

Polymer Miscibility in Organic Solvents and in Plasticizers—A Two-Dimensional Approach

SHOW-AN CHEN,* *Chemical Engineering Department,
Washington University, St. Louis, Missouri 63130*

Synopsis

From thermodynamic considerations based on associated solution models and from the Hansen's three-dimensional solubility parameter concept, it is found that the solvent power of an organic liquid for a given polymer can be characterized by two parameters, δ_h and χ_H , 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 the effects due to temperature and molecular size of the liquid. It is also found that Hansen's solubility sphere for the polymer can be represented as a solubility circle in the proposed χ_H - δ_h plane. The proposed approach is applied successfully to polymer-plasticizer systems.

INTRODUCTION

For the miscibility of polymer-diluent systems, Hansen¹⁻³ proposed that the solubility parameter is a vector composed of the hydrogen-bonding solubility parameter δ_h , polar solubility parameter δ_p , and dispersion solubility parameter δ_d . Using these three components, which are calculable² from the properties of the pure components, he has constructed a three-dimensional solubility diagram 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 $(\delta_{d,P}, \delta_{p,P}, \delta_{h,P})$. Around this point a sphere can be constructed of a radius such that any liquid characterized by a point $(\delta_{d,L}, \delta_{p,L}, \delta_{h,L})$ lying within the sphere is a solvent for the polymer, while a liquid represented by a point outside the sphere is a nonsolvent for the polymer. In the diagrams, the unit length on the axis represented by δ_d is twice the unit length used for δ_p and δ_h . The radius of the sphere must be determined experimentally. This approach enables one to choose suitable solvents for a given polymer without laborious experimental effort and provides a more powerful means than using Flory's interaction parameter for characterization of solvent power. It is also applicable to systems containing mixed liquids, or to systems containing more than one polymeric solute, and can be used to characterize other materials, such as dyes, nonionic emulsifiers, and pigments.

In this work, it is shown from thermodynamic considerations that Han-

* Present address: W. R. Grace & Co., Converted Plastics Group, Duncan, South Carolina 29334.

sen's solubility sphere can be represented as a solubility circle in a proposed solubility plane. Three examples involving the solubilities of poly(vinyl acetate), poly(methyl methacrylate), and polystyrene in various organic liquids, and one example of poly(vinyl chloride) in various plasticizers, have been studied. It is further shown that self-association of the solvent or polymer in a polymer solution favors immiscibility and that mutual association between the polymer and solvent favors miscibility.

THERMODYNAMIC CONSIDERATIONS

For binary liquid mixtures involving hydrogen bonding, the excess Gibbs free energy, ΔG^E , for self-associated solutions, such as alcohol-aliphatic hydrocarbon mixtures, and for mutually associated solutions, such as chloroform-ether mixtures, have been formulated.⁴⁻⁸ In these treatments, the contribution of hydrogen bonding to ΔG^E was considered as a "chemical" contribution. The "physical" contribution to ΔG^E , due to polar and dispersion interactions, was formulated separately from the "chemical" effect. The hydrogen-bonding contribution was taken into account by complex formation. Size effects of these complexes were formulated using the combinatory part of the Flory-Huggins equation and were characterized by the equilibrium constant of the complexing reactions. The physical contribution was formulated using the Scatchard-Hildebrand equation and was characterized using a physical interaction parameter, A_{12} . In this work, the self-associated and mutually associated solution models are extended to polymer solutions. Based on the associated solution model and the three-dimensional solubility parameter concept of Hansen, a generalized functional form of the Gibbs free energy of mixing will be derived from which a two dimensional approach to polymer solubility can be developed.

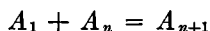
The Self-Associated Solution Model

Consider a mixture of polyolefin and alcohol. Alcohol molecules can self-associate into alcohol complexes having various degrees of aggregation through hydrogen bonding. Thus, the entropy gain from mixing the polymer with alcohol will be smaller than that of mixing with nonhydrogen-bonding liquids at the same composition. Therefore, the solubility of a polyolefin in alcohol may be expected to be weaker than that in nonhydrogen-bonding liquids. Actually, alcohols are often used as nonsolvents in the fractionation of nonpolar or slightly polar polymers.⁹ This immiscibility can be predicted as shown below.

For alcohol-aliphatic hydrocarbon solutions, the excess thermodynamic properties, ΔG^E and ΔH^E , have been formulated using self-associated solution models.⁴⁻⁷ Several common assumptions made in these theories are:

- (a) There is no coupling between hydrogen bonding and physical interaction effects.
- (b) The correction arising from excess volume can be neglected in the formulation of ΔG^E .

(c) The alcohol complexes are formed by successive reactions of the type



and the equilibrium constant for the above reaction is independent of n .

(d) The "combinatorial contribution" to ΔG^E can be expressed by the Flory-Huggins athermal solution equation.

(e) The contribution from the physical interaction between alcohol complexes and solvent to ΔG^E can be expressed by the Hildebrand-Scatchard equation.

Since no restriction on the size of the hydrocarbon has been made, the theories of alcohol-aliphatic hydrocarbon solutions can thus be used for polyolefin-alcohol solutions, provided that an additional term, $\chi_s = 1/z$, which is usually neglected in monomeric solution theories, is introduced. Here, z is the number of nearest neighbors. In the monomeric solution theories, there are two types of expression, the Kretschmer-Wiebe equation⁴ and the modified Wiehe-Bagley equation.⁶ The latter relation involves the additional assumption that the entropy of disorientation of the alcohol complexes can be neglected. Calculations have shown that these two equations work equally well and have the same characteristics.⁷ If we extend the associated solution theories for liquid mixtures to polymer solutions by introducing $\chi_s = 1/z$ into the physical interaction term χ , the chemical potentials of polymer and alcohol can be expressed as follows.

The Kretschmer-Wiebe Equation is

$$\frac{\mu_A - \mu_A^0}{RT} = \ln \frac{\phi_1}{\phi_1^0} - \frac{V_A}{\bar{V}} + \frac{V_A}{\bar{V}^0} + \chi\phi_P^2 \quad (1)$$

$$\frac{\mu_P - \mu_P^0}{RT} = \ln \phi_P + 1 - \frac{mV_A}{\bar{V}} + m\chi\phi_A^2 \quad (2)$$

where

$$\phi_1 = \frac{2K_A\phi_A + 1 - \sqrt{4K_A\phi_A + 1}}{2K_A^2\phi_A} \quad (3)$$

$$\phi_1^0 = \frac{(2K_A + 1) - \sqrt{4K_A + 1}}{2} \quad (4)$$

$$\frac{1}{\bar{V}} = \frac{\phi_P}{mV_A} + \frac{\phi_1}{V_A(1 - K_A\phi_1)} \quad (5)$$

$$\frac{1}{\bar{V}^0} = \frac{\phi_1^0}{V_A(1 - K_A\phi_1^0)} \quad (6)$$

$$\chi = \chi_s + \chi_H \quad (7)$$

$$\chi_s = \frac{1}{z} \quad (8)$$

$$\chi_H = \frac{V_A A_{AP}}{RT} \quad (9)$$

$$A_{AP} = C_{AA} + C_{PP} - 2C_{PA} \quad (10)$$

μ , ϕ , and V are the chemical potential, volume fraction, and molar volume, respectively; and the subscripts A and P refer to alcohol and polymer, respectively. In these equations, C_{PP} and C_{AA} are the cohesive energy densities of the polymer and alcohol, respectively, while C_{PA} is related to the energy of polymer-alcohol interaction. K_A is an alcohol self-association equilibrium constant, which is independent of the aliphatic hydrocarbon structure; it can be calculated from the properties of the pure alcohol.⁷

