low while the virial coefficient remained the same as before. Such behavior suggests that large nonideality extensively suppresses the effects of heterogeneity as was expected from eq 15. Thus, the applicable limits of the method may be broader than suggested above.

Conclusions

The experimental data from sedimentation equilibrium in a single equilibrium run may be expressed as an apparent molecular weight, M_{App}, which is a function of the concentration of the solute, which, in turn, depends on the radial distance. Two methods are proposed for evaluation of the experimental dependences: (1) a plot of $1/M_{\mathrm{App}}$ vs. c and (2) a plot of $1/M_{\mathrm{App}}{}^{1/2}$ vs. c. In both cases the intercept of the straight line through the experimental points yields the molecular weight; the slope yields the second virial coefficient.

For ethyl acetate solutions of polystyrene, which represent moderately nonideal mixtures, both methods yield reasonable molecular weights. For highly nonideal benzene solutions of polystyrene only the square-root plot (2) yields reasonable values of molecular weight; a linear plot (1) yields too high a value.

For narrow fractions of the polymer, such as those used in this study, the method yields values of virial coefficient which are comparable to values obtained by osmometry and light scattering. However, the theoretical analysis predicts, that for polydisperse polymers the method will yield virial coefficients which are too low. Thus, caution is recommended when polymers are studied, which have a broader distribution of molecular weights.

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References and Notes

(1) D. E. Roark and D. A. Yphantis, *Ann. N.Y. Acad. Sci.*, **164**, 245 (1969).
(2) V. L. Seery, E. H. Fisher, and D. C. Teller, *Biochemistry*, **6**, 3315 (1967); **9**, 3591 (1970).
(3) R. W. Green and R. H. McKay, *J. Biol. Chem.*, **244**, 5034 (1969).
(4) T. H. Donnelly, *J. Phys. Chem.*, **70**, 1862 (1966); *Ann. N.Y. Acad. Sci.*, **164**, 147 (1969).
(5) M. Gehatia and D. R. Wiff, *Adv. Chem. Ser.*, **No. 125**, 216 (1973).
(6) Th. G. Scholte, *J. Polym. Sci., Part A-2*, **6**, 91 (1968).
(7) Th. G. Scholte, *J. Polym. Sci, Part A-2*, **6**, 111 (1968).
(8) H. Fujita, "Foundations of Ultracentrifugal Analysis", Wiley, New York, N.Y., 1975.
(9) E. T. Adams, Jr., P. J. Wan, D. A. Soucek, and G. H. Barlow, *Adv. Chem. Ser.*, **No. 125**, 235 (1973).
(10) D. A. Albright and J. W. Williams, *J. Phys. Chem.*, **71**, 2780 (1967).
(11) R. C. Deonier and J. W. Williams, *Proc. Natl. Acad. Sci. U.S.A.*, **64**, 828 (1969).
(12) H. Utiyana, N. Tagata, and M. Kurata, *J. Phys. Chem.*, **73**, 1448 (1969).
(13) P. Munk and D. J. Cox, *Biochemistry*, **11**, 687 (1972).
(14) D. J. DeRosier, P. Munk, and D. J. Cox, *Anal. Biochem.*, **50**, 139 (1972).
(15) R. J. Goldberg, *J. Phys. Chem.*, **57**, 194 (1953).
(16) W. H. Stockmayer and E. F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).
(17) W. R. Krigbaum and P. J. Flory, *J. Am. Chem. Soc.*, **75**, 1775 (1953).
(18) See Flory, ref 19, p 280.
(19) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(20) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
(21) E. G. Richards and H. K. Schachman, *J. Phys. Chem.*, **63**, 1578 (1959).
(22) D. A. Yphantis, *Biochemistry*, **3**, 297 (1964).
(23) P. Munk, R. G. Allen, and M. E. Halbrook, *J. Polym. Sci., Polym. Symp.*, **No. 42**, 1013 (1973).
(24) C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 1107 (1950).
(25) W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **11**, 37 (1953).
(26) G. Meyerhoff, *Z. Phys. Chem. (Frankfurt am Main)*, **4**, 335 (1955).
(27) H. P. Frank and H. Mark, *J. Polym. Sci.*, **10**, 129 (1952).
(28) A. A. Tager and V. M. Andreeva, *J. Polym. Sci., Part C*, **16**, 1145 (1967).
(29) M. J. Schick, P. Doty, and B. H. Zimm, *J. Am. Chem. Soc.*, **72**, 530 (1950).
(30) H. Vink, *Eur. Polym. J.*, **10**, 149 (1974).
(31) C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 862 (1950).
(32) W. R. Krigbaum and P. J. Flory, *J. Am. Chem. Soc.*, **75**, 1775 (1953).
(33) S. G. Chu and P. Munk, to be published.

Polymers in Mixed Solvents

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ABSTRACT: A large discrepancy exists between published experimental values and theoretical predictions of heats of mixing of polymers to infinite dilution in mixed solvents. An even larger error exists for polymer intrinsic viscosities in mixed solvents. The predictions were made on the basis of the Flory–Huggins lattice model theory. We derive expressions using the more recent Prigogine–Flory theory which considers interactions to occur between molecular surfaces, and which is thus sensitive to the molecular surface/volume ratios of the polymer and solvent molecules. The theory also allows for thermodynamic effects associated with volume changes occurring during the mixing process. Both of these changes in theory are important when mixed solvents are used, and the new predictions are very different from those made with the Flory–Huggins theory. They are in good agreement with experiment for a number of systems with varied molecular surface/volume ratios.

