obtained by examining the ratio of the two equilibrium temperatures by means of eq 9. We find that

$$\frac{T_1}{T_2} = \left(\frac{b - 364}{b - 240}\right)\left(\frac{K_2 - 2.64}{K_1 \quad 1.40}\right) \tag{13}$$

where the subscripts 1 and 2 refer to trifluoroethanol and water, respectively. The equilibrium temperature in H_2O can be taken to be approximately 273°K.[6,8] The ratio T_1/T_2 thus depends on the values of b, K_1, and K_2. If it is assumed that K_1 and K_2 do not vary with temperature, then certain conditions can be established. If $K \gg 2.64$ and b is restricted to the physically sensible range $0 < b < 240$, then T_1/T_2 will be much greater than unity and the equilibrium solubility temperature in trifluoroethanol could easily exceed its boiling point. Only if K approaches 2.64 does the ratio T_1/T_2 approach or become less than unity. Under these circumstances heat precipitation would be expected in trifluoroethanol. Although a rationale can be established for the difference in solubility behavior of poly(L-proline) in trifluoroethanol and in water, a quantitative basis cannot be established without the independent determination of the other parameters that are involved.

The thermodynamic data reported here rule out the possibility of liquid–liquid phase separation (with subsequent crystallization of the polymer in the concentrated phase) as the nature of the phase transition involved. Furthermore, since the molecules of high molecular weight do not adopt an extended rodlike conformation, phase separation by the process described theoretically by Onsager[11] and by Flory[12] cannot be operative either. The only other known process that could describe the phenomena is a liquid to crystal transformation, in dilute solution, wherein the polymer undergoes a cooperative structural change from a statistical to an ordered conformation. The above analysis indicates that the thermodynamic data are consistent with the requirements for this type of transition and reasons can be postulated as to why it is not observed in trifluoroethanol.

A phase separation, thermodynamically similar to the heat precipitation of poly(L-proline) in water, is exhibited by cellulose nitrate in dilute ethanol solution.[22] In this case, phase separation also occurs upon heating, at temperatures below θ, and ψ_1 is negative (in the range −2 to −4). A liquid to crystal phase transition is occurring in this case also. The rate of phase separation is strongly temperature dependent here as it is in the heat precipitation of poly(L-proline).[7,8]

The previous conclusion that the origin of the heat precipitation phenomena resides in the Onsager–Flory theories is clearly in error.[7] At that time, investigations were limited to theoretical conformational analysis and to hydrodynamic studies of low molecular weight polymers. These led to the conclusion of an extended molecular conformation in solution. Optical rotatory dispersion studies[3,7] and the observation of a maximum in the circular dichroism spectra at 228 mμ were taken to support this conclusion. The fact that these spectra were maintained up to the point of precipitation appeared to give further support to this mechanism. However, more recent detailed studies have indicated similar optical properties for high molecular weight samples in water[13] and in concentrated $CaCl_2$[23] solutions, where a statistical conformation is clearly established for the macromolecule. It was concluded, therefore, that the optical properties in dilute solution reflect a locally ordered structure rather than an extended, highly ordered molecular conformation. The molecule as a whole thus adopts a statistical conformation. Therefore, the overall molecular conformational change, required for the crystallization process, could take place but would not necessarily manifest itself in any changes in the optical properties.

Acknowledgment. We wish to thank Professor P. J. Flory for making available to us, many years ago, his calculation for the inverted solubility of crystalline long-chain molecules and granting us permission to include it in the present paper.

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Thermodynamic Properties of Liquids, Including Solutions. V. Poly(propylene oxide) in Carbon Tetrachloride

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ABSTRACT: The author's new theory of the thermodynamic properties of solutions is applied to poly(propylene oxide) + CCl_4 solutions, using experimental data by Kershaw and Malcolm. Good agreement is obtained for excess volumes and excess entropies and, for volume fractions up to one-half, for the interaction parameter χ. Certain entropy factors, not allowed for in the elementary theory used, are discussed as possible causes of the deviations at higher concentrations.

The writer's new theory[1–5] of the thermodynamic properties of solutions can reasonably be expected to be applicable, with some modifications, to many polymer solutions. Several systems for which appropriate data are in the literature are now being studied to test this applicability. In a preliminary report[2] the rubber + benzene and poly(propylene oxide) + carbon tetrachloride systems were dealt with. The present paper gives more details of the application of the theory to the latter system, with some minor changes in

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[2] M. L. Huggins, *Polymer*, in press.

