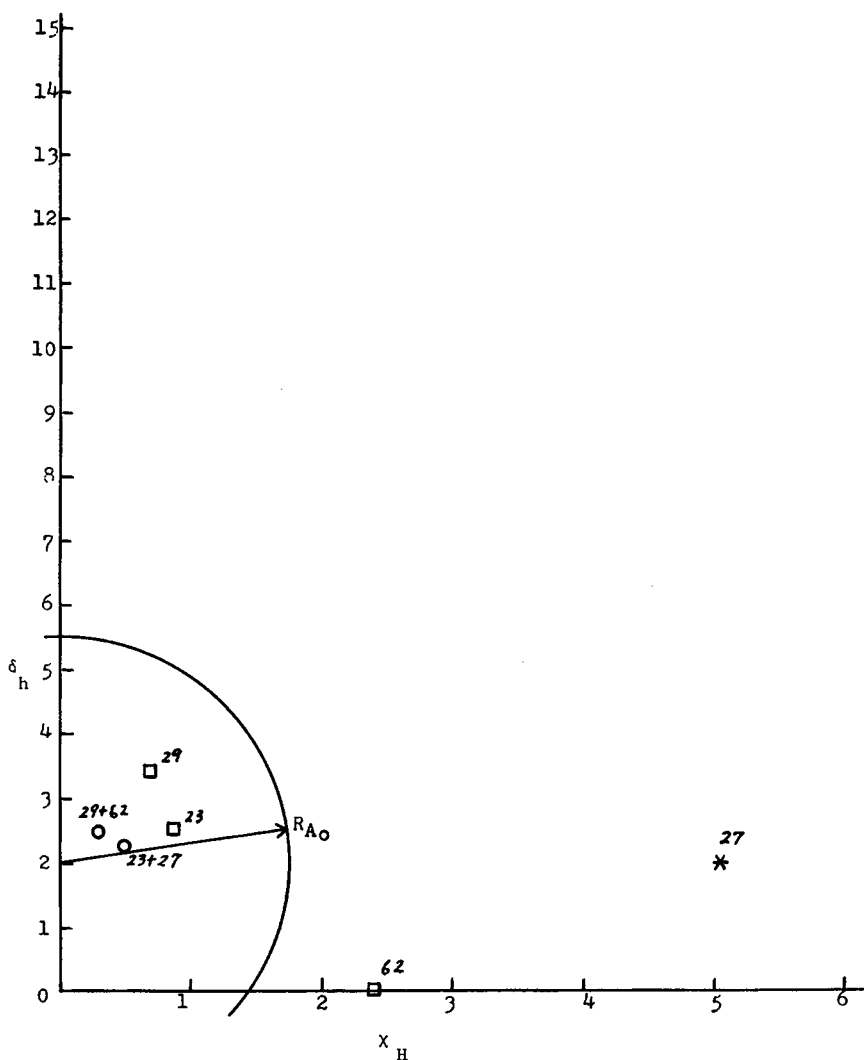
Fig. 2. Solubility of polystyrene in mixed liquids using Hansen's experimental δ_j and R_{A_0} values for the polymer obtained from the solvent placement method. Symbols same as in Fig. 1.

bonding energy which has a nonzero value for any polar substance or any hydrogen-bonding substance. But for liquid mixtures involving no hydrogen bonding such as acetone–hexane system, a method for calculating $\Delta E_h{}^M/V_S$ is not available. Here, we assume that $\Delta E_h{}^M/V_S$ in eq. (18) is also negligible for such systems. Thus, following the above discussions, $\Delta E_j{}^M/V_S$ in eq. (18) can be neglected. By taking square root for both sides of eq. (18) with $\Delta E_j{}^M/V_S$ neglected, an expression for calculating $\delta_{j,S}$ from pure component properties is obtained as