A number of conveniently measured quantities may be used to investigate the interaction of a polymer (component 3) with mixed solvents (components 1 and 2), e.g., the heat of mixing of the polymer to infinite dilution,[2] its intrinsic viscosity,[3,4] or the swelling factor of the cross-linked polymer.[4,5a] These quantities reflect the (1–2) as well as the (1–3) and (2–3) interactions. Thus, the Flory–Huggins theory leads[2] to the following expression for the heat, L, absorbed on dissolving 1 g of polymer in an infinite amount of mixed-solvent of composition φ_1 (volume fraction):

$$L = (zv_3/v)(\varphi_1 w_{H_{13}} + \varphi_2 w_{H_{23}} - \varphi_1\varphi_2 w_{H_{12}}) \quad (1)$$

Here z is the lattice coordination number, v_3 is the specific volume of the polymer, v is the volume of a segment, and the $w_{H_{ij}}$ are the contact interchange energies. It is convenient to define a quantity ΔL representing the deviation of L from a linear interpolation between the values in the pure solvents, L_1 and L_2. Equation 1 predicts[2] that ΔL reflects only the (1–2) interaction:

$$\Delta L \equiv L - (\varphi_1 L_1 + \varphi_2 L_2) = -z(v_3/v)\varphi_1\varphi_2 w_{H_{12}} = -\Delta H_{12}(\varphi_1) \quad (2)$$

Here $\Delta H_{12}(\varphi_1)$ is the heat of mixing the liquids 1 and 2 to form

Table I
Heats of Mixing of Polymers in Mixed Solvents (Comparison of Theory and Experiment)

	Solvents[a] s_1, Å^{-1}	Polymer[b] s_3, Å^{-1}	ΔL(Flory–Huggins)/ ΔL(exptl)[f]	ΔL(Prigogine–Flory)/ ΔL(exptl)[g]
(Benzene–cyclohexane)/PIB	0.96	0.58[c]	1.4	0.9
(Benzene–cyclohexane)/PDMS	0.96	0.60[d]	1.4	0.9
(Benzene–heptane)/PIB	0.92	0.58	1.6	1.1
(Benzene–heptane)/PDMS	0.92	0.60	1.3	0.9
(Chlorobenzene-heptane)/PIB	0.86	0.58	2.0	1.5
(CCl_4–methylcyclohexane)/PDMS	0.89	0.60	1.3	0.9
(Benzene–cyclohexane)/*cis*-polybutadiene	0.96	1.0[e]	0.9	1.0

[a] The average molecular surface/volume ratio of the two solvents. The molecules are considered as spheres with molar "hard-core" volume V^* obtained from α through Flory equation of state. [b] Molecular surface/volume ratio of polymer chain considered as a cylinder. [c] PIB radius = 3.48 Å (B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968)). [d] PDMS radius = 3.36 Å (P. Tancrède, D. Patterson, and V. T. Lam, *J. Chem. Soc., Faraday Trans. 2*, **71**, 985 (1975)). [e] PB radius = 2 Å, ref 14a. [f] Equation 2 and experimental ΔL values from ref 1 and 14b. [g] Equation 15.

a volume of mixed solvent equal to that of the polymer, i.e., v_3, the specific volume of the polymer. According to eq 2, an endothermic excess heat for the mixed solvents leads to a heat of mixing the polymer and the solvent mixture which lies below the linear interpolation of the values in the pure solvents. The quantity ΔH_{12} is readily obtained experimentally, and hence ΔL may be predicted.

The Flory–Huggins theory gives an expression similar to eq 1 for the noncombinatorial part of the free enthalpy (ΔG_M) of dissolving the polymer in the mixed solvent. This leads[3c] through the chemical potentials and the Stockmayer–Fixman equation[5b] to an expression for $\Delta[\eta]$ defined analogously to ΔL:

$$\Delta[\eta] \equiv [\eta] - (\varphi_1[\eta]_1 + \varphi_2[\eta]_2)$$
$$= \frac{1.02 M v_3 \Phi}{N_0 R T}\left\{ z\left(\frac{v_3}{v}\right)\varphi_1\varphi_2 w_{G_{12}}\right\} = \frac{1.02 M v_3{}^2 \Phi}{N_0 R T}\left(\frac{G^E}{V}\right) \quad (3)$$

Here $w_{G_{12}}$ is the (1–2) contact interchange free enthalpy, G^E/V is the known excess free enthalpy per unit volume of the mixed solvents, M is the polymer molecular weight, and Φ is the Flory universal constant. The usual positive value of G^E for the solvent mixture leads to a value of $[\eta]$ in the mixture which is larger than the linear interpolation between the values in the pure solvents (i.e., the free energy of interaction between the coil and the mixture is less than a linearly interpolated value). It is possible that the Stockmayer–Fixman equation overestimates $\Delta[\eta]$, and other equations may be used to relate the coil expansion factor α to the thermodynamic interactions. For instance, ref 2a and 2b use the original Fox–Flory relation, and we choose a modified form of this in the present work.

Experimental determinations of ΔL were made with polydimethylsiloxane and polyisobutylene (see Table I). The mixing of the two solvents was an endothermic process for every system ($\Delta H_{12} > 0$). In conformity with eq 2, negative ΔL were found, corresponding to the breaking of the (1–2) contacts by the polymer. For $\Delta[\eta]$, mixed-solvent systems were used with both signs of G^E. The experiments showed that, as predicted by eq 3, the sign of $\Delta[\eta]$ was the same as that of G^E. Unfortunately, the quantitative predictions of ΔL and $\Delta[\eta]$ are consistently too large. The theoretical negative ΔL are usually ~1.5 times the experimental values, but the discrepancy is much larger for $\Delta[\eta]$. There, using eq 3 based on the Stockmayer–Fixman relation, it was found[3c] that the predicted $\Delta[\eta]$ were about ten times the experimental values. In the earlier work[3b] based on the Fox–Flory approach, the discrepancy involved a factor of ~3, i.e., still unacceptably large.