[3] M. L. Huggins, *J. Polym. Sci.*, in press.

[4] M. L. Huggins, *J. Phys. Chem.*, in press.

[5] M. L. Huggins, to be published.

the recommended parameters and more discussion of the theoretical implications.

A major aim of this theory, after it has been amply tested and extended where necessary, is to make it possible to determine most or all of the needed parameters from experimental data on systems containing only simple low molecular weight compounds. This problem will be dealt with in future papers.

Essentials of the Theory. A solution is assumed to behave thermodynamically as if its molecules were composed of chemically uniform segments, with these segments having surfaces in mutual contact. For each segment type (α, β) the average contacting segment surface area (σ_α^0, σ_β^0) is assumed to be constant at a given temperature. For each kind of segment–segment contact ($\alpha\alpha$, $\beta\beta$, $\alpha\beta$), the average contact energy or volume contribution ($\epsilon_{\alpha\alpha}$, $v_{\alpha\alpha}$, etc.) per unit area of contact is assumed to be constant at a given temperature. The relative total contact areas for the different types are assumed to be governed by an equilibrium constant

$$K = \frac{\sigma_{\alpha\beta}^2}{4\sigma_{\alpha\alpha}\sigma_{\beta\beta}} \tag{1}$$

The poly(propylene oxide) + CCl_4 system is tentatively treated as ditonic, with just two kinds of segments. Each solvent molecule is considered to be a single α-type segment and each of the n-mers in each polymer molecule is considered to be a single β-type segment (even though it is chemically far from homogeneous). It is realized that these assumptions may introduce considerable error, but it seems worthwhile to try them nevertheless, because of the considerable simplification thereby achieved.

From the foregoing assumptions and approximations the excess enthalpy and excess volume of mixing per mole of solution are given by the equations

$$\begin{aligned} \tilde{H}^{\mathrm{E}} &= \epsilon_\Delta x_1 z_\beta g_{\mathrm{K}} \\ \tilde{V}^{\mathrm{E}} &= v_\Delta x_1 z_\beta g_{\mathrm{K}} \end{aligned} \tag{2}$$

with

$$\begin{aligned} \epsilon_{\mathrm{A}} &= \sigma_\alpha^0(2\epsilon_{\alpha\beta} - \epsilon_{\alpha\alpha} - \epsilon_{\beta\beta})/2 \\ v_\Delta &= \sigma_\alpha^0(2v_{\alpha\beta} - v_{\alpha\alpha} - v_{\alpha\beta})/2 \end{aligned} \tag{3}$$

$$x_2 = 1 - x_1 = \phi_2/(nr_{\mathrm{v}}\phi_1 + \phi_2) \tag{4}$$

$$z_\beta = 1 - z_\alpha = \frac{nr_\sigma x_2}{1 + (nr_\sigma - 1)x_2} = \frac{r_{\sigma/\mathrm{v}}\phi_2}{1 + (r_{\sigma/\mathrm{v}} - 1)\phi_2} \tag{5}$$

$$r_{\sigma/\mathrm{v}} = r_\sigma/r_{\mathrm{v}} \qquad r_\sigma = \sigma_\beta^0/\sigma_\alpha^0 \qquad r_{\mathrm{v}} = v_\beta^0/v_\alpha^0 \tag{6}$$

$$g_{\mathrm{K}} = \frac{-2}{z_\alpha z_\beta K'}\,[1 - (1 + z_\alpha z_\beta K')^{1/2}] \tag{7}$$

$$K' = 4\left(\frac{1}{K} - 1\right) \tag{8}$$

Here x, ϕ, and z designate mole fraction, volume fraction, and contacting segment surface fraction, respectively. For random mixing

$$K' = 0 \qquad g_{\mathrm{K}} = 1 \tag{9}$$

If n, the average number of mers per polymer molecule, and r_{v}, the ratio of the mer volume to the molecular volume of the solvent, are known, the theoretical equation for $\tilde{H}^{\mathrm{E}}$ (or $\tilde{V}^{\mathrm{E}}$) contains just three parameters (ϵ_Δ, r_σ, K') to be determined experimentally, either (as in the present case) from data on the system being studied or from data on other systems having the same types of segments. If the assumptions of the theory are strictly correct, the same r_σ and K' parameters apply to both $\tilde{H}^{\mathrm{E}}$ and $\tilde{V}^{\mathrm{E}}$.