The Modified Wiehe-Bagley Equation is

$$\begin{aligned} \frac{\mu_A - \mu_A^0}{RT} = \ln \phi_A - \left(1 + \frac{1}{K_A}\right) \ln(1 + K_A \phi_A) - \frac{\phi_P}{m} \\ + \left(1 + \frac{1}{K_A}\right) \ln(1 + K_A) + \chi \phi_P^2 \quad (11) \end{aligned}$$

$$\frac{\mu_P - \mu_P^0}{RT} = \ln \phi_P + \phi_A - \frac{m}{K_A} \ln(1 + K_A \phi_A) + m \chi \phi_A^2. \quad (12)$$

When $K_A = 0$, both the Kretschmer-Wiebe equation and the modified Wiehe-Bagley equation reduce to the Flory-Huggins equation.

Applying the critical solution conditions

$$\frac{d\mu_A}{d\phi_A} = \frac{d^2\mu_A}{d\phi_A^2} = 0 \quad (13)$$

and an approximation for high polymer solutions at the critical point, $\phi_{P,cr} = 0$,¹⁰ to the Kretschmer-Wiebe equation and to the modified Wiehe-Bagley equation, the expressions for χ_{cr} can be written as follows: From the Kretschmer-Wiebe (K-W) equation

$$\chi_{cr} = \frac{1}{2} \frac{1}{4K_A + 1} \frac{\sqrt{4K_A + 1} - 1 + 2K_A^2}{K_A^2(\sqrt{4K_A + 1} - 1)}, \quad (14)$$

and from the Modified Wiehe-Bagley (W-B) equation

$$\chi_{cr} = \frac{1}{2} \frac{1}{1 + K_A}. \quad (15)$$

The values of K_A in these expressions for alcohol-aliphatic hydrocarbon solutions are of the same order of magnitude;⁷ for ethanol at 25°C, $K_{A,W-B} = 96.55$ and $K_{A,K-W} = 145.7$. If we substitute these K_A values into eqs. (14) and (15), we obtain $\chi_{cr} \cong 0$. For alcohol-aliphatic hydrocarbon solutions, A_{12} values vary from 1.1 to 3.8 in the normal temperature range of 5°C to 60°C;⁷ the corresponding χ values, calculated from the A_{12} values and $z =$

TABLE I
Parameters of Alcohol-Polar Solvent Solutions^a

System	$T, ^\circ\text{C}$	K_A	A_{12}	$\chi_H = V_A A_{12}/RT$
Ethanol-benzene	45	27.87	2.75	0.261
Isobutanol-hexene	60	12.10	1.52	0.220
Methanol-acetone	55	2.90	0.03	0.0015

^a From Chen.⁷

10, range from 0.253 to 0.363. These calculated χ values may be considered as those for polyolefin-alcohol solutions. Thus, χ is generally greater than its critical value, $\chi_{cr} \doteq 0$, in the normal temperature range. This implies that alcohols have poor solvent power, or are nonsolvents, for polyolefins. But an alcohol containing a highly branched alkyl group may dissolve a polyolefin; 2-ethylbutanol-polyisobutylene solution¹ is an example. The reason is that such alcohols may possess extremely small K_A values because of steric hindrance effects due to the branched alkyl groups.

For alcohol-polar solvent solutions, it has been shown that the alcohol-aliphatic hydrocarbon solution theories mentioned above are also applicable.⁷ However, the K_A values for the alcohol in such solutions depend upon the specific polar solvent but are independent of the solution concentration. These K_A values are lower than those in alcohol-aliphatic hydrocarbon solutions. The lowering of K_A is due to the fact that the positive part of a polar molecule can attract the bare hydrogen of an alcohol molecule and thus reduce the degree of self-association of the alcohol. Some typical K_A values for alcohol-polar solvent solutions are listed in Table I. The values, together with eq. (14) or (15), allow us to interpret the immiscibility of slightly polar polymers such as polystyrene and polyisoprene in alcohols.¹ Some examples in which alcohol is used as a nonsolvent in fractionation are listed in Table II. From similar reasoning, we may expect immiscibility of a hydrogen bonding polymer in aliphatic hydrocarbons; poly(vinyl alcohol)¹¹ is an example.

It seems that the occurrence of self-association in the polymer, or in the solvent of a polymer solution, always favors immiscibility. The solvent power of an alcohol for a given polymer (other than a hydrogen-bonding polymer) can be predicted if K_A and χ are calculable from the properties of pure components.

TABLE II
Nonsolvents for Polymers^a

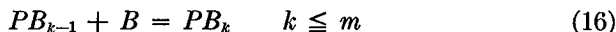
Polymer	Nonsolvent
Polyethylene	<i>n</i> -Propanol
Polystyrene	Methanol
Poly(vinyl chloride)	Methanol
Poly(methyl methacrylate)	Methanol

^a From Miller.⁹

The Mutually Associated Solution Model

In poly(propylene oxide)-methanol- CCl_4 solution, spectroscopic evidence has demonstrated the occurrence of mutual association between methanol molecules and segments of poly(propylene oxide) through hydrogen bond formation.¹² Another example of a mutually associated solution is poly(propylene oxide)-chloroform mixture, for which the Flory interaction parameter is negative,¹² an indication of strong solubility and the occurrence of mutual association.