Equations 2 and 3 have been derived neglecting any preferential sorption by the polymer of one of the solvents. Allowing for this effect lowers[2] L making ΔL more negative, thus increasing the error made by the theory. The calculated value of $[\eta]$ is also lowered[3c,4b] by allowing for preferential adsorption. This would decrease the discrepancy between theory and experiment when $G^E > 0$, but increase it for mixed solvents having $G^E < 0$. Furthermore, the discrepancy is found even when the solvents are of similar quality and preferential adsorption would be expected to vanish[4a] in the middle of the concentration range. Other kinds of deviations from random mixing, occurring in the polar systems, can be shown to result in deviations from the Flory–Huggins theory which are in the correct direction but considerably smaller than found experimentally.

The large discrepancies between theory and experiment must apparently be attributed to deficiencies in the Flory–Huggins theory of the solution thermodynamics. Thus, provided mixed solvents are used, simple heat and viscosity experiments provide a test of the theory. In the case of a single solvent, any inadequacy of the Flory–Huggins theory is hidden by adjustment of the polymer–solvent interaction parameters, e.g., χ, which are left as empirical quantities.

A more recent theory than the Flory–Huggins, namely the Prigogine[6]–Flory[7], departs from the usual volume fractions in dealing with molecular contacts, and employs instead molecular "surface" or "site" fractions, i.e., fractions of the total molecular surface in the mixture which are associated with the different components. It is of interest to note that interaction between molecular surfaces is also an important feature of the theory of Huggins[8] and indeed of early work by Langmuir[9] and others.[9,10] Guggenheim[10] and later Prigogine[6] used a lattice model to evaluate the surface area of a polymer molecule available for intermolecular contact, and both a polymer segment and a solvent molecule were assumed to be of roughly the same size. The surface/volume ratio of a polymer was therefore close to that of a solvent molecule unless the lattice coordination number was made unrealistically small. Indeed, values of $z \sim 3, 4$ were used[3b] successfully to predict $\Delta[\eta]$ results for polymers in mixed solvents. More recently,[7] however, it has been realized that polymer molecules with their side groups may correspond to chains with a cross-sectional diameter considerably greater than the dimensions of the solvent molecules, corresponding to a low molecular surface/volume ratio for the polymer and to a small apparent value of z in the Guggenheim theory.

The ΔL and $\Delta[\eta]$ quantities reflect heat and free enthalpy effects associated with the demixing of a volume of mixed solvent sufficient to provide sites for interaction with the polymer. The Flory–Huggins theory associates the same number of interaction sites with unit volumes of polymer and solvent. However, if the Prigogine–Flory theory is correct, and if the polymer in fact has a smaller molecular surface/volume ratio than the solvents, then it is clear that the Flory–Huggins theory will over-estimate the amount of mixed solvent needed to provide interaction sites with the polymer, and hence also over-estimate ΔL and $\Delta[\eta]$. The Prigogine–Flory theory has now been extensively tested and there is much experimental evidence in many areas in favor of considering molecular interaction to take place between surfaces of molecules. For instance, the usual increase of the χ parameter with polymer concentration is associated with a smaller molecular surface/volume ratio for the polymer than for the solvent.

It is also important that the Prigogine–Flory theory introduces a second contribution to the thermodynamic mixing functions apart from that due to the interaction of molecular surfaces. This arises from volume changes occurring during mixing, i.e., the equation of state effect of Flory. It is particularly important in the chemical potential (χ parameter) of polymer solutions, and explains the phase separation found as a general phenomenon in polymer solutions at high temperatures (LCST). It is evidently of interest to predict ΔL and $\Delta[\eta]$ using the Prigogine–Flory theory. We find that the thermodynamics of ternary systems is indeed sensitive to both the effect of interaction between molecular surfaces and to the effect of volume changes taking place during the mixing process.

Heat of Mixing of Polymer to Infinite Dilution

Using the corresponding states formulation[11] of the Prigogine–Flory theory, and extending the expression for a binary mixture, we write for the molar energy of a ternary mixture,

$$\tilde{U} = U^*\tilde{U}(\tilde{T})$$

$$\begin{aligned} U^* = (&x_1U_1^* + x_2U_2^* + x_3U_3^* - x_1\theta_2V_1^*X_{12} \\ &- x_1\theta_3V_1^*X_{13} - x_2\theta_3V_2^*X_{23}) \end{aligned} \quad (4)$$

Here x_i is the mole fraction of the ith component, the U_i^* and V_1^* are the molar reduction parameters for energy and volume, respectively, θ_i are the surface fractions of components in the final mixture,

$$\theta_i = x_iV_i^*s_i \Big/ \sum_1^3 x_iV_i^*s_i \quad (5)$$

with s_i the molecular surface/volume ratios. The X_{ij} are the contact interaction parameters in the sense of the theory of Flory and collaborators; $\tilde{U}(\tilde{T})$ is the reduced energy as a function of reduced temperature, which for the ternary mixture is given by:

$$\tilde{T} = \sum x_iU_i^*\tilde{T}_i/U^* \quad (6)$$

The quantities $\tilde{U}$ and $\tilde{T}$ for the solvent mixture are given by expressions analogous to eq 4 and 6, whence the molar heat of mixing at zero pressure, ΔU_M, and the quantity L may be obtained:

$$L = \frac{1}{M} \lim_{n_3 \to 0} \partial\{(n_1 + n_2 + n_3)\Delta U_\mathrm{M}\}/\partial n_3 \quad (7)$$