This should not be true, however, if the volume of a mixture depends not only on the relative volumes associated with intermolecular (or, more generally, intersegment) contacts of the different types but also on other concentration-dependent factors, such as the degree of parallel alignment of neighboring elongated molecules or the degree of coiling of long-chain molecules. In some systems containing only simple molecules of low molecular weight, it has been found that the same r_σ and K' parameters can be used for both $\tilde{H}^{\mathrm{E}}$ and $\tilde{V}^{\mathrm{E}}$, but in other systems different parameters are required.[5]

In dealing with the thermodynamic properties of polymer solutions it is customary to use the "Flory–Huggins equation," relating the chemical potential, $\Delta\tilde{G}_1$, to an interaction parameter χ

$$\frac{\Delta\tilde{G}_1}{RT} = \frac{\Delta\tilde{H}_1 - T\Delta\tilde{S}_1}{RT} = \ln\phi_1 + \left(1 - \frac{\tilde{V}_1}{\tilde{V}_2}\right)\phi_2 + \chi\phi_2^2 \tag{10}$$

For our purpose it is convenient to split the parameter χ into an enthalpy part and an entropy part

$$\chi = \chi_{\mathrm{h}} + \chi_{\mathrm{s}} \tag{11}$$

The enthalpy part is related to the excess enthalpy per mole by the equations

$$\chi_{\mathrm{h}} = \frac{\tilde{H}_1}{RT\phi_2^2} \tag{12}$$

$$\tilde{H}_1 = \left(\frac{\partial\tilde{H}^{\mathrm{E}}}{\partial N_1}\right)_{N_2} \tag{13}$$

with substitution, after the differentiation, of x_1 and x_2 for N_1 and N_2, respectively. One obtains the result

$$\chi_{\mathrm{h}} = \frac{\epsilon_\Delta z_\beta}{RT\phi_2^2}\left(\frac{1 - z_\alpha g_{\mathrm{K}}}{1 + z_\alpha z_\beta K' g_{\mathrm{K}}/2}\right) \tag{14}$$

The entropy of mixing of a solution, according to this theory, is the sum of the "combinatorial entropy," measuring the randomness of placing the molecules in the total volume, and the "orientation entropy," measuring the concentration dependence of the randomness of orientation of the molecules and their component segments.

If the molecules are of the same size and the mixing is perfectly random, the theoretical expression for the molal combinatorial entropy is

$$\tilde{S}_{\mathrm{rm}} = -R(x_1 \ln x_1 + x_2 \ln x_2) \tag{15}$$

which leads to Raoult's law. If the molecules are of different sizes,[4] with perfectly random mixing

$$\tilde{S}_{\mathrm{rm}} = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \tag{16}$$

If the mixing is not perfectly random, the molal combinatorial entropy is less than this. It can be computed by adding to $\tilde{S}_{\mathrm{rm}}$ a (negative) combinatorial entropy correction[4] $\tilde{S}_{\mathrm{cc}}$, the magnitude of which depends on the departure of K from unity (or of K' from zero). For the polymer solutions here considered, the experimental data require K to be very close to one, hence $\tilde{S}_{\mathrm{cc}}$ to be negligible. For this case

$$\tilde{S} = \tilde{S}_{\mathrm{rm}} + \tilde{S}_{\mathrm{or}} \tag{17}$$

The excess entropy of mixing, per mole, is defined as the molal entropy of mixing minus that calculated with the assumption of Raoult's law. Hence, from eq 15–17

$$\tilde{S}^{E} = -R[x_1 \ln (\phi_1/x_1) + x_2 \ln (\phi_1/x_2)] + S_{or} \quad (18)$$

Also, from eq 16

$$\tilde{S}_{1,rm} = -R[\ln \phi_1 + (1 - \tilde{V}_1/\tilde{V}_2)\phi_2] \quad (19)$$

Comparing eq 10 and 19, it is seen that, for random mixing, the combinatorial entropy gives no contribution to the interaction parameter χ.

