Review

Free Volume and Polymer Solubility. A Qualitative View[1]

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ABSTRACT: Polymer solvent interaction and the χ parameter have been traditionally associated with the heat of mixing of polymer and solvent liquids and with the difference in contact energies. It is becoming clear that χ is usually mainly entropic and associated with the difference in free volume between polymer and solvent. An attempt is made to place this effect in context in the development of solution thermodynamics, to show how it explains the pressure and temperature dependence of polymer solubility, and to give an intuitive introduction to theories which take it into account.

Many polymer chemists feel that polymer solution thermodynamics achieved an essentially satisfactory form around 1940. Since then, it is thought, the qualitative, physical picture can have changed little in spite of refinements of the Flory–Huggins theory and the excluded volume treatments of dilute solutions. It is now clear, however, that this comfortable feeling is not justified. The traditional ideas do not explain, even qualitatively, many of the most important features of polymer solution thermodynamics. Among these are the origin of polymer–solvent "interactions" and the χ parameter, the temperature dependence of polymer solubility, and the phase separation which takes place in all polymer solutions at an elevated temperature[2] (perversely called a lower critical solution temperature; see Figure 1a).

It turns out that a new factor is needed. In discussing solutions, one can think of the old adage, "Like dissolves like," and thus look for ways in which the polymer and solvent are dissimilar. Traditional ideas concentrate on the dissimilarity of contact energies or cohesive energies between segments of polymer and solvent molecules of *different chemical nature.* The new factor is the dissimilarity between the free volumes of the polymer and solvent liquids, *i.e.*, that the usual solvent is much more expanded than the polymer. This "free volume dissimilarity" is mainly due to the inescapable *difference of size or chain length* between polymer and solvent molecules. A solution of a polymer in a chemically identical homologous solvent of low molecular weight would have no "contact energy dissimilarity" but the free volume dissimilarity remains and is now being found to have important thermodynamic consequences. The effect of free volume dissimilarity was introduced by the theory of solutions proposed in the early 50's by the Brussels group of Prigogine, Mathot, and Trappeniers.[3] It gives a very different picture from the Flory–Huggins theory and is only now attracting attention from polymer chemists. It is, however, the basis of much important recent work by Flory and collaborators.[4] The present article starts with a review of traditional ideas to show where free volume must be brought in, and then gives an intuitive introduction to the Brussels theory.

Strictly Regular Solution Theory. The Flory–Huggins theory (and most work on polymer solution thermodynamics) originates with, and conserves important features of, the theory of strictly regular solutions for mixtures of spherical molecules of equal size. The most important assumption of the theory is that volume changes taking place during mixing may be neglected. Not only is the total ΔV_M zero, but also any effects on ΔH_M and ΔS_M. The entropy of mixing is just the positional or combinatorial ΔS_M associated with the large number of ways of arranging the molecules of different type in the solution. Thus ΔS_M is positive, and with the assumption that mixing is random, it is calculated to have the ideal value, independent of the nature of the liquids being mixed. On the other hand, the heat or energy change on mixing (ΔH_M) is associated with the formation in the mixture of contacts of a new type, (1–2), which replace some of the (1–1) and (2–2) contacts of the pure components according to the quasi-chemical process

$$\tfrac{1}{2}(1\text{–}1) + \tfrac{1}{2}(2\text{–}2) \longrightarrow 1\text{–}2 \qquad (1)$$

ΔH_M is thus proportional to an interchange energy, Δw, related to the contact energies ϵ_{ij} required to break the contacts in eq 1

$$\Delta H_M \propto \Delta w = \tfrac{1}{2}(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \qquad (2)$$

In ΔG_M it is only ΔH_M which depends on the nature of the molecules, or on their interaction, which is characterized by the dimensionless parameter

$$\chi = \frac{z\Delta w}{kT} \qquad (3)$$

Here z is the lattice coordination number, but is not

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(1) Presented at the ceremonial session of the 25th Anniversary Meeting of the Polymer Division of the American Physical Society, Philadelphia, Pa., 1969.