Let consider a simple mutually associated polymer solution and formulate the Gibbs free energy of mixing using the associated solution model in order to understand how the occurrence of mutual association affects the solubility. In a simple mutually associated solution, such as poly(propylene oxide)-chloroform, each solvent molecule contains only one proton donor and each segment of the polymer contains only one proton acceptor. Assume that (a) there is a chemical equilibrium among polymer-solvent complexes PB_k and solvent molecules B , so that



with the equilibrium constant K independent of k ; (b) the Flory-Huggins equation holds for the mixture of polymer-solvent complexes and free solvent; and (c) the effect of excess volume of mixing in the formulation of ΔG^M can be neglected.⁸

The chemical potentials of the polymer and the solvent can then be expressed (see Appendix for detailed derivation) as follows:

$$\frac{\mu_B - \mu_B^0}{RT} = \ln \phi_{0B} - \frac{V_B N}{V_m} + 1 + \chi \phi_P^2 \quad (17)$$

$$\frac{\mu_P - \mu_P^0}{RT} = \ln \phi_0 - \frac{m V_1 N}{V_m} + 1 + \frac{m}{\rho} \chi \phi_B^2 \quad (18)$$

where m = number of repeating units in the polymer, $\rho = V_B/V_1$ = ratio of the molar volume of the solvent to that of the polymer repeating unit.

$$\chi = \chi_S + \chi_H = \frac{1}{z} + \frac{V_B A_{BP}}{RT}, \quad (19)$$

$$\phi_{0B} = \frac{\phi_B + \frac{\rho}{K} + \frac{\phi_P \rho}{m} - \sqrt{\left(\phi_B + \frac{\rho}{K} + \frac{\phi_P \rho}{m}\right)^2 - 4 \frac{\rho \phi_B}{K}}}{2}, \quad (20)$$

$$\phi_0 = \frac{\phi_P}{2} \left[1 - \frac{K \phi_B}{\rho} + \frac{\phi_P K}{m} + \frac{K}{\rho} \sqrt{\left(\phi_B + \frac{\rho}{K} + \frac{\phi_P \rho}{m}\right)^2 - \frac{4 \rho \phi_B}{K}} \right], \quad (21)$$

$$N = \phi_{0B} \frac{V_m}{V_B} + \phi_P \frac{V_m}{m V_1}, \quad (22)$$

$$V_m = x_B V_B + x_P V_1 m, \text{ and} \quad (23)$$

$$\rho > K \geq 0. \quad (24)$$

Applying the critical solution conditions and $\phi_{P,cr} = 0$ to eq. (17), we obtain

$$\chi_{cr} = \frac{1}{2} \left(1 + \frac{\rho K}{(\rho - K)m} \right)^2. \quad (25)$$

It should be noted that χ_{cr} of eq. (25) is always greater than 0.5. If $m = 1000$, $K = 1.99$, and $\rho = 2$, we find $\chi_{cr} = 0.98$. This demonstrates that the occurrence of mutual association between the polymer and the solvent can compensate for some dissimilarities in structure and polarity, and therefore favors miscibility.

The Flory interaction parameter calculated using the method of Blank and Prausnitz¹³ is always positive. Their method fails, as they indicated, for solutions in which the Flory interaction parameters are negative. However, our mutually associated solution model allows us to characterize the solvent power of the solvent in an hydrogen-bonding polymer solution using an equilibrium constant K and a physical interaction parameter. This physical interaction parameter, which absorbs the dispersion and polar interaction effects, is usually positive.

General Considerations

From the associated solution model and the Flory-Huggins equation, the expressions for the chemical potentials of the polymer and solvent can be written in a general functional form:

$$\frac{\Delta G^M}{RT} = f(\phi_S, K) + \chi x_S \phi_P \quad (26)$$

where the subscript S refers to solvent, K is the equilibrium constant of self-association or mutual association, f is a function of ϕ_S and K , and χ is defined by eqs. (7), (8), (9), and (10) after replacing the subscript A by S for solvent.

In alcohol-saturated hydrocarbon solutions, K_A of a specific alcohol was shown to be constant for aliphatic hydrocarbons.⁷ This implies that physical interactions (dispersion interaction and dipole-induced dipole interaction) between alcohol and aliphatic hydrocarbon do not affect K_A . In other words, the self-association equilibrium constant is only dependent on the hydrogen bonding energy of the alcohol. Thus, for self-associated solutions we may replace K in eq. (26) by a hydrogen-bonding solubility parameter, δ_h .

In the mutually associated liquid mixtures, such as solutions of acetylene in various organic solvents, the calculated mutual association equilibrium constant K^{14} seems to be dependent mainly on δ_h of the solvents, as can be seen from Table III. Thus, for mutually associated solutions, we may replace K in eq. (26) by the hydrogen-bonding solubility parameters of the solvent and the solute. Hence, eq. (26) can be written as

TABLE III
Parameters of Acetylene–Organic Solvent Mixtures and
Solubility Parameters of Solvents at 25°C^a

Solvent	K	$\delta_{h,s}$	$\delta_{p,s}$	$\delta_{d,s}$
<i>n</i> -Hexane	0	0	0	7.24
Benzene	0	1.0	0.5	8.95
Tetrahydrofuran	1.08	3.9	2.8	8.22
Acetonitrile	1.13	3.0	8.8	7.50
Butyrolactone	1.28	3.6	8.1	9.26

^a K values are from Harris and Prausnitz;¹⁴ δ_h , δ_p , and δ_d values are from Hansen.²

$$\frac{\Delta G^M}{RT} = f(\phi_S, \delta_{h,s}, \delta_{h,p}) + \chi x_S \phi_P \quad (27)$$

Hansen¹⁻³ has suggested a three dimensional solubility parameter approach to polymer solubility. In his approach, the solubility parameter of any organic substance was divided into three components, δ_d , δ_p , and δ_h , which are calculable from the properties of the pure component. For polar substances, nonzero values of δ_h have been obtained. Let us apply Hansen's concept and assume that eq. (27) is valid for all binary polymer solutions. Then, according to eq. (27), the solvent power of a liquid for a given polymer can be characterized by $\delta_{h,s}$ and χ . Thus, if we use δ_h and χ as two axes and locate the liquid in the χ - δ_h plane, we may be able to determine a solubility region for the polymer. From the analysis of associated solutions described above, we know that the χ values in the soluble region range from zero to some value greater than 0.5. A polymer-liquid mixture having a large value of χ can be miscible if there is sufficient hydrogen bonding between the liquid and the polymer, while one having a small value of χ can be insoluble if there is a self-association of the liquid or the polymer. These conclusions give us some guidance in constructing the solubility region.

TWO-DIMENSIONAL APPROACH TO POLYMER MISCIBILITY

In the preparation of a χ -versus- δ_h plot, it is necessary to calculate χ and δ_h from the properties of the pure components. Methods for calculating or experimentally determining the values of δ_d , δ_p , and δ_h for polymers and liquids have been proposed by Hansen.² Hoy¹⁵ has proposed another method of calculation for liquids and polymers. For binary mixtures of polar liquids, Arkel⁸ considered the energy of vaporization to be a summation of the dispersion and polar contributions, leading to the suggestion that

$$C_{11} = \delta_{d,1}^2 + \delta_{p,1}^2 \quad (28)$$

$$C_{22} = \delta_{d,2}^2 + \delta_{p,2}^2 \quad (29)$$

$$C_{12} = \delta_{d,1}\delta_{d,2} + \delta_{p,1}\delta_{p,2} \quad (30)$$

Applying Arkel's suggestion and the concept of the three-dimensional solubility parameters to eqs. (9) and (10) for the calculation of χ_H , we obtain

$$\chi_H = \frac{V_L}{RT} [(\delta_{d,L} - \delta_{d,P})^2 + (\delta_{p,L} - \delta_{p,P})^2]. \quad (31)$$

If both δ_d and δ_p for the polymer and the liquid are known, χ_H can be calculated from eq. (31).