A nonspherical molecule in a liquid has some randomness of orientation relative to the surrounding molecules, and in general the degree of randomness changes as the environment changes, hence as the concentration of a solution changes. Similarly, the randomness of orientation of the rigid sections of a flexible polymer molecule in a solution must, in general, change with the concentration, and the associated entropy change must contribute to χ_s, the entropy part of the interaction parameter. For the solutions being considered here this is probably the only significant contribution to χ_s, when the polymer concentration is not too great. The theoretical equation for this contribution, derived[4] from the assumptions that have been outlined, is

$$\chi_{s,or} = \frac{-k_s' z_\beta}{r_\sigma \phi_2^2}\left[\frac{(z_\beta - z_\alpha)(1 + z_\alpha z_\beta K')^{-1/2} + z_\alpha g_K}{1 + k_s' z_\alpha g_K}\right] \quad (20)$$

where the parameter k_s' is related to the ratio of $\nu^0(1 - k_s)$, the average randomness of orientation of a polymer segment in pure polymer, to ν^0, that of a polymer segment in infinitely dilute solution

$$k_s' = k_s/(1 - k_s) \quad (21)$$

The parameter k_s' (or k_s) must be determined experimentally. The other two parameters (r_σ and K') are the same as in the equations for $\tilde{H}^E$.

The limiting (infinite dilution) orientation randomness contribution to the interaction parameter is given by the equation

$$\chi_{s,or}^0 = -\frac{k_s}{r_\sigma}\left(\frac{z_\beta}{\phi_2}\right)^2_{\phi_2 \to 0} \quad (22)$$

For a monotonic polymer in a monotonic solvent this reduces to

$$\chi_{s,or}^0 = -k_s r_\sigma / r_v^2 \quad (23)$$

In many solutions—for example, ditonic solutions for which the equilibrium constant K differs considerably from unity—calculation of the combinatorial entropy on the assumption of perfectly random mixing gives an erroneous result. Both the calculated entropy of mixing and the calculated χ_s (for a polymer solution) are in error. A theory to correct for this has been developed and, in a few cases, tested. For the system now being considered, however, we need not be concerned with this correction, since it has been found that K must be quite close to unity to obtain agreement with the $\tilde{V}^E$ and $\tilde{H}^E$ data, and the combinatorial entropy correction to χ_s is negligible.

Application of the Theory. Kershaw and Malcolm[6] have published excellent data on heats and volumes of mixing and on vapor pressures, for solutions of poly(propylene oxide) + CCl_4 at 5.53°. The experimental values of $\tilde{V}^E$, $\tilde{H}^E$, and χ, calculated from their data, are shown as circles in Figures 1-3.

Using smoothed curves to represent the $\tilde{V}^E$ and $\tilde{H}^E$ data, tentative values of these properties at volume fractions of 0.3, 0.5, and 0.7 were obtained. Ratios of these values involve only two unknown parameters (r_σ, K'). The equation, derived from eq 2, is

$$\tilde{H}_{\phi'/\phi}^{E} \text{ or } \tilde{V}_{\phi'/\phi}^{E} = \frac{[1 + (nr_\sigma - 1)x_2'][1 - (1 + K'z_\alpha' z_\beta')^{1/2}]}{[1 + (nr_\sigma - 1)x_2][1 - (1 + K'z_\alpha z_\beta)^{1/2}]} \quad (24)$$

From two ratios ($\tilde{V}_{0.5/0.3}^{E}$ and $\tilde{V}_{0.7/0.5}^{E}$; $\tilde{H}_{0.5/0.3}^{E}$ and $\tilde{H}_{0.7/0.5}^{E}$) for each property, the values of r_σ and K' can be readily determined. The parameters obtained for the two properties were not identical, but were close. Using average values, with the estimated values of $\tilde{V}_{0.5}^{E}$ and $\tilde{H}_{0.5}^{E}$, the third parameter (ϵ_Δ or v_Δ) for each of these properties was calculated. The equation used for this is

$$\epsilon_\Delta \text{ (or } v_\Delta) = \frac{-K'\tilde{H}^{E} \text{ (or } \tilde{V}^{E})}{2[1 + (nr_\sigma - 1)x_2][1 - (1 + K'z_\alpha z_\beta)^{1/2}]} \quad (25)$$