(2) P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).

(3) (a) V. Mathot, Comptes Rendus Réunion sur les changements de Phases, Paris, 1952, p 95; (b) I. Prigogine, N. Trappeniers, and V. Mathot, *Discussions Faraday Soc.*, **15**, 93 (1953); (c) I. Prigogine (with the collaboration of V. Mathot and A. Bellemans), "The Molecular Theory of Solutions," North Holland Publishing Co., Amsterdam, 1957.

(4) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035, 2053, 2061, 2066 (1968); P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, **1**, 279 (1968).

TABLE I

VALUES OF χ AND OF THE ENTHALPY AND ENTROPY CONTRIBUTIONS, χ_H AND χ_S, FOR POLY(METHYL METHACRYLATE) IN VARIOUS SOLVENTS

	$CHCl_3$	Benzene	Dioxane	THF	Toluene	DEK	Acetone	*n*-Xylene
χ	0.365	0.429	0.430	0.446	0.452	0.462	0.481	0.506
χ_H	−0.075	−0.017	0.040	0.026	0.028	0.055	0.028	0.194
χ_S	0.44	0.45	0.39	0.42	0.42	0.41	0.45	0.31

important in the discussion. The χ parameter represents an antipathy between the molecules of different type since it is the ratio of the positive interchange energy, acting against mixing, to the thermal energy favoring mixing.

It was soon found experimentally that Δw or χ, as determined from vapor pressure measurements of ΔG_M, was not the same as found from ΔH_M. To account for this, Δw was reinterpreted[5] empirically to be an interchange free energy with enthalpic and entropic contributions

$$\Delta w \longrightarrow \Delta w_G = \Delta w_H - T\Delta w_S$$

$$\chi = \chi_H + \chi_S = \frac{z\Delta w_H}{kT} - \frac{z\Delta w_S}{k} \qquad (4)$$

The entropy Δw_S was found to be positive, corresponding to the plausible idea of an increase of entropy on forming the new (1–2) contact, and thus χ_S was a *small, negative* correction. Still, it was the empirical nature of Δw_S which led the Brussels group of Prigogine and collaborators to propose a molecular theory of solutions[3e] which no longer requires $\Delta V_M = 0$, and which predicts Δw_S. Although Scott[6a] and Brown[6b] have given equivalent theories, Mathot, Trappeniers, and Prigogine[3] in 1952 extended their theory to include polymer solutions, where free volume changes are of particular importance. Before this, however, a very direct extension of strictly regular solution theory had already given the traditional polymer solution thermodynamics.

Polymer Solution Thermodynamics. A polymer solution differs from a mixture of spherical solute and solvent particles by the linking of the solute particles into chains of polymer segments. Polymer solution thermodynamics asks what is the effect of this chain connectivity. The answer of traditional ideas is: in principle, almost nothing. We assume $\Delta V_M = 0$, and ΔS_M is still just a combinatorial term. The number of ways of arranging the mixture on the solution lattice is, of course, different for a system of spherical molecules, and hence no longer gives the ideal entropy of mixing. Polymer solution thermodynamics has been almost entirely concerned with successive approximate treatments of this combinatorial problem, whether for relatively concentrated solutions as in the 1940's, or for dilute solutions as more recently.

The heat of mixing was taken over essentially unchanged from strictly regular solutions so that it was again proportional to an interchange energy, this time for the creation of a contact between a solvent molecule (or segment thereof) and a polymer segment. The χ parameter was again given by eq 3. Again Δw had to be reinterpreted empirically as an interchange free energy so that χ decomposes into two contributions. (In the Flory terminology χ_H and χ_S are called κ and $^1/_2 - \psi$, respectively.) This procedure seemed justified by the strictly regular solutions precedent. However, consider typical values of the parameters, for instance for poly(methyl methacrylate) in various solvents, as in Table I (values of Schulz and Doll,[7] cited by Tompa[8] in his text). The "small, negative correction," χ_S, is now positive and much larger than χ_H so that χ falls between 0.35 and 0.5 no matter how low χ_H is. This situation is quite general and represents a crucial difficulty in the usual picture. The new positive sign of χ_S corresponds to a negative Δw_S and an inexplicable, large increase of order on forming a polymer–solvent contact. It is clear that solute–solvent interaction has been qualitatively changed by chain connectivity. Traditional ideas offer no explanation for this.

