which does not have a fundamental structural significance. Both the corresponding states and the parachor theories relate the decrease of γ with decreasing M to an increase of the free volume of the liquid, as represented by the reduced volume $\tilde{V}$ or the reduced temperature $\tilde{T} = T/T^*$. One would expect a relation to exist between the decrease of γ from γ_∞, *i.e.*, $\gamma(M)/\gamma_\infty - 1$ and the decrease of $1/T^*$ from $1/T^*_\infty$, *i.e.*, $T^*_\infty/T^* - 1$. We have found that for the polymers considered here, $\gamma(M)/\gamma_\infty - 1$ is directly proportional to $(T_\infty^*/T^* - 1)^{2/3}$. Elementary arguments stemming from the significance of T^* show that $T_\infty^*/T^* - 1$ should be very close to proportional to M^{-1}, and this has been found to be the case for the present systems. Thus $\gamma(M)/\gamma_\infty - 1$ is proportional to $M^{-2/3}$ which is equivalent to eq 1.

Conclusions

We draw the following conclusions from this study.

(1) The solubility parameter relation for γ gives poor results when V is replaced in eq 4 by the polymer repeat unit, but the modified form, eq 16, gives reasonable results. Nevertheless, the temperature dependence of γ is too small and the Gaines-LeGrand relation, eq 1, is not accurately predicted.

(2) Both the corresponding states and parachor theories give satisfactory predictions of the temperature and molecular weight dependences of γ. It is probably fair to consider the corresponding states approach as a justification of the more empirical parachor method. However, the parachor is clearly far superior as regards practical utility since it requires only density data, whereas the corresponding states theory requires thermal expansion coefficients, and compressibilities or CED data. We suggest that the comparison of the parachor and corresponding states theory predictions should be continued as equation of state and surface tension data become available for more polymers.

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Prediction of the χ Parameter by the Solubility Parameter and Corresponding States Theories

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ABSTRACT: Values of the polymer-solvent interaction parameter, χ, are predicted using the solubility parameter theory and the corresponding states theory in the form given by Flory and collaborators. The theories predict a similar effect on χ of changing molecular parameters such as the solvent chain length, polymer and solvent cohesive energy, and polymer flexibility. Surprisingly similar predictions are also given for the temperature and pressure dependence of χ. The corresponding states theory treats the changes of volume occurring in polymer and solvent during mixing. The simple solubility parameter theory can also take these changes into account, although this is not apparent in its derivation.

According to the solubility parameter theory[2] (SPT) the polymer(2)-solvent(1) interaction parameter, χ, is related to the difference between the solubility parameters, δ, of the two components through

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + \beta \tag{1}$$

$$= \frac{(\Delta E^{\mathrm{v}})_1}{RT}\left[1 - \frac{\delta_2}{\delta_1}\right]^2 + \beta \tag{2}$$

$$\delta = \left[\frac{\Delta E^{\mathrm{v}}}{V}\right]^{1/2} \tag{3}$$

Here ΔE^{v} and V are the molar energies of vaporization and molar volumes; β is an empirical constant absent in the original theory applied to mixtures of quasi-spherical molecules, but found necessary for polymer systems.[2a] These simple equations have been of great utility in predicting polymer solubility and other polymer properties. The success of the theory is attested by its continued development,[3,4] particularly for systems with polar and hydrogen-bonded solvents, and until recently it was the only theory used extensively.

In the last few years, however, the corresponding states theory (CST) of Prigogine[5] has attracted attention, particularly in the modified form of Flory and collaborators.[6a] This theory also gives[6b] the temperature and pressure dependence of the χ parameter which is generally considered to be beyond the powers of the SPT, and predicts a concentration dependence for χ which is completely ignored by the older theory. Fur-

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(1) On leave of absence from the Institute of Macromolecular Chemistry, Czechoslovak Academy of Science, Prague, Czechoslovakia.

(2) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," Reinhold, New York, N. Y., 1950; (a) Chapter 20; (b) Chapter 7; (c) Chapter 8.

(3) H. Burrell, *Off. Dig. Fed. Soc. Paint Technol.*, **27**, 726 (1955).