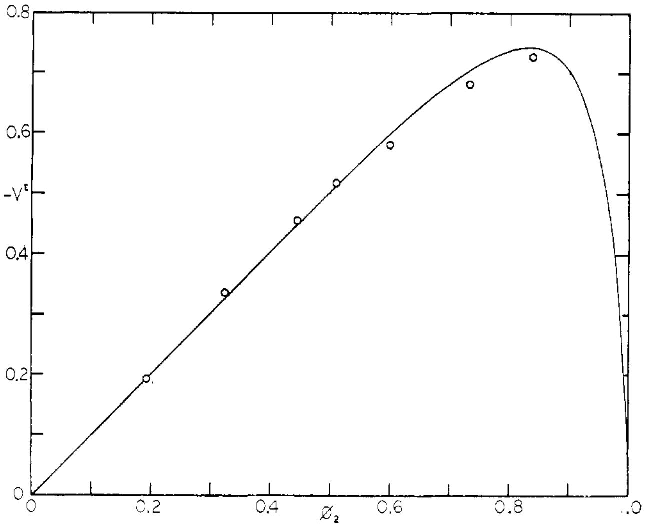

Figure 1. Excess volume of mixing per mole of solution, in milliliters. The curve is theoretical: $r_\sigma = 0.54$; $K' = 0$; $v_\Delta = -1.124$; ○, data by Kershaw and Malcolm.[6]

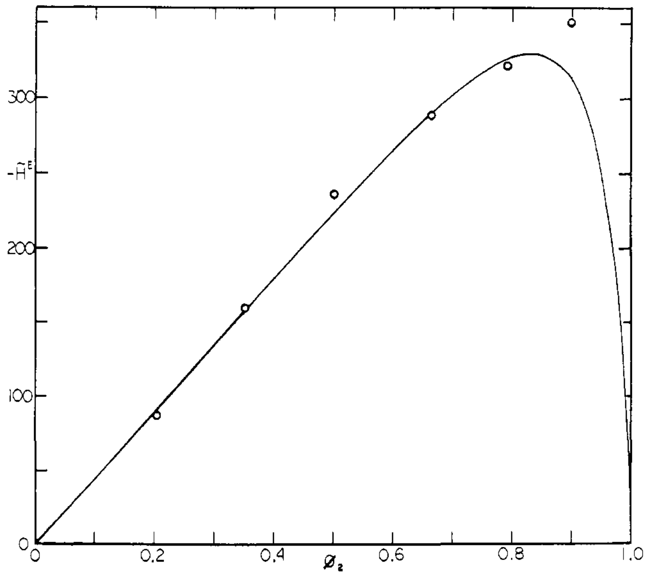

Figure 2. Excess enthalpy of mixing per mole of solution, in calories. The curve is theoretical: $r_\sigma = 0.54$; $K' = 0$; $\epsilon_\Delta = -499$; ○, data by Kershaw and Malcolm.[6]

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[6] R. W. Kershaw and G. N. Malcolm, *Trans. Faraday Soc.*, **64**, 323 (1968).

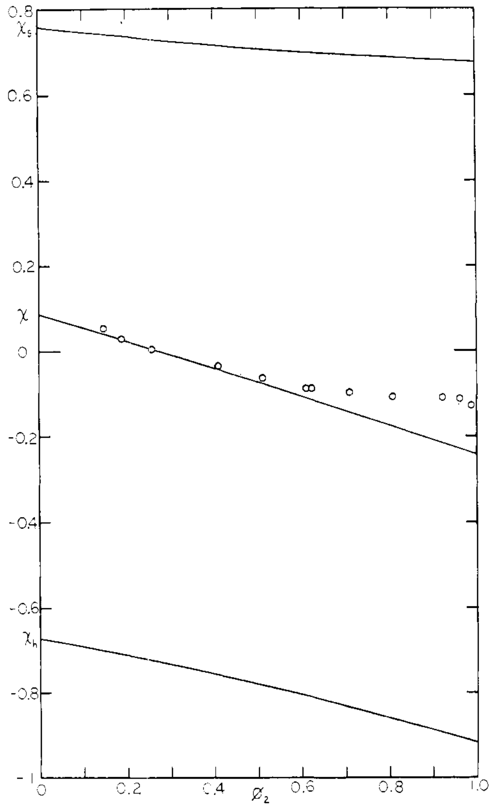

Figure 3. The interaction parameter and its enthalpy and entropy components. The curves are theoretical: $r_\sigma = 0.54$; $K' = 0$; $\epsilon_\Delta = -499$; $k_s' = -0.358$; ○, from vapor pressure data by Kershaw and Malcolm.[6]

Equation 2, with the parameters obtained in this way, then gave the concentration dependence of $\tilde{H}^E$ and $\tilde{V}^E$. The curves (quite close to those in Figures 1 and 2) gave good agreement with the experimental points.