where M is the molecular weight of the polymer. Substituting (4) and (6) into (7) we obtain:

$$\begin{aligned} L = s_3v_3^*[&\theta_{10}(X_{13}/s_1) + \theta_{20}(X_{23}/s_2) \\ &- \theta_{10}\theta_{20}(X_{12}/s_1)]\tilde{Q}(\tilde{T}_0) + P_3^*v_3^*[\tilde{U}(\tilde{T}_0) \\ &- \tilde{U}(\tilde{T}_3) + (\tilde{T}_3 - \tilde{T}_0)\tilde{U}'(\tilde{T}_0)] \end{aligned} \quad (8)$$

where v_3^* is the specific volume reduction parameter of the polymer, $P_3^* = U_3^*/V_3^*$ is the reduction parameter for pressure, and

$$U'(\tilde{T}) \equiv \partial\tilde{U}/\partial\tilde{T} \equiv \tilde{C}_\mathrm{p}(\tilde{T});\ \tilde{Q}(\tilde{T}) \equiv -\tilde{U}(\tilde{T}) + \tilde{T}\tilde{C}_\mathrm{p}(\tilde{T}) \quad (9)$$

The zero subscript, e.g., θ_{10}, $\tilde{T}_0$, refers to the mixed solvent. Equation 2 suggests the definition of the quantity

$$\Delta L = L - (\theta_{10}L_1 + \theta_{20}L_2) \quad (10)$$

evaluated from eq 8 to be:

$$\begin{aligned} \Delta L/v_3^* = &-\theta_{10}\theta_{20}(s_3/s_1)X_{12}\tilde{Q}(\tilde{T}_0) \\ &+ \theta_{10}[P_3^* - (s_3/s_1)X_{13}][\tilde{Q}(\tilde{T}_0) - \tilde{Q}(\tilde{T}_1)] \\ &+ \theta_{20}[P_3^* - (s_3/s_2)X_{23}][\tilde{Q}(\tilde{T}_0) - \tilde{Q}(\tilde{T}_2)] \\ &- P_3^*\tilde{T}_3[\tilde{U}'(\tilde{T}_0) - \theta_{10}\tilde{U}'(\tilde{T}_1) - \theta_{20}\tilde{U}'(\tilde{T}_2)] \end{aligned} \quad (11)$$

Equation 11 permits the calculation of ΔL, but we consider instead an approximation. This is based on $\tilde{T}_3$ being considerably lower than either $\tilde{T}_1$ or $\tilde{T}_2$, which for most solvents are close together. Taking $\tilde{T}_2 = \tilde{T}_1$ and using eq 6

$$\frac{\tilde{T}_0 - \tilde{T}_1}{\tilde{T}_1} = \frac{\theta_{10}\theta_{20}X_{12}}{\theta_{10}P_1^* + \theta_{20}P_2^*(s_1/s_2)} \ll 1 \quad (12)$$

whence, expanding reduced quantities in eq 11 around $\tilde{T}_1$, we have

$$\frac{\Delta L}{v_3^*} = \theta_{10}\theta_{20}X_{12}\left[-\left(\frac{s_3}{s_1}\right)\tilde{Q}(\tilde{T}_1) + \frac{(\tilde{T}_1 - \tilde{T}_3)\tilde{T}_1P_3^*U''(\tilde{T}_1)}{\theta_{10}P_1^* + \theta_{20}P_2^*\left(\frac{s_1}{s_2}\right)}\right] \quad (13)$$

which replaces the Flory–Huggins eq 2. Equation 13 is general, however, and below we put it in a form suitable for calculations.

Qualitative Interpretation of (13). The significance of the two terms in eq 13 is shown by decomposing the mixing process into three steps: (a) the mixed solvents are separated into the pure components 1 and 2; (b) portions of θ_{10} and θ_{20} of the polymer are mixed with the pure liquids 1 and 2 (these heats give the linear term in L: $\theta_{10}L_1 + \theta_{20}L_2$); (c) the polymer solutions are mixed to give the final ternary system. The sum of the heat changes in steps (a) and (c) gives ΔL. It is clear that (c) remakes most, viz., a fraction $1 - \theta_3$, of the (1–2) contacts which were replaced by (1–1) and (2–2) in (a). A certain fraction, θ_3, are not remade since they have been taken up by the polymer molecules. The resulting heat effect is equal to the heat of demixing a sufficient quantity of mixed solvent to furnish a *molecular surface area equal to that associated with 1 g of polymer.* This heat, as given by the theory, is identically the first term of eq 13. This term therefore differs from $-\Delta H_{12}$ in eq 2 simply because the Flory–Huggins theory takes polymer and solvent liquids to have equal molecular surface areas per unit volume, and therefore in the Flory–Huggins theory $-\Delta H_{12}$ refers to a volume of mixed solvent equal to the *volume of 1 g of polymer.*