(4) C. M. Hansen, *J. Paint Technol.*, **39**, 104, 505, 511 (1967), and references cited.

(5) I. Prigogine, A. Bellemans, and V. Mathot, "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam, and Interscience, New York, N. Y., 1957, Chapter 16.

(6) (a) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035, 2053, 2061, 2066 (1968); (b) D. Patterson, *J. Polym. Sci., Part C*, **16**, 3379 (1968).

thermore the bases of the two theories appear to be quite different. The familiar squared term of eq 1 reflects[2b] the relative weakness of the (1–2) contact compared with the (1–1) and (2–2) contacts in the pure liquids as expressed by the interchange energy

$$\Delta w = \frac{1}{2}(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \tag{4}$$

Use is made of the geometric mean rule $\epsilon_{12} \simeq (\epsilon_{11}\epsilon_{22})^{1/2}$ to give

$$\Delta w \simeq \frac{1}{2}(\epsilon_{11}{}^{1/2} - \epsilon_{22}{}^{1/2})^2$$

Thus χ is related to a dissimilarity between contact energies ϵ_{11} and ϵ_{22} in the pure liquids. On the other hand, the CST associates the noncombinatorial free energy of mixing and hence the χ parameter with two dissimilarities[7] between the components: (1) in contact energies and (2) in free volumes or thermal expansions. Like the SPT, the CST was primarily concerned with mixtures of quasi-spherical molecules. The new contribution (2) is in fact small for these systems but becomes dominant for polymer solutions where it accounts for a good deal of characteristic behavior, such as phase separation at high temperatures. One is tempted to conclude that the SPT, apparently ignoring these free volume effects, must give way to the newer theory. In the present work we amplify a previous argument[8] that δ, through its definition (eq 3) in fact reflects the free volume or thermal expansion of the liquid. Model calculations show that there is a semiquantitative agreement between the predictions of the two theories in a whole range of test cases. These include the temperature and pressure dependence of χ. Scott has warned[9] against using the SPT to make such detailed predictions. We believe that the theory, probably fortuitously, is capable of more than would be expected from its derivation.

We first recall a well-known modification[2c] of the SPT designed to take account of an overall volume during the mixing process. The original Hildebrand–Scatchard work used the solubility parameters to obtain the energy change (ΔE_{M}) on mixing the components under constant total volume of the system,[2b] *i.e.*, a hypothetical pressure, which can be negative, is applied to the solution so that the ΔV_{M} is eliminated. The entropy of mixing under these conditions was assumed to be totally combinatorial in nature, so that χ, representing the noncombinatorial part of the free energy of mixing, would be completely energetic in origin and equal to the first term of eq 1. Later work,[2c] however, explicitly considered the constant pressure condition, determining the effects of relaxing the hypothetical pressure so that ΔV_{M} is not necessarily zero. It was shown that ΔE_{M} and ΔS_{M} would be modified by the volume of mixing, but in such a way as to cancel completely in the free energy. Thus χ is again given by eq 1 but the first term cannot still be considered as energetic in origin. (The empirical constant β was justified[2a] as a correction to the Flory combinatorial entropy. β, although combinatorial in origin, was attached to χ in order to preserve the Flory form of the chemical potential expression.)

The CST approaches the role of volume changes in a quite different way. The components start from their different "free volumes" [10] which change in opposite directions during the mixing process to attain the same free volume characteristic of the solution. Associated with the free volume changes are changes of H, S, and G. As stressed by Flory[11] the volume changes of the components could cancel to give $\Delta V_{\mathrm{M}} = 0$ and mixing at constant volume, but they still make a large net contribution to the other thermodynamic mixing functions, including the entropy. The free energy of mixing at constant pressure now contains a large contribution from the volume changes, which is verified experimentally by the presence of the lower critical solution temperature in polymer solutions. This indicates that the SPT treatment of volume changes is inadequate, but at the same time the success of eq 1 in polymer solution thermodynamics demands an explanation. This seems to be that δ, as defined by eq 3, does depend on the free volume of the liquid through both ΔE^{v} and V. Furthermore the effect of free volume is to cause eq 1 to give predictions which are qualitatively similar to those of the CST. For instance, a series of homologs of increasing molecular weight will have increasing δ values because of the decreasing free volume of the homologs. The high polymer of the series with a homolog as solvent will thus have a nonzero $(\delta_1 - \delta_2)^2$ value solely due to the free-volume difference. Furthermore the theory gives qualitatively correct temperature and pressure dependencies of χ through