Substituting the r_σ, K', and ϵ_Δ parameters into eq 14 gives the concentration dependence of χ_h. Subtracting χ_h for one concentration (*e.g.*, $\phi_2 = 0.4$) from the value of χ at that concentration, read from a smooth curve through the experimental points, gives χ_s at that concentration. If the only significant contribution to χ_s at that concentration is $\chi_{s,or}$, eq 20 can then be used to compute the k_s' required to give agreement. With this known, the concentration dependence of χ_s and, by adding χ_h, that of χ can be calculated and the latter compared with the experimental points.

This procedure led to curves close to those shown in Figure 3. Agreement was good up to volume fractions of about one-half. Attempts were made, unsuccessfully, to obtain agreement also at higher concentrations, by modifying r_σ, K', and ϵ_Δ (but using only combinations that would give at least fair agreement with the $\tilde{H}^E$ and $\tilde{V}^E$ data points) and by including a contribution, $\chi_{s,cc}$, for the combinatorial entropy correction when K' differed from zero. The curves in the three figures were drawn for $r_\sigma = 0.54$, $K' = 0$. The $\tilde{V}^E$, $\tilde{H}^E$, and χ curves for $r_\sigma = 0.54$, $K' = -0.8$, for example, are practically identical with those shown, and those for $r_\sigma = 0.48$, $K' = 0$ do not differ very much.[2,3] The curves for χ_h and χ_s are fairly sensitive to the choice of parameters, but their sum, χ, is relatively insensitive.

Discussion

The elementary theory and its equations give good agreement with the experimental data for $\tilde{V}^E$ and $\tilde{H}^E$, at least up to volume fractions of about 0.8, and for χ up to about 0.5. The departures between 0.5 and 0.8, at least, must be due to inaccuracies or incompleteness in the theory for χ_s.

This result is not surprising. The simple theory includes no correction for the combinatorial entropy for changes in the effective molecular weight of the polymer as a result of aggregation or entanglement or for entrapment of the solvent molecules, at the higher concentrations. The theory does not allow for a decrease in the orientation entropy at high concentrations, resulting from the same causes. It does not even allow for the greater probability of a second contact between polymer segments after a first contact has been made. Some of these factors have been considered by the writer previously,[7-9] but they were not taken into account in the development of the equations used here. Work is in progress on extensions of the simple theory to allow for these factors.

Another possible cause of differences between the experimental results and the theoretical predictions is the assumption that each mer can be treated as if it were chemically uniform, whereas actually it consists of two parts that are chemically very different and should behave differently as regards their interactions with other groups of atoms. Perhaps this assumption introduces appreciable error only at high polymer concentrations, when there is much polymer–polymer interaction. Studies of the effects of similar approximations in low molecular weight systems and of this and other polymer–solvent systems without making this assumption should be enlightening. Such studies must await the accumulation of the needed parameters from data on simple systems.

It should be noted that the maximum departure of the theoretical curve for χ from the experimental points is only about one-tenth of a unit, hence only about one-tenth the magnitude of χ_h or χ_s.

A detailed comparison of the theory used in this work with other theories of the thermodynamic properties of solutions can best be made after this theory has been applied to a number of systems containing only simple molecules of low molecular weight, but a brief discussion and comparison with the theory of Barker,[10,11] which was used by Kershaw and Malcolm, is certainly in order here.

The fundamental ideas underlying Barker's theory are quite similar to those underlying the theory used in this paper. The present theory, although developed independently, can be considered a refinement of Barker's, just as his is a refinement of earlier theories by Staverman,[12,13] Guggenheim,[14] Tompa,[15] Prigogine,[16] and others.