$$\delta_{j,S} = \sqrt{\phi_1{}^0 \delta_{j,1}{}^2 + \phi_2{}^0 \delta_{j,2}{}^2} \qquad j = d, p, h. \tag{19}$$
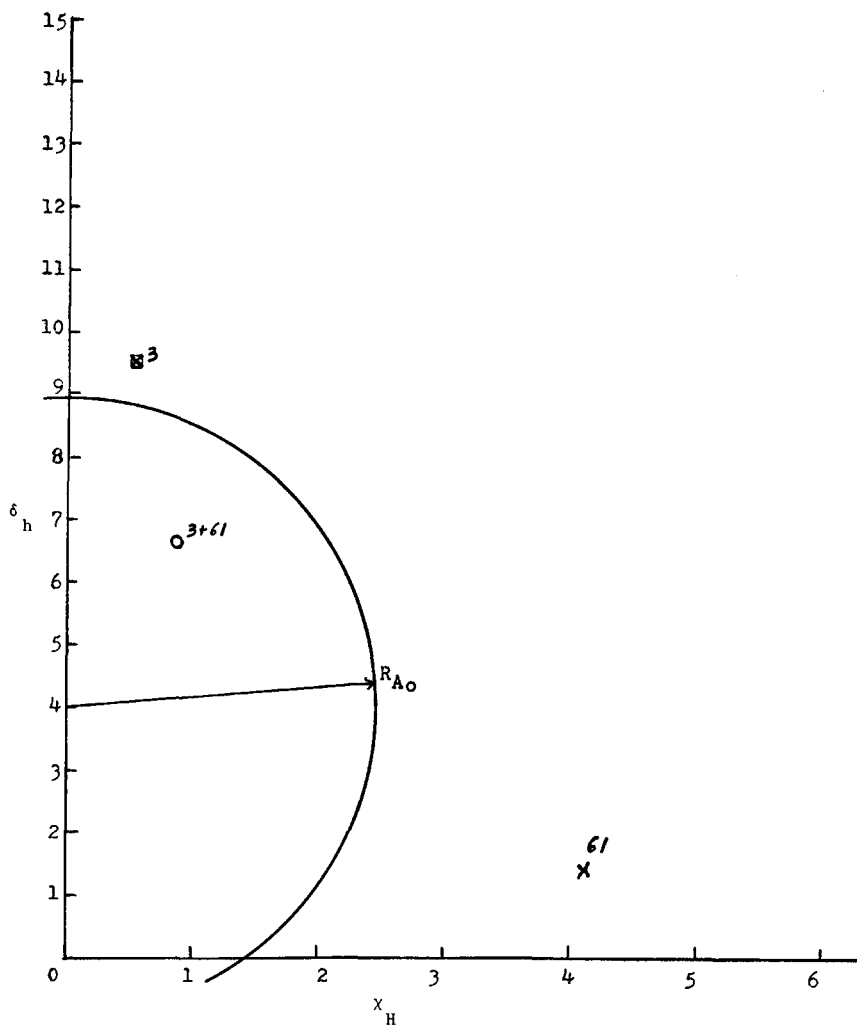
Fig. 3. Solubility of poly(vinyl acetate) in mixed liquids using Hansen's experimental δ_j and R_{A_0} values for the polymer obtained from the solvent placement method. Symbols same as in Fig. 1.

Via the same reasoning, as expression for $\delta_{j,s}$ of a multicomponent liquid mixture can be written as

$$\delta_{j,s} = \sqrt{\sum_{i=1}^{n} \phi_i{}^0 \delta_{j,i}{}^2} \qquad j = d, p, h. \tag{20}$$

THE TWO-DIMENSIONAL APPROACH TO POLYMER MISCIBILITY IN MIXED LIQUID

In using the 2-D approach to predict the solvent power of a mixed liquid for a given polymer, we first calculate δ_h of the mixed liquid using eq. (19)

TABLE I
Solubility of Poly(methyl Methacrylate) in Mixed Liquids.   Comparison
Between the 2-D Approach and Hansen's 3-D Approach