In calculating Flory's interaction parameter, Blanks and Prausnitz¹³ considered that the solubility parameter for the polymer or solvent can be separated into two components, a polar solubility parameter and a dispersion solubility parameter. An expression identical to eq. (31) has been used in calculating Flory's interaction parameters. In polar-nonpolar systems, polar-induced polar interactions are also involved, in addition to the dispersion-dispersion interactions. For such a system they proposed

$$\chi_H = \frac{V_L}{RT} \left[(\delta_{d,L} - \delta_{d,P})^2 + \frac{T^*}{T} (\delta_{p,L}^2 - 2\Psi) \right] \quad (32)$$

where Ψ , a function of the product of δ_d and δ_p , was determined empirically. The temperature T^* is that at which δ_p was determined.

In our case, use of the three-dimensional solubility parameter concept requires an empirical evaluation of Ψ for polar-nonpolar systems.

Construction of a Polymer Solubility Region in the χ_H - δ_h Plane

Solution thermodynamics indicates that large χ_H values, or large difference in the δ_h values of polymer and liquid, favors immiscibility in a polymer solution. In the χ_H - δ_h plane, a given polymer can be located at the point $(0, \delta_{h,P})$, while a solvent candidate for this polymer may appear at $(\chi_H, \delta_{h,L})$. Since both δ_h and χ_H are always positive, the location of any polymer or liquid should be within, or at, the boundary of the first quadrant of the plane. A good solvent lies closer to $(0, \delta_{h,P})$ than a nonsolvent or a poor solvent does.

The solubility data and experimental and calculated values of δ_d , δ_p , and δ_h for liquids and polymers were taken from Hansen's work,¹⁻³ while the χ_H values were calculated using eq. (31). Hansen's polymer solubility data were determined by visual inspection of solutions at a concentration of about 0.5 g polymer per 5 ml liquid. He has classified 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. In this work, the solubilities of three polymers, poly(methyl methacrylate), polystyrene, and poly(vinyl acetate), in 85 liquids were studied. It was found that if we assume that χ_H has double the scale of the δ_h axis, a solubility circle about $(0, \delta_{h,P})$ as its center can be obtained for any given polymer. Liquids lying within this circle are good solvents, and those lying near and outside the circle are poor solvents and nonsolvents, respectively. For nonpolar liquids, such as hexane, cyclohexane, carbon disulfide, and carbon tetrachloride, the χ_H values were also calculated using eq. (31); the loca-

tions of these nonpolar liquids in the plots were in agreement with the experimental data. This indicates that Ψ of eq. (32) can be neglected in the present approach.

Using estimated δ_i values for the polymers and liquids, the two-dimensional (2-D) plots of these three polymers were constructed and are shown in Figures 1, 2, and 3, where i refers to d , p , or h . The unit of δ_i is (cal/

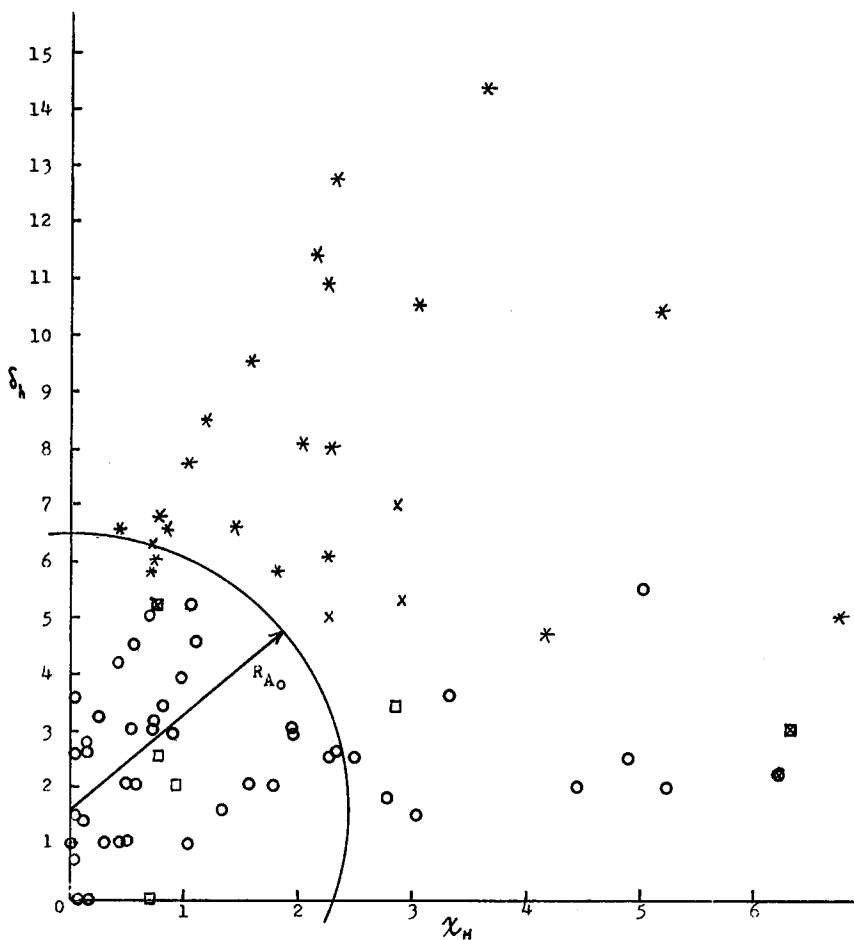


Fig. 1. Solubility of polystyrene in 85 liquids using estimated δ_i values for the polymer and liquids: (O) soluble, group 1; (⊗) nearly soluble, group 2; (□) strongly swollen, group 3; (⊠) swollen, group 4; (×) slightly swollen, group 5; (*) no visible effect, group 6.

$\text{cm}^3)^{1/2}$, and χ_H is dimensionless. The accuracy of the 2-D approach was also compared to that of Hansen's 3-D approach in which the experimental values of δ_i and R_{A_0} were used, as shown in Table IV. Columns 4, 6, 8, and 9 of Table IV indicate satisfactory predictions from the present approach. The R_{A_0} values in these three figures were chosen in such a way that predic-

TABLE IV
Comparison Between the Present 2-D Approach and Hansen's 3-D Approach

Polymer	No. of group 1 liquids used ^a	No. of group 6 liquids used ^a	Present 2-D approach ^b						Hansen's 3-D approach ^c			
			No. of group 1 liquids lying outside the S.C.			No. of group 6 liquids lying inside the S.C.			Using Hansen's δ_i & R_{A_0} values	Using Hansen's δ_i & R_{A_0} values	No. of group 1 liquids lying outside the S.S.	No. of group 6 liquids lying inside the S.S.
			Using estd. δ_i values	Using Hansen's exptl. δ_i & R_{A_0} values	Using estd. δ_i values	Using Hansen's exptl. δ_i & R_{A_0} values						
Polystyrene	49	24	8	4	2	0	7	0	7	0		
Poly(vinyl acetate)	58	7	10	16	0	0	13	0	13	0		
Poly(methyl methacrylate)	34	23	3	8	4	3	11	3	11	0		

^a The total number of liquids used for each polymer are 85.