In the Barker treatment, as applied by Kershaw and Malcolm, the molecules are considered to be composed of chemically different segments or "elements," of two types for the polymer and one type for CCl_4. Each element hypothetically occupies a site of a lattice of arbitrarily assumed coordination number 4. Each element is assigned a number of contact points, the numbers being chosen by consideration of the molecular geometry. The present theory avoids these approximations by introducing the concept of molecular surfaces, with each segment type having an average

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contacting surface area. The surface areas might be estimated from molecular models, but the fraction of the total surface area, for each type, that makes contact with others is difficult to evaluate *a priori*, at least in the present state of our knowledge. (The individual contacting surface areas need not be evaluated, but only their ratios.) In the present treatment the approximation that the polymer molecules contain only a single kind of segment is tried out. With this approximation, only one ratio of contacting surface areas is required. It is evaluated empirically. It would be better, of course, to treat the polymer molecules as composed of two or three kinds of segments; this can be readily done after the appropriate r_σ and K' values have been determined from data on other systems.

In both theories it is necessary to determine an interchange energy (the energy of replacement of like contacts by unlike contacts) for each two types of segments. Kershaw and Malcolm, dealing with three types of segments, must evaluate three interchange energy parameters. One they assume to be zero, another they estimate from data on cyclohexane + CCl_4 mixtures, and the third is given the empirical value required to give agreement with the experimental H^{E} value at one concentration ($\phi_2 = 0.5$).

In both theories the relative numbers (or areas) of contacts of the different types are governed by one or more equilibrium constants, each related to the interchange energies by an equation[1] of the form

$$K_{\alpha\beta} = A \exp(-\Delta\epsilon_{\alpha\beta}/kT) \qquad (26)$$

Barker assumes $A = 1$ and $k =$ the gas constant R (for interchange energies per mole of contacts). Since the writer is doubtful about the justification for these assumptions, he prefers, at least until after the temperature dependence of the parameters for more systems has been studied, to consider each K as an independent parameter, to be determined empirically from experimental data, either on the system being studied or on another system having the same kinds of contacts.

In both theories, part of the entropy is related to the randomness of distributing the contacts (or unit contact areas) of the different types. This randomness, in turn, is related to the relative numbers of the different types of contacts as determined by the above-mentioned equilibrium relationship. For the system here considered, this part of the entropy is essentially that calculated assuming perfect randomness, leading[4] to the relationships of eq 18 and 19.

Barker[11] also assumes a contribution, to the excess entropy of mixing, of changes in the extent of vibrational or other motion of the contacting molecules or parts of molecules relative to their contact "points." This corresponds to the orientational randomness entropy, $\tilde{S}_{\mathrm{or}}{}^{\mathrm{E}}$, in the present theory. The magnitude of the contribution and its concentration dependence are determined by Barker with the aid of measurements of the temperature dependence of G^{E}. Kershaw and Malcolm (like the writer) adjust a parameter to give agreement, at one concentration, between TS^{E} and the difference between the experimental excess enthalpy and excess free energy.

Some comment should be made about the assumption, made by Prigogine,[16] Flory,[17] and others, that the excess enthalpy and entropy of mixing are related to the excess volume of mixing in the same way that the enthalpy and entropy changes on heating or compressing a pure liquid are related to its volume changes. This assumption is based on the concepts that the entropy of mixing is primarily dependent on the "free volume" and that the excess volume of mixing measures a free volume change. The writer believes this reasoning to be fallacious. The volume change on mixing measures principally the change in volume when contacts between like molecules or molecular segments are replaced by contacts between unlike molecules or segments. This replacement may or may not affect the free volume. It will affect the entropy indirectly, by altering the randomness of distribution of the molecules and intermolecular contacts (the combinatorial entropy) and the randomness of orientation of the molecules and segments (the orientation entropy), but these effects should not follow the "equation of state" relations.

It should be emphasized that the primary purpose of this paper is not to show that the new theory gives better agreement with experiment for this system than does any other theory, but rather to show that the fundamental assumptions of this theory are not in contradiction with the data and to illustrate procedures that can be used in applying the theory to polymer solutions. As has been pointed out, the theory presents the hope that most or all of the parameters required for predicting the thermodynamic properties of polymer solutions can be obtained from experimental measurements on mixtures of simple compounds of low molecular weight.

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