Liquid no.[a]	Liquid	Group of solvent power	Location in the proposed S.C.[b]	Location in Hansen's S.S.[c]
5	n-butanol	6	outside	outside
25	methylal	5	outside	outside
Mixed liquid[d]	5 + 25	1	outside	outside
23A	furan	4	outside	outside
42	aniline	4	inside	inside
Mixed liquid	23A + 42	1	inside	inside
23A	furan	4	outside	outside
56	α-bromonaphthaline	6	outside	outside
Mixed liquid	23A + 56	1	outside	outside
20	oxitol	5	inside	inside
42	aniline	4	inside	inside
Mixed liquid	20 + 42	1	inside	inside
21	diacetone alcohol	5	inside	inside
23A	furan	4	outside	outside
Mixed liquid	21 + 23A	1	inside	inside
23A	furan	4	outside	outside
38	acetonitrile	6	inside	outside
Mixed liquid	23A + 38	1	inside	inside
38	acetonitrile	6	outside	outside
57	benzene	5	outside	outside
Mixed liquid	38 + 57	1	inside	inside
39	nitromethane	6	outside	outside
62	hexane	5	outside	outside
Mixed liquid[d]	39 + 62	1	inside	inside
39	nitromethane	6	outside	outside
57	benzene	5	outside	outside
Mixed liquid	39 + 57	1	inside	inside
42	aniline	4	inside	inside
56	α-bromonaphthaline	6	outside	outside
Mixed liquid	42 + 56	1	inside	inside

[a] Same as that listed in Hansen's work.[2,3]

[b] S.C. = Solubility circle.

[c] S.S. = Solubility sphere.

[d] The mixed liquid, which dissolves the polymer as determined expeimentally,[2] is composed of two equal volumes of liquid.

and χ_H of the polymer–mixed liquid using eq. (13).   Using the values of these two parameters, we then locate the mixed liquid in the χ_H–δ_h plane. If the mixed liquid is located within the solubility circle of the polymer, it is a good solvent for the polymer; if it is located on the boundary or outside the circle, it is a poor solvent or nonsolvent for the polymer.

Polymer solubility data and experimental values of δ_d, δ_p, and δ_h of polymers and liquids were taken from Hansen's work.[2,3]   The solubility data were determined by visual inspection of solutions at concentration of about

TABLE II

Solubility of Polystyrene in Mixed Liquids and Comparison Between
the 2-D Approach and Hansen's 3-D Approach[a]

Liquid no.	Liquid	Group of solvent power	Location in the proposed S.C.	Location in Hansen's S.S.
23	diethyl ether	3	inside	outside
27	propylene carbonate	6	outside	outside
Mixed liquid	23 + 27	1	inside	inside
62	hexane	3	outside	outside
29	acetone	3	inside	inside
Mixed liquid	62 + 29	1	inside	inside

[a] Footnotes same as for Table I.

TABLE III

Solubility of Poly(vinyl Acetate) in Mixed Liquids and Comparison
Between the 2-D Approach and Hansen's 3-D Approach[a]

Liquid no.	Liquid	Group of solvent power	Location in the proposed S.C.	Location in Hansen's S.S.
3	ethanol	4	outside	outside
61	tetralin	5	outside	inside
Mixed liquid	3 + 61	1	inside	inside

[a] Footnotes same as for Table I.

0.5 g polymer per 5 ml mixed liquid composed of two equal volumes cf nonsolvent or poor solvent. Hansen classified the polymer–liquid mixtures into six groups: (1) soluble, (2) nearly soluble, (3) strongly swollen, slightly soluble, (4) swollen, (5) slightly swollen, and (6) no visible effect. The solvent powers of the mixed liquids he reported were of group (1).

The solubilities of poly(methyl methacrylate), polystyrene, and poly(vinyl acetate), which have been given as examples in the previous article,[1] in mixed liquids were again studied. It was found that most mixed liquids that dissolve the polymers as determined experimentally are located inside the solubility circles, as shown in Figures 1, 2, and 3, and that the prediction using the 2-D approach is satisfactory. A comparison of the applicability between the 2-D approach and Hansen's 3-D approach for the polymer-mixed liquid systems, as presented in Tables I, II, and III, shows that both approaches work equally well for the systems studied. For poly(methyl methacrylate), both approaches fail to predict the solvent power of these two mixed liquids, n-butanol–methylal and furan–α-bromonaphthaline.