It should be mentioned that the newer excluded volume treatments for dilute solutions do not solve the difficulty. They can be regarded as combinatorial problems, to use the lattice terminology, but applied to dilute solutions. The polymer–solvent interaction is represented by the excluded volume between segments, β, related to the potential of average force, $w(r)$. This free energy quantity cannot be convincingly evaluated, so that in practice β is identified with the χ parameter of the older theories through[9]

$$\beta = 2V_1(^1/_2 - \chi)/N_0 \qquad (5)$$

where V_1 is the solvent molar volume and N_0 Avogadro's number.

The Lower Critical Solution Temperature. A much more dramatic difficulty arose with the discovery[2] that every polymer solution separates into two phases on increasing the temperature, as well as on lowering the temperature to the well-known critical solution temperature with which the Flory Θ point is associated. Figure 1a shows schematically a typical phase diagram and Figure 1b the temperature dependence of the χ parameter. It is clear that the temperature dependence is not predicted by the monotonically decreasing $\chi(T)$ relationship given by eq (4) of form $\chi = a/T + b$. (This is more usually expressed in the Flory terminology, $^1/_2 - \chi = \psi - \kappa = \psi(1 - \Theta/T)$.) The new critical solution temperature must be called a lower critical solution temperature since it lies at the bottom of a two-phase region, and in spite of its being a higher

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(5) E. A. Guggenheim, *Discussions Faraday Soc.*, **15**, 24 (1953).

(6) (a) R. L. Scott, *J. Chem. Phys.*, **25**, 193 (1956); (b) W. B. Brown, *Phil. Trans. Roy. Soc.*, **A250**, 175 (1957).

(7) G. V. Schulz and H. Doll, *Z. Elektrochem.*, **56**, 248 (1952).

(8) H. Tompa, "Polymer Solutions," Butterworth and Co., Ltd., London, 1956, p 170.

(9) W. H. Stockmayer, *J. Polym. Sci.*, **15**, 595 (1955).

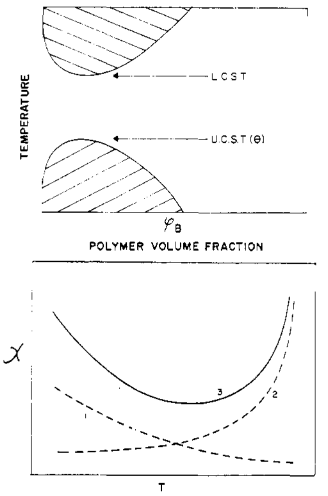

Figure 1. (a) Phase diagram of a polymer solution showing the phase separation occurring at high temperatures above the LCST. (b) The temperature dependence of the χ parameter: curve 3, total χ; curve 2, contribution to χ due to free volume dissimilarity between polymer and solvent; curve 1, contribution to χ due to contact energy dissimilarity between polymer and solvent.

temperature than the usual upper critical solution temperature. The thermodynamic conditions for a LCST are that ΔH_M is exothermic and that the entropy of dilution is negative, *i.e.*, that as the solution is diluted there is actually an ordering of the system. Thus, the normal positive combinatorial ΔS_M has been outweighed by a large negative Δw_S term or positive χ_S. This peculiar condition is realized in very few mixtures of molecules of similar size, *e.g.*, aqueous amine solutions where ordering of water around the solute apparently produces the negative Δw_S. However, it occurs for *every* polymer solution so far as is known.