$$\left[\frac{\partial \ln \delta}{\partial T}\right]_P \simeq -\alpha_P \tag{5}$$

$$\left[\frac{\partial \ln \delta}{\partial P}\right]_T = +\beta_T \tag{6}$$

where α_P and β_T are the thermal expansion coefficient and isothermal compressibility. Both of these quantities are much larger for the solvent than for the polymer. The decrease of δ as T increases is much more rapid for the solvent than for the polymer so that at high enough temperature $(\delta_1 - \delta_2)^2$ will reach a value sufficient to cause phase separation. Similarly χ is predicted to decrease with pressure when $\delta_1 < \delta_2$ and increases when $\delta_1 > \delta_2$ which is in reasonable agreement with experiment. In order to make a quantitative comparison of the predictions of the two theories we require the CST expression for χ.

Detailed Expressions for the χ Parameter

Corresponding States Theory. In the CST[6b] the molecule is characterized by the molecular parameters shown in eq 7 obtainable from equation of state

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[7] D. Patterson, *Macromolecules*, **2**, 672 (1969).

[8] D. Patterson, *Rubber Chem. Technol.*, **40**, 27 (1967).

[9] J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice Hall, Englewood Cliffs, N. J., 1962, p 103.

[10] By "free volume" we mean the degree of expansion of the liquid over the close-packed volume, measured by the reduced volume, $\tilde{V}$, in the CST.

[11] P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).

$$T^* = \frac{U^*}{S^*} = \frac{\epsilon^*}{(c/q)k}$$
$$P^* = \frac{U^*}{V^*} = \frac{q\epsilon^*}{r\sigma^3} \qquad (7)$$

properties of the liquid. Here r, q, and c are effective numbers of segments from the point of view of, respectively, volume, energy, and entropy, and we can set $q \simeq r$; ϵ^* and σ are the intermolecular energy and distance parameters for the interaction between segments. The quantity $3c$ is equal to the number of external degrees of freedom of the molecule. The structural factor $c/q \simeq c/r$ reflects the flexibility or molecular mobility of the chain, and also its length. It is linear in $1/r$; *i.e.*, $c/r = a + b/r$, a being a measure of the flexibility.

The following general expression was derived[6b] for the χ parameter at low polymer concentration and at zero pressure

$$\chi = -\frac{U_1}{RT}\nu^2 + \frac{C_{p,1}}{2R}\tau^2 \qquad (8)$$

or in the reduced form, where the tilde superscript indicates a reduced quantity

$$\frac{\chi}{c_1} = -\frac{\tilde U_1}{\tilde T_1}\nu^2 + \frac{\tilde C_{p,1}}{2}\tau^2 \qquad (8a)$$

where U_1 is the configurational energy of the solvent, essentially the negative of the energy of vaporization, and $C_{p,1}$ is the configurational heat capacity or temperature derivative of U_1. The second term of eq 8 reflects differences in free volume between the components through the parameter τ

$$\tau = 1 - \frac{T_1^*}{T_2^*} \qquad (9)$$

It is helpful to notice from the definition of T^* that τ depends on the ratio of the contact energies ϵ^* of the components and also, through the structural factors, on their relative flexibilities and chain lengths. In the first term, ν^2 is a measure of the relative weakness of the (1–2) contact to the average of (1–1) and (2–2) contacts. It has usually been fixed by experiment, but if the geometric mean rule is valid

$$\nu^2 = \left[1 - \left(\frac{\epsilon_{22}}{\epsilon_{11}}\right)^{1/2}\right]^2 \qquad (10)$$