In selecting a liquid pair to form a good mixed solvent for a given polymer, it is required that liquids 1 and 2 satisfy the following conditions: (a) the absolute value of the difference between the hydrogen-bonding solubility parameters of the polymer and mixed liquid, $(\delta_{h,P} - \delta_{h,S})$, should be

small enough; and (b) A_{12}, a measurement of dissimilarities of the dispersion and polar contributions between these two liquids, should be large enough to make $\chi_{PS,H}$ small so that

$$(\delta_{h,P} - \delta_{h,S})^2 + 4(\chi_{PS,H})^2 < R_{A1}, R_{A2}, \text{ and } R_{A0} \qquad (21)$$

where R_{A0} is the radius of the solubility circle and R_{A1} (or R_{A2}) is the distance between locations of the polymer and liquid 1 (or liquid 2) in the 2-D plane.

This approach should also be applicable for polymer miscibility in mixed plasticizer or mixed plasticizer–solvent systems because a plasticizer also behaves as a diluent for polymers.

DISCUSSION

1. If δ_h values equal zero, eqs. (1) and (6) reduce to the Flory-Huggins equation and eq. (12) can be considered as an expression for the Flory interaction parameter of a polymer–mixed solvent system. Applying regular solution theory and the assumption of equal molar volume of solvents 1 and 2 to the Flory-Huggins equation, Scott[15] reached an expression similar to eq. (12) for χ_{PS} of polymer–mixed solvent systems. Despite these two assumptions made in Scott's derivation, his expression for χ_{PS} has been applied by Dondos and Patterson[16] to systems in which the regular solution theory is completely inapplicable, one of the values of the Flory interaction parameter in the ternary solution being negative. However, these two assumptions appear to be unnecessary in our derivation. Thus, eq. (12), if considered as an expression for the Flory interaction parameter of polymer–mixed solvent system, can be used in all cases including that for which values of the Flory interaction parameters are negative.

2. Other methods for calculating δ_S and $\delta_{S,j}$ have been proposed by Burrell[17] and by Hansen,[2,3] respectively, as

$$\delta_S = \phi_1 \delta_1 + \phi_2 \delta_2 \qquad (22)$$

and

$$\delta_{S,j} = \phi_1 \delta_{j,1} + \phi_2 \delta_{j,2} \qquad j = d, p, h. \qquad (23)$$

Values of δ_S and $\delta_{S,j}$ calculated using eqs. (22) and (23) are close to those calculated using the proposed mixing rule, eq. (17) with $\Delta E^M/V_S$ neglected and eq. (19), for binary liquid mixtures of equal volume concentration, but may have a significant difference for mixtures in which one component is diluted.

References

1. S.-A. Chen, *J. Appl. Polym. Sci.*, **15**, 1247 (1971).
2. C. M. Hansen, *J. Paint Technol.*, **39** (505), 104 (1967).
3. C. M. Hansen, *J. Paint Technol.*, **39** (511), 505(1967).
4. M. L. Huggins, *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942); *J. Amer Chem. Soc.*, **64**, 1712 (1942).

5. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes*, 3rd ed., Dover Publications, New York, 1964.

6. S.-A. Chen, Doctoral Thesis, Washington University, St. Louis, Missouri, June, 1969.

7. C. B. Krestchmer and R. J. Wiebe, *J. Chem. Phys.*, **22**, 1697 (1954).

8. H. Renon and J. M. Prausnitz, *Chem. Eng. Sci.*, **22**, 229 (1967).

9. H. G. Harris and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **8**, 180 (1969).

10. G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

11. G. Gee and W. J. C. Orr, *Trans. Faraday Soc.*, **42**, 507 (1946).

12. G. Allen, C. Booth, G. Gee, and M. N. Jones, *Polymer*, **5**, 367 (1964).

13. J. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworths, London, 1959.

14. K. H. Meyer, *Natural and Synthetic High Polymers*, Interscience, New York, 1950, p. 672.

15. R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949).

16. A. Dondos and D. Patterson, *J. Polym. Sci. A-2*, **5**, 230 (1967).

17. H. Burrell, *Official Digest*, Oct., 726 (1955).