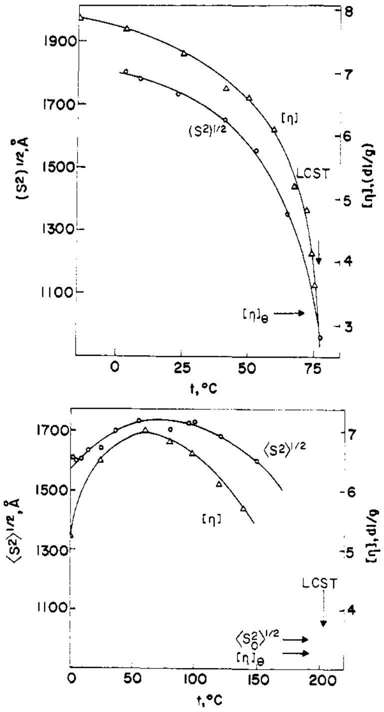

Figure 2. (a) Polyisobutylene-*n*-pentane: radius of gyration and intrinsic viscosity *vs.* temperature. (b) Polyisobutylene–dibutyl ether: radius of gyration and intrinsic viscosity *vs.* temperature.

The new feature which explains the LCST, and χ_S, is the dissimilarity in free volume between the dense polymer liquid and the expanded solvent. Mixing, with some exaggeration, is like the condensation of a gas (solvent) into a dense medium (polymer). Although the free volume of the solution is intermediate between those of the polymer and solvent, the over-all volume change is negative. Associated with this contraction there is an exothermic heat effect and a negative contribution to ΔS_M. Each mixing function becomes the sum of two contributions

$$\Delta V_M = \underset{+}{\Delta V_M(\text{contact energy diss})} + \underset{-}{\Delta V_M(\text{free vol diss})}$$

giving

$$\Delta H_M = \underset{+}{\Delta H_M\,(\text{contact energy diss})} + \underset{-}{\Delta H_M\,(\text{free vol diss})}$$

Both contributions count in χ_H. Also

$$\Delta S_M = \underset{+}{\Delta S_M(\text{combinatorial})} + \underset{-}{\Delta S_M(\text{free vol diss})}$$

Here the χ_S parameter is due to the second contribution only, since χ by definition does not include the combinatorial entropy given, for instance, by the well-known Flory–Huggins expression. The total effect of free volume in ΔG_M or χ could be of either sign depending on the relative contributions to χ_H and χ_S. In fact, the effect on the entropy can be shown to be more important so that the contact energy dissimilarity and the free volume dissimilarity both give unfavorable, positive contributions to ΔG_M and χ (*cf.* like dissolves like)

$$\chi = \underset{+}{\chi(\text{contact energy diss})} + \underset{+}{\chi(\text{free vol diss})}$$

The two contributions are shown schematically in Figure 1b as functions of *T*. The first contribution may be equated to the original Flory–Huggins term, decreasing with *T*. However, as temperature rises, the free volume dissimilarity between polymer and solvent increases, and with it the new contribution to χ. The total χ finally turns upward, ΔH_M becomes exothermic, the entropy of dilution negative, and the LCST occurs at the critical value of χ.

Characteristics of the LCST. The critical value of χ is still given by the Flory–Huggins combinatorial entropy approximation, *i.e.*

$$\chi_c = {}^1/_2(1 + r^{-1/2})^2 \qquad (6)$$

where r is the ratio of molar volumes of polymer and solvent. Thus χ_c increases as the molecular weight of the polymer is decreased. Decreasing molecular weights of polymer therefore come out of solution at increasing temperature at the LCST which, like the UCST, may be used for fractionation.[10a]

Polymer dimensions and the second virial coefficient decrease[10b] toward the LCST as χ increases. Figure 2a shows the radius of gyration and [η] of polyisobutyl-

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(10) (a) G. Allen, C. H. Baker, and C. Clemson, *Polymer*, **7**, 525 (1966); J. S. Rowlinson and C. D. Myrat, *ibid.*, **6**, 645 (1965); (b) G. Delmas and D. Patterson, *ibid.*, **7**, 513 (1966).