It is usual to put $q \sim r$ so that the ratio $\epsilon_{22}/\epsilon_{11}$ may be obtained from the experimentally accessible P_2^*/P_1^* if $\sigma_2 = \sigma_1$. For simplicity we assume this to be the case in what follows so that

$$\nu^2 = [1 - (P_2^*/P_1^*)^{1/2}]^2 \qquad (11)$$

An expression similar to eq 8 has been derived for χ as a function of pressure[12]

$$\frac{\chi}{c_1} = -\frac{\tilde U(\tilde P)}{\tilde T}\nu^2 + \frac{\tilde C_{p,1}(\tilde P)}{2}\left[\tau + \frac{\tilde\beta_{T,1}\tilde P}{\tilde\alpha_P\tilde T}\pi\right]^2 \qquad (12)$$

where

$$\pi = P_1^*/P_2^* - 1 \qquad (13)$$

A significant feature of the derivations of eq 8 and 12 is that only the second order has been retained of the difference parameters ν, τ, and π. Flory and collaborators have given an expression for χ at zero pressure using their CST (eq 49–51 of ref 5) based on a particular model of the liquid state

$$\chi = \frac{P_1^*V_1^*}{RT\tilde V_1}\left[\left(\frac{s_2}{s_1}\right)^2\frac{X_{12}}{P_1^*} + \frac{\alpha_P T}{2}\left\{\left(\frac{P_2^*}{P_1^*}\right)\tau - \frac{s_2X_{12}}{s_1P_1^*}\right\}^2\right] \qquad (14)$$

The Flory model assumes a van der Waals liquid with

$$-\tilde U = \tilde V^{-1} \qquad (15)$$

and a cell partition, and gives the following equation of state

$$\frac{\tilde P\tilde V}{\tilde T} = 1/(1 - \tilde V^{-1/3}) - 1/\tilde V\tilde T \qquad (16)$$

However eq 14 and 8 are in fact very similar. Equations 15 and 16 show that in the Flory model

$$\frac{\alpha T}{\tilde V} = \tilde C_p \qquad (17)$$

and eq 14 can be put in the form

$$\chi = -\frac{U_1}{RT}\left(\frac{s_2}{s_1}\right)^2\frac{X_{12}}{P_1^*} + \frac{C_{p,1}}{2R}\left\{\frac{P_2^*}{P_1^*}\tau - \frac{s_2X_{12}}{s_1P_1^*}\right\}^2 \qquad (18)$$

The difference between eq 18 and 8 lies in nomenclature and in the neglect of third powers of small differences in eq 8. A general derivation of eq 18 can be given.[13] In calculations we have replaced τ in eq 8 and 12 by the complete expression

$$\left(\frac{P_2^*}{P_1^*}\tau - \frac{s_2X_{12}}{s_1P_1^*}\right)$$

and have taken the ratio (s_2/s_1) to be unity. In using eq 12 to give the pressure dependence of χ we have adopted the Flory model to give the thermodynamic properties of the solvent and, obtaining

$$\frac{\chi}{c_1} = \frac{\nu^2}{\tilde V_1\tilde T_1} + \frac{\tilde C_p}{2}\left[\left(\frac{P_2^*}{P_1^*}\tau - \frac{X_{12}}{P_1^*}\right) + \frac{\tilde P\tilde V^2}{\tilde P\tilde V^2 + 1}\pi\right]^2 \qquad (19)$$

with

$$\tilde C_p^{-1} = \left(1 - \frac{2}{3}\tilde V^{-1/3}\right) - 2(1 - \tilde V^{-1/3})/(\tilde P\tilde V^2 + 1) \qquad (20)$$

By setting $\tilde P = 0$, a zero pressure form is obtained which is equivalent to eq 8a with the solvent thermodynamic properties taken from the Flory model.

Solubility Parameter Theory. Turning to the SPT, eq 3 and 15 give

$$\delta = -\left(\frac{U}{V}\right)^{1/2} = \frac{P^{*1/2}}{\tilde V} \qquad (21)$$

On substituting in eq 1 the χ parameter as a function of temperature and pressure is given by the simple equation

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(12) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).