The second term of eq 13 has no analogue in the Flory–Huggins eq 2 since it involves the difference in reduced temperatures of the polymer and the solvents. The fraction $1 - \theta_3$ of (1–2) contacts broken in step (a) is remade in step (c), but this happens *in the presence of the polymer.* This produces a zero net heat effect in the Flory–Huggins theory, but not in the newer theory where polymer affects the energy of the (1–2) contacts, at least in the prevailing "one fluid" form. The energy of a solution is not expressible as the sum of contact energies, and indeed the Prigogine–Flory theory offers a possible explanation of the "ternary term" which has been found necessary[4] in applying Flory–Huggins polymer solution thermodynamics to ternary systems. The second term in eq 13 corresponds to the net thermodynamic effect of breaking the (1–2) contacts at a higher reduced temperature, $\tilde{T}_1$, than prevails when they are remade in the presence of the polymer. Equation 13 of ref 2 gives an expression in Prigogine's nomenclature for this second term and it may be shown to be identical with the term found here. Reference 2 evaluated the term using the Prigogine cell theory or experimental values for the change of ΔH_{12} with temperature and found the second term to be nonnegligible. However, if we use the Flory model to evaluate $\tilde{U}''(\tilde{T}_1)$, we now find the second term is only 5% of the first term in eq 13 and it may be neglected. It is then of interest to compare the calculated values of ΔL using the two theories. In eq 13 the X_{12} parameter may be related to the heat of mixing quantity ΔH_{12} of eq 2

$$\Delta H_{12} = (s_0/s)(v_3{}^*\tilde{V}_3/\tilde{V}_1)\theta_{10}\theta_{20}X_{12}\tilde{Q}(\tilde{T}_1) \tag{14}$$

$$s_0 = \varphi_{10}s_1 + \varphi_{20}s_2$$

i.e., a volume fraction average of s_1 and s_2. Equation 13 becomes

$$\Delta L(\text{Prigogine–Flory}) = -\frac{\tilde{V}_1}{\tilde{V}_3}\left(\frac{s_3}{s_0}\right)\Delta H_{12} \tag{15a}$$

In treating intrinsic viscosities below, we find it necessary to put $s_1 \simeq s_2$. In practice, the surface/volume ratios for solvents are similar, so that in eq 15 we can make the same approximation, $s_0 \simeq s_1$, whence

$$\Delta L(\text{Prigogine–Flory}) = -\frac{\tilde{V}_1}{\tilde{V}_3}\left(\frac{s_3}{s_1}\right)\Delta H_{12} \tag{15b}$$

or

$$\frac{\Delta L(\text{Prigogine–Flory})}{\Delta L(\text{Flory–Huggins})} = \frac{\tilde{V}_1}{\tilde{V}_3}\left(\frac{s_3}{s_1}\right) \tag{15c}$$

Comparison with Experiment. The systems studied in ref 2 involve polyisobutylene (PIB) or polydimethylsiloxane (PDMS) as polymeric components. Six typical systems are re-examined in Table I which shows (columns 2 and 3) that the molecular surface/volume ratios (s_3) of both PIB and PDMS are considerably smaller than the average surface/volume ratios of the solvents (s_1). Corresponding to this, the Flory–Huggins theory (eq 2) gives too large predictions for ΔL, taken here at equimolar concentration of the mixed-solvent medium. This is shown in column 4 of Table I where the ratio ΔL(Flory–Huggins)/ΔL(exptl) is considerably larger than unity for the PIB and PDMS systems. [Values of ΔL(Flory–Huggins) may be found in ref 2.] On the other hand, ΔL(Prigogine–Flory) was calculated using eq 15 obtaining $\tilde{V}_1$ and $\tilde{V}_3$ from the thermal expansion coefficients of these components Now the ratio ΔL(Prigogine–Flory)/ΔL(exptl) is much more satisfactory, i.e., closer to unity (column 5). However, we have no explanation for the poor results from both theories in the case of the (chlorobenzene–heptane)/PIB system.

Polybutadiene is a polymer with an unusually[14a] high surface/volume ratio similar to that for benzene and cyclohexane. This means that for the (benzene–cyclohexane)/polybutadiene system the Flory–Huggins and Prigogine–Flory predictions should be similar. Heats of mixing of polybutadiene with benzene–cyclohexane have been measured,[14b] and Table I shows that now both of the theoretical predictions are very good.

Intrinsic Viscosities in Mixed Solvents

The intrinsic viscosity of a polymer in a single solvent may be related to the thermodynamic interaction parameter χ through any one of a number of relations. For instance, the Stockmayer–Fixman relation[5b] gives

$$[\eta] = K_\theta M^{1/2} + \frac{1.02 M v_3{}^2\Phi}{N_0 V_1}(\tfrac{1}{2} - \chi) \tag{16}$$

The original Fox–Flory relation,[12] as modified by Stockmayer,[13] gives

$$[\eta] = K_\theta M^{1/2}\alpha^3$$

$$\alpha^5 - \alpha^3 = 0.98 C_M(\tfrac{1}{2} - \chi)M^{1/2} \tag{17}$$

with C_M as given in ref 12. In the case of a ternary system, the expression $0.5 - \chi$ is replaced by the function Y:

$$Y = \frac{V_1}{2RT}(M_{33} - \epsilon^2 M_{11}) \tag{18}$$

Here, as described in ref 4a, the M_{ii} are special double differentiations, with respect to volume fractions, of the solution free enthalpy. The quantity ϵ represents[4a] the selective sorption by the coil of one of the solvents. In the present treatment, the corresponding states approach is used to give the noncombinatorial part of the solution free enthalpy, i.e.,

$$G(x_1,x_2,x_3) = U^*\tilde{G}(\tilde{T}) \tag{19}$$

The Flory–Huggins expression with volume rather than segment fractions was used for the combinatorial contribution to G, and the final expression for Y becomes:

$$\begin{aligned} Y = {} & \tfrac{1}{2}(\varphi_{10} + l\varphi_{20}) \\ & + \frac{V_1}{RT}\left[\left(\frac{S_3{}^2}{S_0 S_1}\right)\left(\xi_{13}\theta_{10} + \frac{S_1}{S_2}\xi_{23}\theta_{20} - \xi_{12}\theta_{10}\theta_{20}\right)\tilde{U}(\tilde{T}_0)\right. \\ & \left. - \frac{A^2(\theta_{10})}{2[\varphi_{10}\pi_1{}^*\tilde{T}_1 + \varphi_{20}\pi_2{}^*\tilde{T}_2]}\tilde{C}_P(\tilde{T}_0) - \frac{1}{2}\epsilon^2 M_{11}\right] \end{aligned} \tag{20}$$