ene in n-pentane from 0° to the LCST of 76°. Here χ is due almost entirely to the free volume difference and follows Figure 1b, curve 2. The molecular weight of the polymer sample used is very high ($\sim 9 \times 10^6$) so that the LCST should correspond to $\chi = {}^1/_2$ and a Θ point. In fact, the second virial coefficient does fall to zero at this temperature and the dimensions of the molecule become the same, to within experimental error,[11] as in benzene at 25°, the well known Θ point associated with the UCST. If now some contact energy difference is introduced between the PIB and the solvent by taking butyl ether as solvent instead of pentane, both contributions to χ occur, so that curve 3 of Figure 1b is required. The dimension (and A_2) pass through a maximum[10b] as shown in Figure 2b.

The Brussels Theory of Polymer Solution Thermodynamics. The advantage of this theory is the possibility of taking into account the expansion of the components and the solution. The expansion of a chain-molecule liquid reflects the thermal energy of only some of the degrees of freedom of the molecule. These are the external degrees of freedom of low enough frequency and hence high enough amplitude to affect the volume. Translational and rotational degrees of the molecule in the gas phase will give such external degrees in the liquid. Low-frequency torsional oscillations of the chain will also count. The total $3c$ external degrees have thermal energy $3ckT$ which is opposed by the cohesive energy. This is proportional to ϵ^* the depth of the interaction potential between neighboring nonbonded segments, and also to the number of these external, intermolecular contacts made by the chain molecule. For present purposes this may be taken proportional to the number of segments, r, or to the number of atoms in the chain backbone, n. (A segment is chosen so that the molecular volume is proportional to r.) Expansion and free volume are characterized by a dimensionless ratio of the above two energies, *viz.*, the reduced temperature

$$\tilde{T} = \frac{U_{\text{thermal}}}{U_{\text{cohesive}}} = \left(\frac{c}{r}\right)\frac{kT}{\epsilon^*} = T/T^* \qquad (7)$$

In this expression, c/r is one-third the number of external degrees of freedom per segment. For a series of chemically identical homologues, c/r decreases as r or n increases. For example, a monomer has three external degrees of freedom, so that $c/r = 1$. Only two external degrees are gained by going to the dimer since one degree is associated with the high-frequency stretch between segments. Thus, $c/r = 5/6$, and $\tilde{T}$, or the free volume, has decreased relative to that of the monomer liquid. For longer molecules the parameter c/r depends on the extent to which torsional oscillation is free in the chain, *i.e.*, on the chain flexibility, dropping asymptotically to a value characteristic of chain flexibility and side-group motion in the high polymer. For spherical molecules (monomers), $\tilde{T}$ depends only on the cohesive energy parameter ϵ^* since $c/r = 1$. For a chain-molecule liquid, however, $\tilde{T}$ and free volume also depend on how the segments are connected into chains, *i.e.*, on the length and flexibility, through the c/r parameter, called a structural parameter.

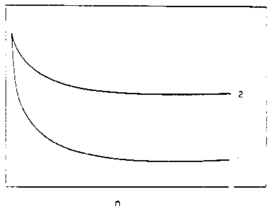

Figure 3. Dependence of reduced temperature, $\tilde{T}$ on n, number of atoms in principal chain for two homologous series: (1) with small chain flexibility, *e.g.*, alkanes; (2) with large chain flexibility, *e.g.*, dimethylsiloxanes.

The two curves of Figure 3 show $\tilde{T}$ schematically as a function of n for two series of homologs: (1) where rotation around bonds is relatively hindered as in the n-alkanes and (2) where the chain is very flexible as in the dimethylsiloxane series. The difference in free volumes at any temperature is much greater between polyethylene and say, pentane, than between polydimethylsiloxane and its homolog of $n = 5$, *i.e.*, hexamethyldisiloxane. This is reflected in the values of the LCST of these two systems. For polyethylene–pentane[12] the LCST is 90°, similar to PIB–pentane[13] at 76°, and corresponds to 0.77 of the critical temperature of pentane. For polydimethylsiloxane–hexamethyldisiloxane[13] the system goes to 221° or 0.95 of T_c before the free volume difference increases enough to cause the LCST.