(13) D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, in press.

$$\frac{\chi}{c_1} = \frac{1}{\tilde{V}_1 \tilde{T}_1}\left[1 - \left(\frac{P_2^*}{P_1^*}\right)^{1/2}\left(\frac{\tilde{V}_1}{\tilde{V}_2}\right)\right]^2 + \beta \qquad (22)$$

Comparison of Predictions of the Theories

We shall compare the values of χ parameters predicted by the two theories to show the effect of (1) variation of the molecular parameters at 300°K and constant negligible pressure; (2) variation of the temperature at constant negligible pressure; (3) variation of the pressure at constant temperature.

Variation of Molecular Parameters. Homologous Series of Solvents. For convenience a particular polymer is adopted of infinite molecular weight with $T_2^* = 7000$°K and $P_2^* = 100$ cal/cm^3 (corresponding to a hydrocarbon such as polyethylene), and $a = {}^1/_3$. A homologous series of solvents is considered and we take as an example (reasonable for n-alkanes)

$$\begin{aligned}(c_1/r_1) &= {}^1/_3 + 1/r_1 \\ r_1 &= (n + 1)/2\end{aligned} \qquad (23)$$

where n is the number of carbons. The polymer and the solvent chain therefore have the same flexibility. The dependence of χ on chain length of the solvent is shown in Figure 1a for three values of the ratio $\epsilon_{11}^*/\epsilon_{22}^*$. This ratio and eq 23 allow T_1^* and P_1^* to be calculated together with $\tilde{T}_1$. Using the Flory equation of state (eq 16), $\tilde{V}_1$ and $\tilde{V}_2$ are found whence the χ parameter may be calculated from eq 22 for the SPT, and from eq 19, with $\tilde{P} = 0$, for the CST. Figure 1b shows the value of χ plotted against the solvent solubility parameters. When $\epsilon_{11}^*/\epsilon_{22}^* > 1$, *e.g.*, polydimethylsiloxane in the n-alkane series, both theories predict a minimum in χ. This occurs at $\delta_1 = \delta_2$ in the SPT and at a value of δ_1 very close to δ_2 in the CST. Thus the only difference between the predictions is in the absolute values of χ which are some 0.3 higher than for the CST. The usual size[14] of the empirical constant β ($\simeq$0.34) presents a difficulty if it is to be explained as an error in the Flory–Huggins combinatorial entropy approximation. The present result suggests that β should be interpreted as bringing the SPT χ values in line with those from the CST. When $\epsilon_{11}^*/\epsilon_{22}^* = 1$, *e.g.*, polyethylene or polyisobutylene in n-alkanes, the solvent of infinite chain length is identical with the polymer and both theories predict a zero value for χ if $\beta = 0$. In the region of usual solvent chain length, however, the CST still predicts χ values about 0.3 higher than the SPT which we interpret as the justification of the β parameter. With $\epsilon_{11}^*/\epsilon_{22}^* < 1$, the minimum value of χ reappears, but at a value of δ_1 less than that of the polymer. It is thus not always correct to put the polymer χ value equal to that of the homolog which gives maximum swelling of the polymer. This is seen[15] in the case of the swelling of rubbers, *e.g.*, SBR, neoprene, and butadiene–acrylonitrile, in the alkanes. The rubbers have values of the solubility parameters about 9–10 whereas maximum swelling with the n-alkane series usually occurs in heptane where $\delta_1 = 7.4$.