^b S.C. = solubility circle; δ_i = δ_d , δ_p , or δ_h .

^c S.S. = solubility sphere.

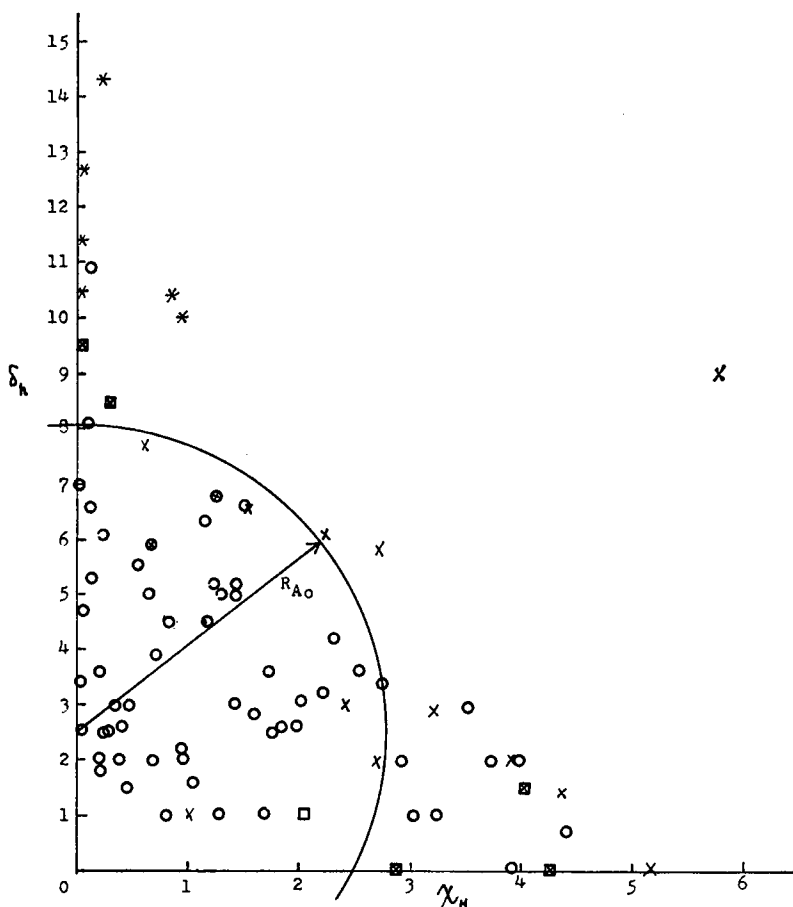


Fig. 2. Solubility of poly(vinyl acetate) in 85 liquids using estimated δ_i values for the polymer and liquids. Symbols same as in Fig. 1.

tions from the present 2-D approach and Hansen's 3-D approach can be compared.

For the three polymers studied, both experimental δ_i values for the polymers and liquids and the radius of Hansen's solubility sphere, R_{A_0} , obtained from a solvent placement method, were also used in constructing the 2-D plot (Figs. 4, 5, and 6). The accuracy of the prediction shown in columns 5 and 7 of Table IV is about the same as that (shown in columns 4 and 6) using calculated δ_i values for the polymers and liquids. It should be noted that the unit length used for R_{A_0} is the same as that used for δ_h in the 2-D plots. Thus, Hansen's polymer solubility sphere can be expressed as a circle in the present 2-D plane.

The solubility circle for a given polymer can be determined by first locating the polymer and all available liquids in the χ_H - δ_h plane and then determining the solvent power for a few liquids located at different distances

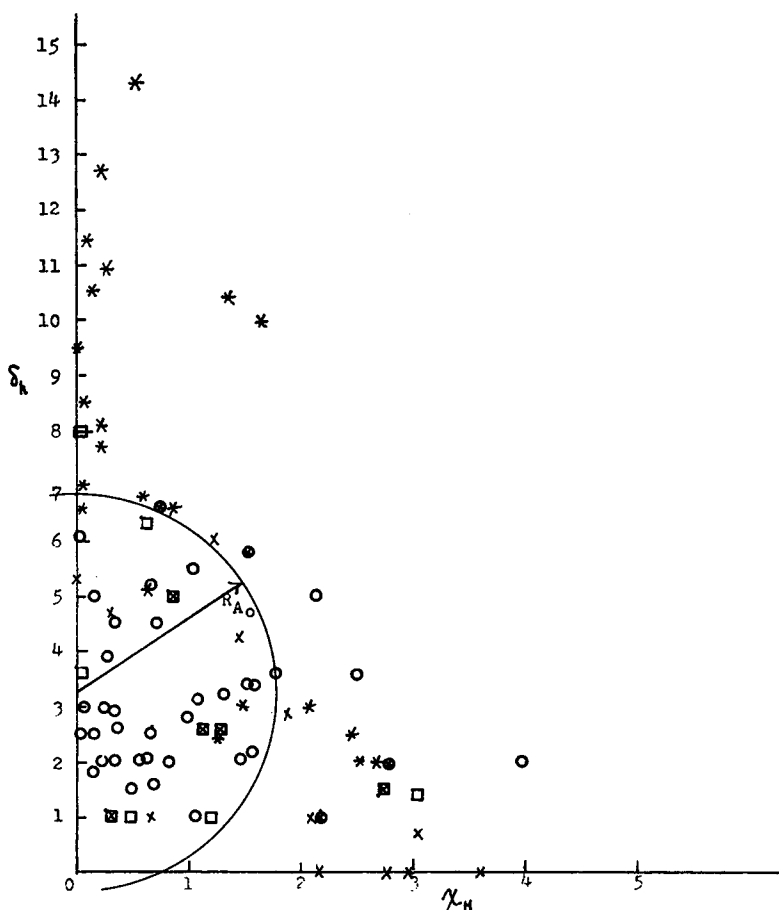


Fig. 3. Solubility of poly(methyl methacrylate) in 85 liquids using estimated δ_i values for the polymer and liquids. Symbols same as in Fig. 1.

from the polymer. We may find that several liquids among the liquids examined are of nonsolvent, i.e., solvent power group 5 or 6. The smallest polymer-nonsolvent distance is the radius of the solubility circle for this polymer.