According to the Brussels theory, temperature enters the partition function only in its reduced form. At a constant reduced pressure (essentially zero for liquids at saturation pressure), molar or specific thermodynamic quantities are related to dimensionless reduced quantities through reduction parameters which depend only on the chain length. Here U is the configurational

$$\begin{aligned} V(n,T) &= V^*(n)\cdot\tilde{V}(\tilde{T}) = rv^*\cdot\tilde{V}(\tilde{T}) \\ U(n,T) &= U^*(n)\cdot\tilde{U}(\tilde{T}) = r\epsilon^*\cdot\tilde{U}(\tilde{T}) \\ G(n,T) &= U^*(n)\cdot\tilde{G}(\tilde{T}) = r\epsilon^*\cdot\tilde{G}(\tilde{T}) \end{aligned} \qquad (8)$$

or external intermolecular energy, essentially the energy of the liquid compared to that of the perfect gas. It is a negative quantity. The combinatorial entropy is not included in G, but only that due to intersegmental contacts. The starred reduction parameters can be regarded as the intrinsic molecular quantities at 0°K, while the reduced quantities are the factors by which these intrinsic quantities must be multiplied to allow for thermal expansion and free volume at higher temperatures. Thus, $\tilde{V}$ is a very direct measure of free volume. Note that here free volume is rather similar to the Bueche[14] theory concept, where an additional free volume is associated with the chain ends. With Bueche, a short-chain liquid has higher free volume than a long-chain one because every molecule, short or

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(11) There should be a small variation of the "unperturbed" dimensions found at different Θ temperatures. In principle, measurements at the UCST and LCST in the same solvent could be an attractive way of measuring this variation.

(12) P. Ehrlich and J. J. Kurpen, *J. Polym. Sci., Part A-1*, 3217 (1963).

(13) D. Patterson, G. Delmas, and T. Somcynsky, *Polymer*, **8**, 503 (1967).

(14) F. N. Kelley and F. Bueche, *J. Polym. Sci.*, **50**, 549 (1961).

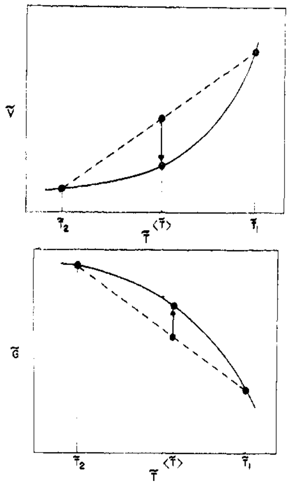

Figure 4. (a) Schematic representation of reduced volume, $\tilde{V}$, against reduced temperature, $\tilde{T}$, showing the decrease in the average of $\tilde{V}$ of the components which takes place on mixing. (b) Schematic representation of reduced Gibbs free energy, $\tilde{G}$, against reduced temperature $\tilde{T}$, showing the increase in the average of $\tilde{G}$ of the components which takes place on mixing.

long, only has two ends. With Prigogine, the role of the ends is played by the five external degrees (three translations and two rotations in the gas phase) which every molecule has independent of its length.

Simha and collaborators[15] have tested $V(n,T)$ data for the following series: n-alkanes from methane to polyethylene, polystyrenes from the dimer to the infinite polymer, and polyethylene oxides, polydimethylsiloxanes, and fluorinated alkanes differing in degree of polymerization. Amazingly enough, all these data can be reduced to a single $\tilde{V}(\tilde{T})$ curve, shown schematically in Figure 4a, demonstrating that the corresponding states law is valid to a considerable degree. It may be that this $\tilde{V}(\tilde{T})$ curve is universal for all dispersion force liquids whether composed of spherical or of chain molecules.