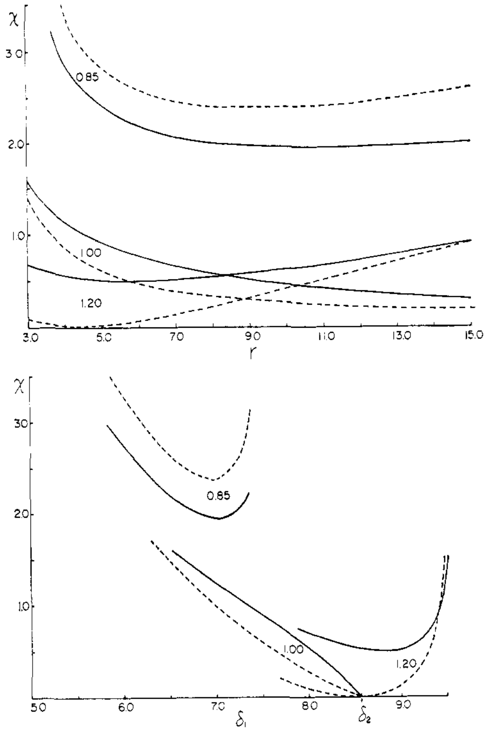

Figure 1. (a) The interaction parameter, χ, as a function of the solvent chain length, r_1, at $T = 300$°K, $P = 0$ for the following values of $\epsilon_{11}^*/\epsilon_{22}^*$: 0.85, 1.00, and 1.20. Full line from CST; dashed line from SPT. (b) The interaction parameter, χ, as a function of the solvent chain length, r_1, at $T = 300$°K, $P = 0$, plotted against the solubility parameter of the solvent (δ_1), for the following values of $\epsilon_{11}^*/\epsilon_{22}^*$: 0.85, 1.00, and 1.20. Full line from CST; dashed line from SPT.

Solvents of Different Cohesive Energy. It is also instructive to consider the variation of χ in the two theories when the $\epsilon_{11}^*/\epsilon_{22}^*$ ratio is varied at constant chain length of the solvents, as presented in Figure 2. As the cohesive forces in the solvent increase, its solubility parameter increases and for both theories χ reaches a minimum either at or very close to the solubility parameter of the polymer. However, the minimum of χ does not occur in either theory at $\epsilon_{11}^*/\epsilon_{22}^* = 1$ which would correspond to polymer and solvent being

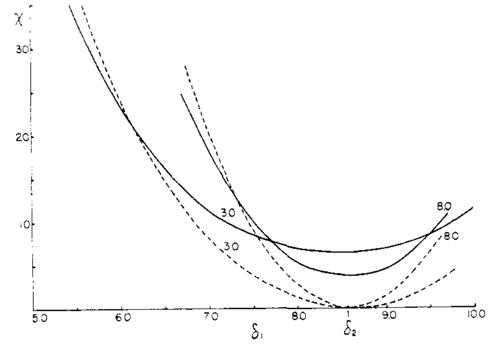

Figure 2. The interaction parameter, χ, as a function of the $\epsilon_{11}^*/\epsilon_{22}^*$ at $T = 300$°K, $P = 0$, plotted against the solubility parameter of the solvent (δ_1). The curves are for two values of the solvent chain length, r_1: 3.0 and 8.0. Full line from CST; dashed line from SPT.

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(14) R. F. Blanks and J. M. Praunsnitz, *I.E.Ch. Fund.*, 3, 1 (1964).

(15) G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).

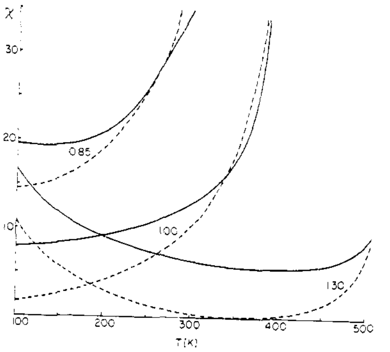

Figure 3. The interaction parameter, χ, as a function of temperature at $P = 0$, for the chain length of the solvent, $r_1 = 3.5$. The curves are for the following values of $\epsilon_{11}^*/\epsilon_{22}^*$: 0.85, 1.00, and 1.30. Full line from CST; dashed line from SPT.