An Application to Polymer-Plasticizer Systems

The 2-D approach proposed above was applied to poly(vinyl chloride)-plasticizer systems. It was found that, if the δ_i values for poly(vinyl chloride) (PVC) obtained from Hansen's solvent placement method are used, the migration loss of the plasticizer from a plasticized PVC increases with increasing the distance between the center (the location of PVC) and the plasticizer. The results are shown in Table V. If estimated δ_i values for PVC are used, the relationship between the migration loss of DOP (di-2-ethylhexyl phthalate) and its location in the 2-D plane does not follow

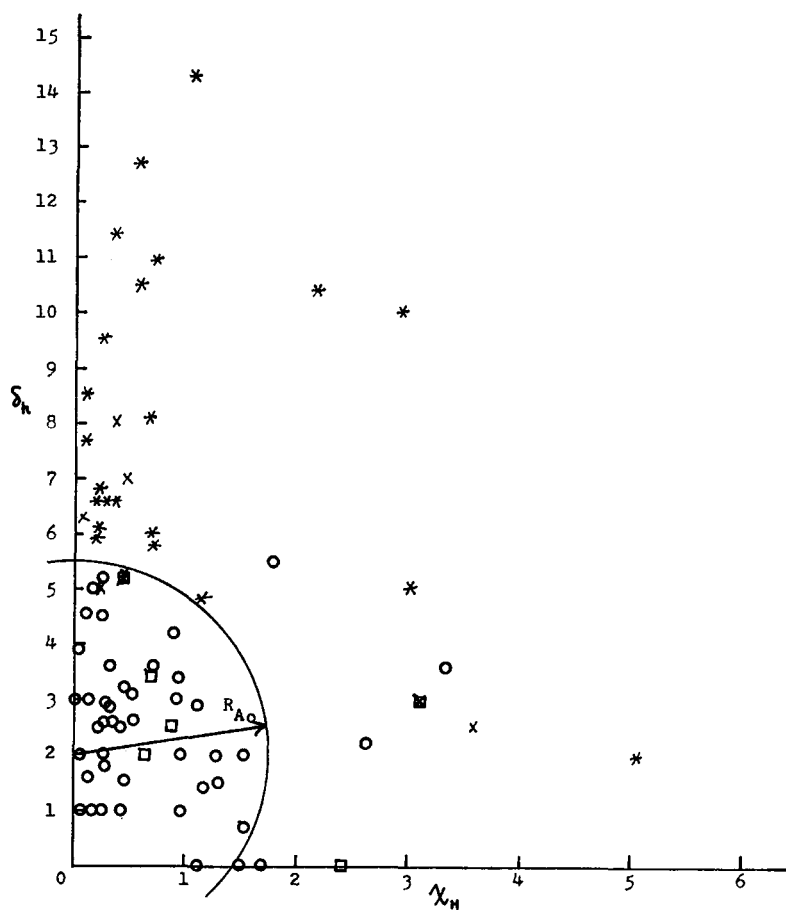


Fig. 4. Solubility of polystyrene in 85 liquids using Hansen's experimental δ_i and R_{A_0} values for the polymer and liquids obtained from the solvent placement method. Symbols same as in Fig. 1.

the above conclusion. This might be due to the fact that the homomorph idea is inapplicable to molecules containing a chlorine atom,¹⁻³ hence the estimated δ_i values for PVC are invalid. In the present 2-D plot, R_A , the distance between the center and the location of the plasticizer, can be calculated using

$$R_A^2 = (\delta_{h,P} - \delta_{h,L})^2 + 4(\chi_H)^2. \quad (33)$$

Thus, from the present approach we are able to select a suitable plasticizer for a given polymer.

R_A values for each plasticizer in Hansen's 3-D solubility system were also calculated using the δ_i values for PVC estimated from pure component properties and using those obtained from Hansen's solvent placement method; these values are listed in Table V for comparison. Column 4 of

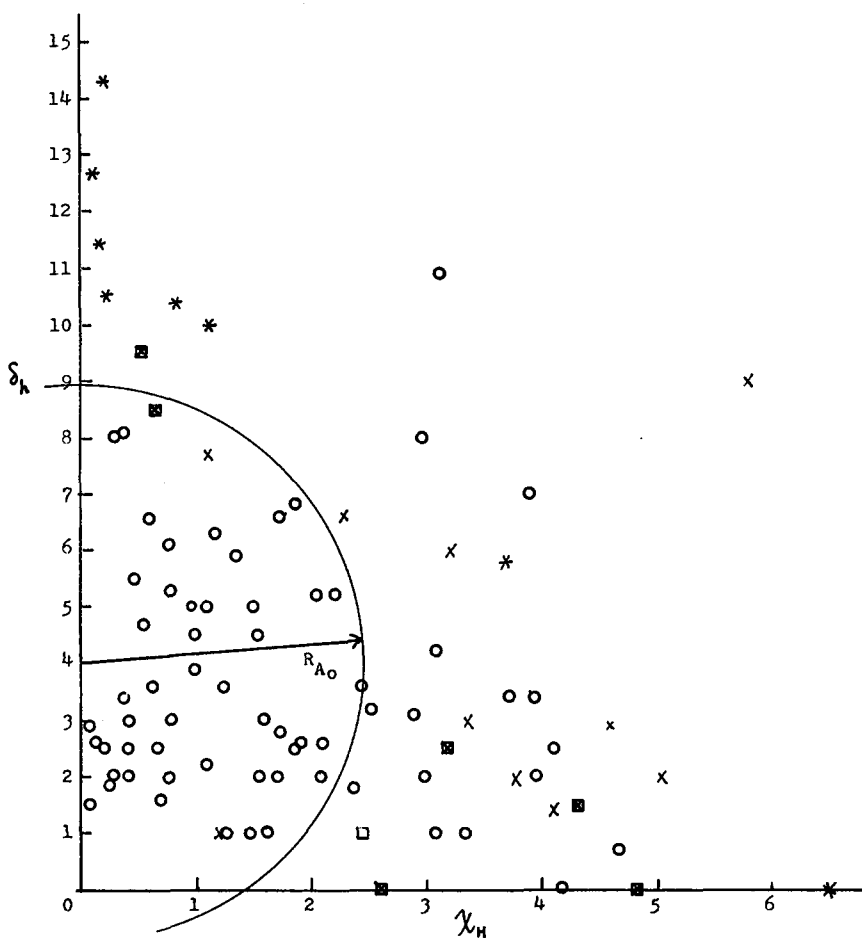


Fig. 5. Solubility of poly(vinyl acetate) in 85 liquids using Hansen's experimental δ_i and R_{A_0} values for the polymer and liquids obtained from the solvent placement method. Symbols same as in Fig. 1.

Table V gives no solubility prediction, while column 5 gives a solubility prediction with one exception.

CONCLUSIONS

1. For a polymer solution such as poly(vinyl alcohol) in alcohol, in which both mutual and self-associations occur, miscibility or immiscibility may mainly depend on the relative importance of mutual association between the polymer and the liquid or self-association in the polymer or in the liquid.