The Mixing Functions. The theory assumes that the mixture behaves as a pure liquid with an averaged reduction parameter for any thermodynamic quantity and an averaged reduced temperature $\langle\tilde{T}\rangle$. For a *polymer and solvent of the same chemical nature*, the averages are very simple and close to being linear in volume fraction. One can see qualitatively that contraction on mixing is predicted. In Figure 4a, the reduced temperatures, $\tilde{T}_1$ and $\tilde{T}_2$ of the solvent and polymer, respectively, give $\tilde{V}_1$ and $\tilde{V}_2$. Multiplying by v^*, one obtains the volumes per segment in the two pure liquids. The average of these volumes per segment falls on the dotted line. On the other hand, the volume per segment in the solution falls below, on the full curve, and hence a contraction occurs on mixing.

The corresponding curve for the intermolecular $\tilde{G}(\tilde{T})$ give ΔG_M and the χ parameter. In Figure 4b, it is clear that ΔG_M depends on two features of the diagram. The first of these is the size of the interval between $\tilde{T}_1$ and $\tilde{T}_2$, which is characterized by the parameter

$$\tau = (1 - \tilde{T}_2/\tilde{T}_1) = (1 - T_1^*/T_2^*) \tag{9}$$

Using eq 7 for $\tilde{T}$ and putting $\epsilon_1^* = \epsilon_2^*$ in the present case

$$\tau = 1 - \frac{(c/r)_2}{(c/r)_1} \tag{10}$$

The τ parameter therefore owes its origin to the difference in structural parameters between polymer and chemically identical solvent, or essentially to the polymer chain connectivity. Its value is obtained from the thermal expansion coefficients of the polymer and solvent liquids. The second feature of Figure 2b on which ΔG_M depends is the curvature of $\tilde{G}$ against $\tilde{T}$, *i.e.*, $(\partial^2\tilde{G}/\partial\tilde{T}^2)_p = -\tilde{C}_p(\tilde{T})/\tilde{T}$, ΔG_M being positive when the curvature is negative (concavity downward). Furthermore the curvature varies with $\tilde{T}$, *i.e.*, on the composition of the mixture. It is for this reason that χ is predicted to vary with composition in the Prigogine and Flory theories. For a very dilute solution $\tilde{C}_p$ can be related to the C_p of the pure solvent, and according to the theory

$$\chi = \frac{C_{p,1}(P,T)}{2R}\tau^2 \qquad \chi_H = -\frac{T}{2R}\frac{\partial C_{p,1}}{\partial T}\tau^2$$
$$\chi_S = \frac{C_{p,1} + T\partial C_{p,1}/\partial T}{2R}\tau^2 \tag{11}$$

As the critical temperature of the solvent is approached under the equilibrium vapor pressure, C_p tends to infinity and with it χ. Qualitatively eq 11 gives curve 2 of Figure 1b and predicts the LCST.

For a polymer in a *solvent of different chemical nature*, the traditional term due to contact energy dissimilarity enters

$$\chi = \frac{(-U)_1}{RT}\nu^2 + \frac{C_{p,1}}{2R}\tau^2$$
$$\tau = 1 - \left(\frac{(c/r)_2}{(c/r)_1}\cdot\frac{\epsilon_1^*}{\epsilon_2^*}\right) \tag{12}$$

χ is still mainly a structural effect, but also due to the differences of ϵ^*. In eq 12, $(-U)_1$ is essentially the solvent energy of vaporization and ν^2 is a parameter characterizing molecular differences between polymer and solvent segments. All parameters may be obtained from equation of state data on polymer and solvent liquids. The first term of eq 12 gives curve 1 of Figure 1b, and both terms together give the total χ (curve 3).