from the same homologous series, *e.g.*, polyethylene and pentane. The solubility parameter also reflects the free volume of the liquid and hence the molecular chain length. Thus $\delta_1 = \delta_1$ occurs when ϵ_{11}^* is somewhat greater than ϵ_{22}^*, the greater cohesive energy of the solvent causing its free volume to approach that of the polymer, decreasing the value of χ at the expense of introducing a contact energy difference which increases χ. The correct balance for a minimum value is found at $\delta_1 = \delta_2$ in the SPT. The same balance between contact energy difference and free volume difference is seen in the CST. When $\epsilon_{11}^*/\epsilon_{22}^* = 1$ the ν^2 parameter disappears but the second, free volume term of χ remains large. An increase of $\epsilon_{11}^*/\epsilon_{22}^*$ ratio gives a nonzero value of ν^2 but χ continues to decrease due to the decrease of the free volume term. Interpreting β as being the difference between χ parameters given by the two theories, one notices that β is negative for a very small value of the ratio $\epsilon_{11}^*/\epsilon_{22}^*$. However, in this region the polymer would certainly be insoluble in the "solvent" and hence the result is not inconsistent with the choice of $\beta \simeq 0.34$ for the usual polymer–solvent systems.

Flexibility of the Polymer. It is also of interest to note that both the SPT and CST show that the χ parameter depends on the flexibility of the components. We have varied the (c_2/r_2) parameter of the polymer for constant values of $\epsilon_{11}^*/\epsilon_{22}^*$ and chain length of the solvent. As (c_2/r_2) is decreased, corresponding to a decreased flexibility and free volume of the polymer, δ_2 is increased with a corresponding effect on the χ value calculated from the SPT. The free volume term of the CST expression for χ is changed in a similar way and the theories give similar results for the change of χ with change of polymer flexibility.

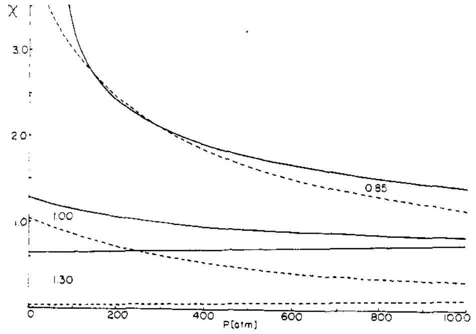

Figure 4. The interaction parameter, χ, as a function of pressure at $T = 300$°K for the chain length of the solvent $r_1 = 3.5$. The curves are for the following values of $\epsilon_{11}^*/\epsilon_{22}^*$: 0.85, 1.00, and 1.30. Full line from CST; dashed line from SPT.

The Temperature Dependence of χ. One of the successes of the CST has been its ability to predict an increase of the χ parameter with increasing T leading to phase separation at sufficiently high temperature. This is due to the second, free volume term in the expression for χ, which increases without limit as the critical temperature of the solvent is approached. It is not so well known that the SPT can predict qualitatively similar behavior. Figure 3 shows χ *vs.* temperature for fixed chain length of the solvent and flexibility of the polymer, but with the three values of $\epsilon_{11}^*/\epsilon_{22}^*$. With $\epsilon_{11}^*/\epsilon_{22}^* = 1$ the contact energy term in the CST vanishes and with the Flory model used here the free volume term increases montonically with increasing temperature imposing the same dependence on the χ parameter. The same behavior is predicted by the SPT. For $\epsilon_{11}^*/\epsilon_{22}^* = 1$, $\delta_1 < \delta_2$, and as T increases, δ_1 decreases rapidly compared with δ_2. Hence $(\delta_1 - \delta_2)$ increases with temperature, predicting an increase of χ.

Thus both theories can predict the phase separation of polymer solutions at the lower critical solution temperature. For $\epsilon_{11}^*/\epsilon_{22}^* > 1$ corresponding, for instance, to polyisobutylene–benzene, $\delta_1 > \delta_2$ at normal temperatures. The rapid decrease of δ_1 with temperature therefore carries it past δ_2 and the SPT predicts a decrease of χ below its value at the upper critical solution temperature, then an increase toward the lower critical solution temperature. Both theories predict χ increasing with T in the normal temperature range when $\epsilon_{11}^*/\epsilon_{22}^* < 1$ and hence when $\delta_1 < \delta_2$. An example of such a choice of parameters would be polystyrene–cyclohexane which must have χ decreasing with T around 34°, the well-known Θ temperature. Such a decrease of χ with T is also predicted by the two theories but at unrealistically low temperatures. This error in the CST, and possibly also in the SPT, is due to an overemphasis of the free volume term in the present model.