2. Since the present two-dimensional approach can be used to characterize and predict the solvent power of organic liquids for polymers, the hydrogen-bonding contribution to ΔG^M in all kinds of mixtures can be separated from the physical contribution (a sum of dispersion and polar contri-

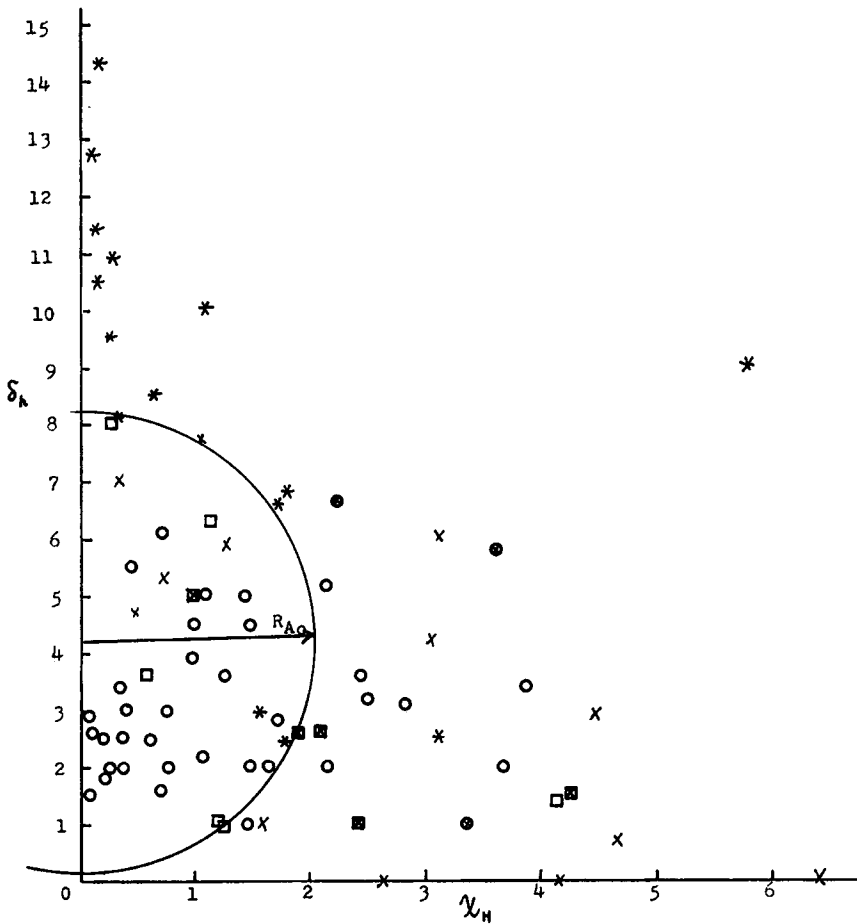


Fig. 6. Solubility of poly(methyl methacrylate) in 85 liquids using Hansen's experimental δ_h and R_{A_0} values for the polymer and liquids obtained from the solvent placement method. Symbols same as in Fig. 1.

butions), at least in a practical sense; and the dispersion and the polar contributions have a similar nature, as indicated in eq. (31).

3. For a better prediction, a more precise relative scale between the δ_h and χ_H axes may be obtained by studying the solubilities of a large number of polymers.

4. The present 2-D approach may be extended to polymer solubility in mixed liquids (or plasticizers) and to polymer-polymer compatibility in blends.

Appendix: Mutually Associated Solution Model

With the assumptions mentioned in the text in treating the mutually associated solution model, let us consider a mole of polymer solution containing x_B moles of solvent and x_p moles of polymer. The Gibbs free energy of mixing, ΔG^M , can be expressed as

TABLE V
Prediction of PVC-Plasticizer Miscibility Using the Present 2-D and Hansen's 3-D Approach

Plasticizer ^a	R_A via present 2-D approach		R_A via Hansen's 3-D approach		Migration loss, ^b wt-%	Volatility loss, ^b wt-%
	Using estd. δ_i values for PVC	Using Hansen's exptl. δ_i values for PVC	Using estd. δ_i values for PVC	Using Hansen's exptl. δ_i values for PVC		
DBP	2.97	1.90	1.66	2.84	soluble (no separation on cooling)	—
TCP	8.06	2.71	3.62	2.00	0.5	0.3
DOP	2.00	4.39	2.00	3.47	6.0	1.7
DOA	9.91	21.8	3.28	5.53	17.6	3.4

^a DBP = Dibutyl phthalate; TCP = Triercyl phosphate; DOP = Dioctyl phthalate or di-2-ethylhexyl phthalate; DOA = Dioctyl adipate.

^b From Riser and Palm¹¹ and Buttrey.¹⁷

$$\frac{\Delta G^M}{RT} = \sum_{k=0}^m n_k \ln \phi_k + n_{0B} \ln \phi_{0B} + \chi x_B \phi_P, \quad (\text{A-1})$$

where n_k = number of moles of the complex PB_k , n_{0B} = number of moles of free solvent molecules, and

$$\phi_k = \frac{n_k(mV_1 + kV_B)}{n_{0B}V_B + \sum_{k=0}^m n_k(mV_1 + kV_B)} \quad (\text{A-2})$$

$$\phi_{0B} = \frac{n_{0B}V_B}{n_{0B}V_B + \sum_{k=0}^m n_k(mV_1 + kV_B)} \quad (\text{A-3})$$

The chemical potentials of the complex PB_k and the free solvent can be derived from eq. (A-1) as

$$\begin{aligned} \mu_k - \mu_k^0 &= \left(\frac{\partial \Delta G^M}{\partial n_k} \right)_{P,T,n_{j \neq k},n_{0B}} \\ &= RT \left[\ln \phi_k - \frac{N(mV_1 + kV_B)}{V_m} + 1 + \chi \left(x_B \frac{mV_1 \phi_B - kV_B \phi_P}{V_m} + k\phi_P \right) \right] \end{aligned} \quad (\text{A-4})$$

$$\mu_{0B} - \mu_{0B}^0 = \left(\frac{\partial \Delta G^M}{\partial n_{0B}} \right)_{T,P,n_k} = RT \left[\ln \phi_{0B} - \frac{V_B N}{V_m} + 1 + \chi \phi_P^2 \right] \quad (\text{A-5})$$

where μ_k^0 and μ_{0B}^0 are the chemical potentials of pure PB_k complex and free solvent, respectively, both species being in a random state; V_m is the molar volume of the polymer solution and equal to

$$\begin{aligned} V_m &= x_B V_B + x_P m V_1 \\ &= n_{0B} V_B + \sum_{k=0}^m n_k (m V_1 + k V_B); \end{aligned} \quad (\text{A-6})$$

N is the total number of moles of complexes and free solvent per mole of polymer solution and equal to

$$N = n_{0B} + \sum_{k=0}^m n_k \quad (\text{A-7})$$

According to Prigogine,¹⁸

$$\mu_P = \mu_0 \quad (\text{A-8})$$

$$\mu_B = \mu_{0B}. \quad (\text{A-9})$$

Also $\mu_P^0 = \mu_0^0 \quad (\text{A-10})$

$$\mu_B^0 = \mu_{0B}^0 \quad (\text{A-11})$$

Applying eqs. (A-8), (A-9), (A-10), and (A-11) to eqs. (A-4) and (A-5), we obtain

$$\frac{\mu_P - \mu_P^0}{RT} = \ln \phi_0 - \frac{mV_1 N}{V_m} + 1 + \frac{m}{\rho} \chi \phi_B^2 \quad (\text{A-12})$$

$$\frac{\mu_B - \mu_B^0}{RT} = \ln \phi_{0B} - \frac{V_B N}{V_m} + 1 + \chi \phi_P^2. \quad (\text{A-13})$$

Equations (A-12) and (A-13) are identical to eqs. (18) and (17), respectively.