The following nomenclature has been used: $S_i = s_i/\tilde{V}_i$; $\xi_{ij} = X_{ij}/\tilde{V}_i$; $\pi_i{}^* = P_i{}^*/\tilde{V}_i$; $S_0 = \varphi_{10}S_1 + \varphi_{20}S_2$; $l = V_1/V_2$ (ratio of solvent molar volumes). The reduced temperature $\tilde{T}_0$ of the mixed solvent is given by eq 6, putting $x_3 = 0$, and the quantity $A(\theta_{10})$ is given by:

$$\begin{aligned} A(\theta_{10}) = \pi_3{}^*\tilde{T}_3 - \tilde{T}_0\Bigl\{\pi_3{}^* + \frac{S_3}{S_1}(\xi_{12}\theta_{10}\theta_{20} \\ - \xi_{13}\theta_{10} - \frac{S_1}{S_2}\xi_{23}\theta_{20})\Bigr\} \end{aligned} \tag{21}$$

The application of eq 20 and 21 has been simplified by assuming $\tilde{T}_1 = \tilde{T}_2$, $S_1 = S_2$, $P_1{}^* = P_2{}^*$, $\tilde{V}_1 = \tilde{V}_2$, etc., and that the preferential adsorption, ϵ, is zero. In this approximation the two solvents have the same free volumes and molecular surface/volume ratios. We use the subscript 1 to denote the solvents and for computation on an actual system suggest that 1 subscript quantities might be volume fraction averages of the pure solvent quantities as in eq 14 or simple arithmetric averages. We then obtain an expression for the quantity ΔY, namely

$$\begin{aligned} \Delta Y &= Y(\theta_{10}) - (\theta_{10}Y_1 + \theta_{20}Y_2) \\ &= \frac{X_{12}\theta_{10}\theta_{20}}{RT\tilde{V}_1}V_1(-\tilde{U}(\tilde{T}_1))\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2\left[\left(\frac{s_3}{s_1}\right)^2\right. \\ &\quad \left. - \left(1 - \frac{T_1{}^*}{T_3{}^*}\right)\left(\frac{\tilde{T}_1\tilde{C}_p(\tilde{T}_1)}{-\tilde{U}(\tilde{T}_1)}\right)\left(\frac{P_3{}^*}{P_1{}^*}\right)\left(\frac{P_3{}^*}{P_1{}^*} + \frac{s_3}{s_1}\right)\right] \end{aligned} \tag{22}$$

Here the X_{12} parameter may be related to the experimental G^E of the mixed-solvent system through

$$G^E = X_{12}\theta_{10}\theta_{20}V_1(-\tilde{U}(\tilde{T}_1))/\tilde{V}_1 \tag{23}$$

and if one uses the Flory model of the liquid state

$$\tilde{T}_1\tilde{C}_p(\tilde{T}_1)/-\tilde{U}(\tilde{T}_1) = \alpha_1 T \tag{24}$$

where α_1 is the thermal expansion coefficient of either solvent. Thus

$$\Delta Y = \frac{G^E}{RT}\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2\left[\left(\frac{s_3}{s_1}\right)^2 - \left(1 - \frac{T_1{}^*}{T_3{}^*}\right)\alpha_1 T\left(\frac{P_3{}^*}{P_1{}^*}\right)\left(\frac{P_3{}^*}{P_1{}^*} + \frac{s_3}{s_1}\right)\right] \tag{25}$$

This may be contrasted with the Flory–Huggins expression with a similar assumption of zero preferential adsorption:

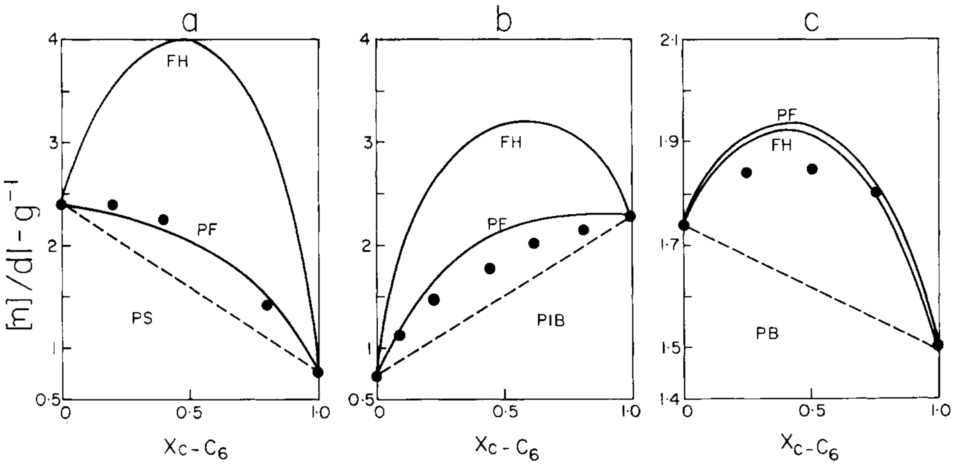

Figure 1. Intrinsic viscosities of polymers in benzene–cyclohexane as functions of cyclohexane mole fraction: (●) experimental points; lines calculated using modified Fox–Flory [η]–Y relation and (FH), Flory–Huggins eq 26 or (PF), Prigogine–Flory eq 25 for Y. (a) Polystyrene of 881 000 $\bar{M}_v$ at 34 °C; experimental data from ref 3a. (b) Polyisobutylene of 490 000 $\bar{M}_v$ at 25 °C; experimental data from ref 3b. (c) *cis*-1,4-Polybutadiene of 161 000 $\bar{M}_v$ at 25 °C.