The Pressure Dependence of the χ Parameter. The CST predicts[7] a pressure dependence of the χ parameter through the effect on the free volume of the two components. Figure 4 shows that the pressure dependence is predicted in a quite similar fashion by the SPT where the δ of the relatively compressible solvent is increased more rapidly by pressure than that of the polymer. The Flory equation of state, eq 16, again gave $\tilde{V}_1$ and $\tilde{V}_2$ for use in eq 22 for the SPT and eq 19 for the CST. When $\epsilon_{11}^*/\epsilon_{22}^* \leq 1$, $\delta_1 < \delta_2$ and hence $\mathrm{d}\chi/\mathrm{d}P < 0$ in the SPT and also in the CST. When $\epsilon_{11}^*/\epsilon_{22}^*$ is sufficiently greater than unity, however, $\delta_1 > \delta_2$ and the solvent becomes less compressible than the polymer. Then pressure can increase the $(\delta_1 - \delta_2)$ term giving $\mathrm{d}\chi/\mathrm{d}P > 0$.

The Influence of (s_2/s_1) Parameter. In the above computations the s_2/s_1 parameter of eq 18 was set equal to unity. Further computations were made with values of s_2/s_1 less than unity which may, in fact, be encountered in polymer–solvent systems.[6a] The shapes of the curves in the figure are not changed but the absolute values of the χ parameter are decreased, which decrease the values of the β parameter. However the conclusion of the similarity of results calculated from the SPT and CST remains unaffected.

Conclusions

Remarkably similar predictions are obtained using the SPT and the CST plus Flory model of liquid state. The CST has drawn attention to the important role played by free volume in polymer solution thermodynamics. It seems that the SPT is also successful in treating free volume effects. We believe that the great popularity of the solubility parameter approach, particularly in industrial laboratories, is entirely justified.

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Analysis of Polydisperse Systems at Sedimentation Equilibrium. I. Simple Solvent Systems

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ABSTRACT: An analytical procedure is developed which permits the complete characterization of polydisperse systems. The computational algorithm involves a nonlinear "least squares" determination of the unknown coefficients for an equation describing sedimentation equilibrium. It is demonstrated that by the appropriate modification of the functional form or the selective application of constraints on the coefficients the same basic algorithm can encompass the requirements of associating heterogeneous systems with sufficient flexibility to accept the data forms produced by the interference, photoelectric scanning, and schlieren optical systems. The possibility of treating several other aspects of the analysis of systems at sedimentation equilibrium is noted as well as the applicability of the basic computational procedure to general problems of data analysis.

The analytical ultracentrifuge is an experimental tool of great power. Not the least aspect of this instrument is its potential for determining molecular weights of macromolecules. In the absence of significant heterogeneity, molecular weights can be determined with ease and reliability. Such systems are, however, neither extremely common nor are they particularly exciting. A large proportion of real systems will contain contaminants which may or may not be experimentally important. Even more significant are systems which involve association as a function of concentration and/or solvent composition. Two approaches have been available for the interpretation of sedimentation equilibrium experiments in these cases. The most generally employed analytical procedures have involved the determination of apparent average molecular weight distributions.[1–9] For the special cases where association occurs these distributions have been analyzed for the molecular weights and association constants. Likewise for systems involving self-association the direct determination of the monomer molecular weight and association constants by fitting the data to specific model systems has been proposed.[10,11]

It is the purpose of this paper to demonstrate that an analysis of the total observed radial distribution can provide a direct determination of the molecular weights and concentration distributions of each component not only for associating systems but also for the general case of a heterogeneous system.[12] At the same time the considerations required for optimum experimental design will be considered. For a thorough analysis of sedimentation phenomena it would be necessary to include the possibility of preferential interactions and of density gradients not ordinarily allowed for in simple analyses. In the present work we will only indicate the direction to be taken for these two considerations as they will be considered in depth subsequently.

Theory

The sedimentation equilibrium relationship, presented by Svedberg and Pederson[14] in their classic treatise on the ultracentrifuge, has been the basis for most equilibrium analyses performed. This relationship is normally expressed according to eq 1, in which M is the

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