At chemical equilibrium, according to eq. (16), we have

$$\mu_{k-1} + \mu_{0B} = \mu_k. \quad (\text{A-14})$$

Substituting eqs. (A-4) and (Z-5) into eq. (A-14), we obtain

$$\frac{\Delta\mu_k^0}{RT} \equiv \frac{\mu_{0B}^0 + \mu_{k-1}^0 - \mu_k^0}{RT} = \ln \frac{\phi_k}{\phi_{k-1}\phi_{0B}} - 1. \quad (\text{A-15})$$

$\Delta\mu_k^0$ can be formulated by considering contributions from polymer chain disorientation and hydrogen bonding separately.⁷ Flory¹⁰ has calculated the entropy of a polymer in solution due to the chain length effect by considering the formation of the solution to occur in two steps: disorientation of the polymer molecules and mixing of the disoriented polymers:

$$\Delta S_{\text{disorientation}} = R \{ \ln i + (i-1)[\ln(z-1)/e] \} \quad (\text{A-16})$$

Therefore,

$$(\Delta\mu_k^0)_{\text{disorientation}} = -T(\Delta S_k)_{\text{disorientation}} \quad (\text{A-17})$$

$$= -RT \left\{ \ln \frac{m+k\rho}{[m+(k-1)\rho]\rho} + [\ln(z-1)/e] \right\} \quad (\text{A-18})$$

$$(\Delta\mu^0)_{\text{hb}} = h_{\text{hb}} - T s_{\text{hb}} \quad (\text{A-19})$$

$$\Delta\mu_k^0 = (\Delta\mu_k^0)_{\text{disorientation}} + (\Delta\mu^0)_{\text{hb}}. \quad (\text{A-20})$$

Combining eqs. (A-17), (A-18), (A-19), (A-20), and (A-15), we obtain

$$\ln \left\{ \frac{\phi_k}{\phi_{k-1}\phi_{0B}} \frac{[m+(k-1)\rho]\rho}{m+k\rho} \right\} = \ln(z-1) - \frac{h_{\text{hb}} - T s_{\text{hb}}}{RT} \quad (\text{A-21})$$

If we define the reaction equilibrium constant as

$$K \equiv \frac{C_k}{C_{k-1}C_{0B}V_1}, \quad (\text{A-22})$$

then

$$\ln K = -\frac{h_{\text{hb}} - T s_{\text{hb}}}{RT} + \ln(z-1) \quad (\text{A-23})$$

where

$$C_k = \frac{n_k}{V_m}, \quad C_{0B} = \frac{n_{0B}}{V_m}.$$

From eq. (A-22),

$$C_k = KV_1 C_{k-1} C_{0B} = (KV_1 C_{0B})^k C_0. \quad (\text{A-24})$$

ϕ_0 , ϕ_{0B} , and N can be solved from the following mass balance equations:

$$\phi_B = \phi_{0B} + \sum_{k=0}^m V_B k C_k = \phi_{0B} + \frac{K\phi_{0B}\phi_0}{m \left(1 - \frac{K}{\rho} \phi_{0B} \right)^2} \quad (\text{A-25})$$

$$\phi_P = \sum_{k=0}^m m V_1 C_k = m V_1 C_0 \frac{1 - (KV_1 C_{0B})^m}{1 - KV_1 C_{0B}}. \quad (\text{A-26})$$

For high polymers, eq. (A-26) can be approximated by

$$\phi_P = \frac{mV_1C_0}{1 - KV_1C_{0B}} \quad (\text{A-27})$$

Upon solving eqs. (A-25) and (A-27) for ϕ_0 and ϕ_{0B} , we obtain eqs. (20) and (21). Applying eqs. (A-3) and (A-6) to eq. (A-7), we obtain eq. (22).

This work was initiated during the later part of the author's residence at Washington University, St. Louis. During his stay, he received financial aid from the Paint Research Institute, which was greatly appreciated. He also wishes to thank Dr. E. B. Bagley for helpful comments.

References

1. C. M. Hansen, *J. Paint Technol.*, **39**, No. 505, 104 (1967).
2. C. M. Hansen, *J. Paint Technol.*, **39**, No. 511, 505 (1967).
3. C. M. Hansen, Doctoral Thesis, *The Three-Dimensional Solubility Parameter and Solvent Diffusion Coefficient*, Danish Technical Press, Copenhagen, 1967.
4. C. B. Kretschmer and R. J. Wiebe, *J. Amer. Chem. Soc.*, **71**, 3176 (1949).
5. H. Renon, and J. M. Prausnitz, *Chem. Eng. Sci.*, **22**, 229 (1967).
6. I. A. Wiehe and E. B. Bagley, *Ind. Eng. Chem., Fundam.*, **6**, 209 (1967).
7. S. A. Chen, Doctoral Thesis, *Thermodynamics of Associated Solutions*, Washington University, St. Louis, June 1969.
8. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes*, 3rd ed., Dover Publications, New York, 1964.
9. M. L. Miller, *The Structure of Polymers*, Reinhold, New York, 1966.
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953.
11. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Interscience, New York, 1966.
12. J. F. Heil, Ph.D. Thesis, University of California at Berkeley, 1965; *A.I.Ch.E. J.*, **12**, 678 (1966).
13. R. F. Blank and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **3**, 1 (1964).
14. H. G. Harris and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **8**, 180 (1969).
15. K. L. Hoy, *Tables of Solubility Parameters*, Union Carbide Corp., South Charleston, W. Va., 1969.
16. G. R. Riser and W. E. Palm, *Polym. Eng. Sci.*, **1** (Apr. 1967).
17. D. N. Buttrey, *Plasticizers*, Franklin Publishing Co., Palisade, N. J., 1960.
18. Prigogine, I., *The Molecular Theory of Solutions*, North-Holland Publishing Co., Amsterdam, 1957.

Received September 2, 1970

Revised November 30, 1970