$$\Delta Y = G^{\mathrm{E}}/RT \qquad (26)$$

The two terms in eq 25 or 22 have a significance analogous to that of the terms in eq 13 for ΔL, as shown by referring to the three-step process of mixing the polymer with the mixed solvent. The first term corresponds to a net replacement of (1–2) contacts by (1–1) and (2–2) as characterized by the X_{12} parameter or G^{E}. This first term is analogous to the whole of the Flory–Huggins eq 26, but it appears in eq 25 with the important multiplying factor $(\tilde{V}_1/\tilde{V}_3)^2(s_3/s_1)^2$ which decreases with polymer surface/volume ratio. The second term in eq 25 or 22 depends on the difference of polymer and solvent reduced temperatures, and corresponds to the effect of the polymer on the free enthalpy of the (1–2) contacts. In contrast to the situation for ΔL where the second term of eq 13 is small, the second term in eq 25 or 22 is now important. For the (benzene–cyclohexane)/polystyrene system, for instance, the second term is 0.7 of the first and the total ΔY(Prigogine–Flory) is only $\sim 0.1\Delta Y$(Flory–Huggins).

A relation is required to transform the quantity ΔY into a value of [η] for the polymer coil or into $\Delta[\eta]$ as defined in eq 3. The simplest relation is the Stockmayer–Fixman which makes $\Delta[\eta]$ directly proportional to ΔY, i.e.,

$$\Delta[\eta] = \frac{1.02 M v_3^2 \Phi}{N_0 V_1}\Delta Y \qquad (27)$$

where V_1 is the molar volume of either solvent. Using the Flory–Huggins expression, eq 26, we recover eq 3, already used in ref 3c. The new Prigogine–Flory eq 25 gives values of ΔY, and corresponding values of $\Delta[\eta]$ from eq 27, which may be very different from the Flory–Huggins values. We now believe that the linear Stockmayer–Fixman relation over-estimates the change of [η] due to a change of Y, particularly for high M. Thus, in spite of the attractive simplicity of eq 27, we return in the present work to the modified Fox–Flory relation between [η] and Y, eq 17.

Comparison with Experiment. Figure 1 shows the comparison between theories and experiment for three systems. In each case the mixed solvent is benzene–cyclohexane and the polymers are polystyrene, polyisobutylene, and polybutadiene. Equation 17 relates [η] to Y for which two predictions are made, viz., the Flory–Huggins eq 26 and the Prigogine–Flory eq 25. Predictions were also made allowing for preferential adsorption in the Flory–Huggins theory, as originally done by Shultz and Flory[3a] or in ref 3b. No significant difference in predictions was found and hence the results are not shown here. The calculation procedure involved fitting the [η] values in the pure solvents. In the PS and PIB cases one of the solvents was a theta solvent (χ = 0.5) and the χ parameter was known for the other solvent (see ref 3b). The fit then gave values for K_θ and C_{M}. In the case of the polybutadiene system, neither solvent was a theta solvent and the χ parameters were unknown. A value of K_θ was obtained from the literature and C_{M} was calculated, so that fitting [η] at the two ends of the concentration range yielded Y or χ values. For all three systems, knowing Y at the two ends and using eq 25 or 26 for ΔY, values of [η] were obtained at intermediate concentrations. Values of G^{E} for benzene–cyclohexane are from ref 16. In applying eq 25 one needs values of s, $\tilde{V}$, T^*, and P^* for the polymers and average values for the solvents. For polystyrene,[17] s = 0.47 Å^{-1}. The other s values are in Table I and values of the other quantities wee taken from the thermodynamic literature.

The Flory–Huggins theory performs worst with the (benzene–cyclohexane)/PS system (Figure 1a) where the surface to volume ratio of the polymer is very low (0.47 Å^{-1}) compared with the solvent (0.96 Å^{-1}). Here the calculated $\Delta[\eta]$ is about six times the experimental and a high maximum is predicted in [η], but not found. The prediction is slightly better when PS is replaced by PIB (Figure 1b) which has a somewhat higher surface/volume ratio (s = 0.58 Å^{-1}). Most polymers would appear to have similar surface/volume ratios and ref 3c gives many other examples where the Flory–Huggins theory is badly in error. Figures 1a and 1b show that, in contrast, the Prigogine–Flory predictions are good. This is because of the s_3/s_1 term in eq 25 for ΔY which decreases the predicted ΔY to only 0.1–0.2 of the Flory–Huggins value. It is of interest that the second, "free volume" term in eq 25 is not negligible but varies little with the polymer. For very low s_3/s_1 ratios <0.4 the second term would be larger than the first and negative $\Delta[\eta]$ would be predicted in spite of $\Delta G^{\mathrm{E}} > 0$.

Figure 1c shows the results for polybutadiene which has an unusually high surface/volume ratio (s = 1.0 Å^{-1}), the same as that of the solvents. Corresponding to this, the predictions of the two theories are now similar, and both are good. In eq 25 s_3/s_1 is ~1 rather than ~0.5 for the other two systems. The quantity ΔY predicted by the Prigogine–Flory theory is now as large as with the Flory–Huggins, so that both theories predict a maximum in [η], which is found experimentally. The different [η] and ΔL behavior of polybutadiene as compared with the other polymers is in harmony with the different phase behavior of this polymer described in ref 14a.