Models of the Liquid State. Various models have been used to predict the empirical, universal $\tilde{V}(\tilde{T})$ curve found by Simha and also the quantities $(-U)$ and C_p of eq 12. So far they are all cell model theories with configurational partition function

$$Q = \Psi^{3cN}e^{-U(V)/kT}$$

Ψ being the Hirschfelder–Eyring cell partition function. The difference between theories lies in the volume dependence assumed for $U(V)$. Prigogine and collaborators originally used a dependence inspired by the 6–12 Lennard-Jones potential, while Flory[4]

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[15] R. Simha and A. J. Havlik, *J. Amer. Chem. Soc.*, **86**, 197 (1964); V. S. Nanda and R. Simha, *J. Phys. Chem.*, **68**, 3158 (1964).

has recently used the inverse volume dependence characteristic of a van der Waals liquid. Such models give a zero value to the configurational C_v, and Prausnitz[16] has added a term to give a finite C_v. It appears that all the equations of state have similar small inadequacies. They predict too sharp a temperature dependence of the thermal expansion coefficient at any value of T, and too slow an increase of the compressibility. This results in a temperature variation of the reduction parameters. The Flory model is probably best, is easy to use, and has been extensively applied.[4]

To illustrate the effect of free volume difference we have made an *a priori* calculation for χ, χ_H, and χ_S at 25° for two mixtures considered above and using eq 11 so that any contact energy dissimilarity is ignored. For polyisobutylene–pentane, the values are χ 0.5, χ_H -0.4, χ_S $+0.9$, whereas for polydimethylsiloxane–hexamethyldisiloxane they are χ 0.1, χ_H -0.1, χ_S 0.2. One sees again that the quantities are much larger for the mixture of less flexible hydrocarbons than for the more flexible silicones.

Effect of Pressure of Polymer Solution Thermodynamics. There is normally a large difference of compressibilities between polymer and solvent. Hence pressure decreases the free volume difference and increases polymer solubility. Figure 5 shows data of Ehrlich[12] on the critical line on a P, T diagram for polyethylene in pentane (curve d). The pressure dependence of the LCST is 0.5°/atm. Similar qualitative behavior is shown by $C_p(P, T)$ in the expression (11) for χ, since it is decreased by pressure. The theory[17] reproduces experiment quite well by setting χ and hence $C_p(P, T)$ constant along the critical line, and using the Flory model to give the functional dependence of C_p on P and T.

In the same way, polyethylene becomes soluble in compressed butane, propane, and ethane by raising the pressure above experimental critical lines in Figure 5. The theory again gives qualitative agreement with experiment, as shown.

Conclusion

This discussion tries to emphasize the qualitative nature of the free volume factor. A more detailed survey of theory and experiment has been published.[18] It gives a discussion, unfortunately in a different mathematical nomenclature from the present, of the very useful solubility parameter theory of χ. The success of this theory may be due to the fact that the solubility parameter is a single quantity which involves the intermolecular forces and also the free volume of the liquid. Incidentally, Hildebrand seems to have been the first to use free volumes in polymer solutions with his derivation of the combinatorial entropy of mixing molecules of different sizes.[19]

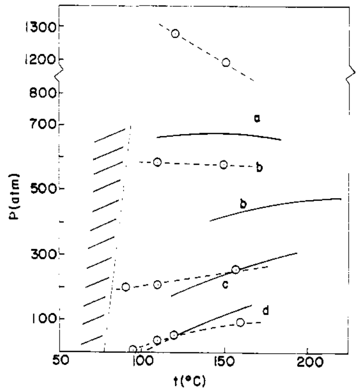

Figure 5. Projections on the P, T plane of critical lines for polyethylene in alkane solvents. The region on the left corresponds to the solid phase of polyethylene: dotted lines, experimental results of Ehrlich and Kurpen[12] using polyethylene of 246,000 molecular weight; full lines, from theory;[17] (a) polyethylene–ethane; (b) propane; (c) butane; (d) pentane.

It may be that the LCST would repay interest by more polymer chemists. Also the use of pressure as a thermodynamic variable in polymer solutions seems of considerable interest. The equation of state of chain-molecule liquids is increasing in importance, as emphasized by Flory. The free volume theories can be applied to other properties such as the surface tension[20] of chain-molecule liquids. It is also possible that the quantitative treatment of free volume by the theories may be of use in developing free-volume theories of the glass transition. Last, it is interesting to speculate that changes of free volume on mixing could affect the relative numbers of different rotational conformations of chain molecules. This would result in a new contribution to polymer solution thermodynamics, particularly to ΔH_M.

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