The good results with the Prigogine–Flory approach may be partly fortuitous. For instance, use of the Stockmayer–

Fixman relationship between $[\eta]$ and Y would worsen the agreement. The same would be true for the Flory–Huggins theory, however, so that whatever the $[\eta]$–Y relation the Prigogine–Flory predictions must be superior. Thus heats of solution and intrinsic viscosities of polymers in mixed-solvent media provide evidence of the essential validity of the concept of interaction between molecular surfaces, as embodied in the Prigogine–Flory and Huggins theories.

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References and Notes

(1) (a) Czechoslovak Academy of Sciences; (b) McGill University.

(2) G. Delmas, D. Patterson, and S. N. Bhattaharyya, *J. Phys.Chem.*, **68**, 1468 (1964).

(3) (a) A. R. Shultz and P. J. Flory, *J. Polym. Sci.*, **15**, 231 (1955); (b) R. Noel, D. Patterson, and T. Somcynsky, *ibid.*, **42**, 561 (1960); (c) A. Dondos and D. Patterson, *J. Polym. Sci., Part A-2*, **7**, 209 (1969).

(4) (a) J. Pouchlý, A. Živny, and K. Šolc, *J. Polym. Sci., Part C*, **23**, 245 (1968); (b) J. Pouchlý and A. Živny, *J. Polym. Sci., Part A-2*, **10**, 1481 (1972); (c) J. Pouchlý, A. Živny, and K. Šolc, *Collect. Czech. Chem. Commun.*, **37**, 988 (1972).

(5) (a) G. M. Bristow, *Trans. Faraday Soc.*, **55**, 246 (1959). (b) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963].

(6) I. Prigogine (with the collaboration of V. Mathot and A. Bellemans), "The Molecular Theory of Solutions", North-Holland Publishing Co., Amsterdam, 1957.

(7) P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).

(8) M. L. Huggins, *J. Phys. Chem.*, **74**, 371 (1970).

(9) See, for example, C. H. Deal and E. L. Derr, *Ind. Eng. Chem.*, **60**, 28 (1968).

(10) E. A. Guggenheim, *Proc. R. Soc. London, Ser. A*, **183**, 213 (1945).

(11) D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, **49**, 98 (1970).

(12) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter 12.

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

(14) (a) G. Delmas and P. de St. Romain, *Eur. Polym. J.*, **10**, 1133 (1974); (b) H. Eid and G. Delmas, unpublished.

(15) F. Danusso, G. Moraglio, and G. Gianotti, *J. Polym. Sci.*, **51**, 475 (1961).

(16) J. R. Goates, R. J. Sullivan, and B. J. Ott, *J. Phys. Chem.*, **63**, 589 (1959).

(17) From the geometrical calculation in P. J. Flory and H. Höcker, *Trans. Faraday Soc.*, **67**, 2258 (1971).

The Generation of True Cosolvency by Pressure. Solubility Limits of High Molecular Weight Polystyrene in Mixtures of Acetone and Diethyl Ether

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ABSTRACT: For sufficiently high molecular weights of polystyrene, complete miscibility with mixtures of acetone and diethyl ether can never be achieved under atmospheric pressure, irrespective of the composition of the mixed solvent. This is in contrast to the situation for low molecular weight samples, which exhibit the phenomenon of true cosolvency. It is, however, possible to re-establish this effect by pressure; for $M_w = 2.5 \times 10^6$ critical conditions are achieved for the first time at 35 bars under the condition that the temperature is −10 °C and the mole fraction of acetone 0.4. On further increasing the pressure a critical surface develops out of this point. This surface resembles a closed horn and circumscribes the conditions of complete miscibility. The combination of the Prigogine–Patterson theory and Scott's single liquid approximation proves successful again for a theoretical interpretation of the experimental findings.

In the course of our investigations on mixed solvents[1,2] we have also reported on a phenomenon we called true cosolvency.[3] This term was chosen to indicate that for the system under investigation, namely acetone/diethyl ether/polystyrene (AC/DEE/PS), the polymer is, for given atmospheric pressure, at no temperature completely miscible with either acetone or diethyl ether alone, while this is the case with the mixed solvent. Ordinary cosolvency, on the other hand, is characterized by the fact that at least one of the two components of the mixed solvent becomes completely miscible with the polymer when the temperature is changed under isobaric conditions.

The effect of true cosolvency was independently also observed by Cowie and McEwen,[4] who stated that this phenomenon cannot be observed for the above mentioned system under atmospheric conditions if the molecular weight of the polystyrene exceeds approximately one million. Since we knew from our pressure investigations on a polystyrene sample of $M_w = 1.1 \times 10^5$ that the mixing volumes are negative at the lower critical solution temperature as well as at the upper critical solution temperature, we asked ourselves whether the effect of true cosolvency could be re-established for molecular weights higher than one million by the increased mixing tendency at higher pressures.

In addition it seemed interesting to check whether our hitherto quite successful theoretical approach[2,3,5] also proves useful for the prediction of molecular weight influence.

Experimental Section

Apparatus. For the investigation of the demixing conditions for systems which can only be made homogenous at elevated pressures, an apparatus had to be constructed that allows stirring of its contents in order to promote dissolution at elevated pressures. For this purpose we used a cell, holding a deepening below the light beam passing it. The magnetic stirrer contained in this cavity is moved by a strong permanent magnet outside the cell.

A schematic picture of the entire measuring device is given in Figure 1. Since most of this representation is self-explanatory, a very brief statement of the experimental procedure should suffice. Readers interested in more details are referred to ref 5.

Experimental Procedure. Measurements were performed for one approximately critical polymer concentration only, since previous results[5] have shown that the demixing conditions are nearly independent of the precise polymer concentration, as long as one is not too far from the extrema in the isothermal or isobaric sections