Polymer-Cosolvent Systems. IV. Upper and Lower Critical Solution Temperatures in the System Methylcyclohexane-Diethyl Ether-Polystyrene

J. M. G. Cowie* and I. J. McEwen

Department of Chemistry, University of Stirling, Stirling, Scotland. *Received October 19, 1973*

ABSTRACT: Phase equilibria in the quasi-ternary system methylcyclohexane (1), diethyl ether (2), and polystyrene (3) have been studied. The upper and lower critical solution temperatures have been measured as a function of both polymer chain length and solvent composition and pseudoideal conditions have been established for the system. The Prigogine-Flory theory has been used to predict phase separation in the ternary mixtures with limited success, but an improvement between theory and experiment can be obtained when more extensive mixture thermal expansion data are available. The system exhibited cosolvency and the selective adsorption behavior, studied for one fraction at room temperature, was in accord with previous observations in related systems.

A cosolvent system can be described as one in which mixtures of two liquids dissolve a polymer which is insoluble in either liquid separately, under the conditions of study. The enhanced solubility of the polymer, observed in such binary liquid systems, was explained originally on the basis of the Hildebrand concept of solubility parameters (δ) and solution was expected when the average δ of the liquid mixture was closer to that of the polymer than the δ for each component liquid. Two of the systems studied previously[1,2] comply with this requirement, but we have also reported a system[3] in which the solubility parameters of both liquids are larger than that of the polymer. In the latter case cosolvency cannot be explained using the simple Hildebrand picture and it has been suggested that the sign of the excess free energy of mixing $\Delta G_M{}^E$ for the binary mixture is a more realistic guide to potential cosolvent liquid pairs.[1,4] Thus when $\Delta G_M{}^E > 0$, the two liquids are relatively incompatible and 1-2-3 contacts are favored.

The quasi-ternary solutions studied here also provide an example of an asymmetric δ system, where now the values of δ for the liquids are both lower than that of the polymer. While in the initial work[1,3] the cosolvent behavior of only one fraction of polystyrene was examined, it was subsequently found[2] that a more realistic picture could be obtained if the critical temperatures of a number of fractions of differing molecular weight are measured, as this enables one to establish the general solubility behavior of the polymer in the mixed solvent.

The cosolvent system reported here is methylcyclohexane (1), diethyl ether (2), polystyrene (3) for which we have measured the upper critical solution temperatures (ucst) and lower critical solution temperatures (lcst) as a function of chain length and solvent composition. Light scattering has been used to study the preferential adsorption of solvent on one polymer fraction at ambient temperature, and also to verify the pseudo-ideal conditions indicated by cloud point measurements.

The Prigogine-Flory theory[5,6] of corresponding states can be applied to quasi-binary systems to predict the variation of cst with chain length. Here we attempt to assess the applicability of this theory to ternary systems using simple approximations.

Experimental Section

Polymer Samples. The polystyrene fractions used were narrow molecular weight distribution fractions obtained from the Pressure Chemical Co.

Light Scattering. Measurements were made using a Sofica PGD 42000 instrument and unpolarized blue light (λ 436 nm) at an angle of 90°. The primary standard was benzene, for which a value of $R_{90} = 48.5 \times 10^{-6}$ cm^{-1} was selected, and measurements were monitored repeatedly with this or a secondary glass standard. Clarification of solutions was effected by passage through Millipore filters (0.45 μm porosity) into cylindrical cells, optically ground by the Hellma Co. The cells were closed with tight-fitting Teflon stoppers which minimized solvent evaporation and were effective even when measurements were made at elevated temperatures. Values of the refractive index increment (dn/dc), for blue light, were measured with a Brice-Phoenix differential refractometer. Solutions were contained in a stoppered cell to minimize differential solvent evaporation.

Critical Solution Temperatures. Solutions in the concentration range 0-20% (v/v) were prepared and injected into capillary tubing (2-mm i.d.) sealed at one end. They were finally sealed under vacuum, such that the tubes were two-thirds full, and warmed slowly in a bath of silicone oil. Phase separation was recorded by noting the temperature at which the image of a copper wire, placed behind the tubes, became blurred. The lcst was taken to be the minimum temperature of the resulting cloud point curve and this procedure[2] was used for each fraction in each mixed solvent composition. The ucst was measured in a similar fashion only now the maximum of the corresponding low temperature cloud point curve was taken. The reproducibility of the threshold temperatures was ±0.5 K.

Results

Selective Adsorption. The system was first studied by measuring the solubility of one fraction ($M_w = 1.56 \times 10^5$) at room temperature. The light-scattering behavior of the polymer in various solvent compositions is shown in Figure 1. In all cases the plots had negative slopes and were usually curved. This suggested initially that the cosolvency effect was very poor and that the system was perhaps aggregated. Calculation of M_w, however, indicated that the values, though different from M_w measured in a single solvent, did not necessarily represent an aggregated polymer solution. When measurements are carried out in mixed solvent systems, variations in M_w are quite often found and these reflect the preferential adsorption of one of the components of the liquid mixture by the polymer chains. This appears to be the situation for this system and the extent of the selective adsorption can be estimated by calculating the magnitude of the selective adsorption parameter λ^* defined by[7]

$$\lambda^* = [(M^*/M)^{1/2} - 1][(dn/dc)/(dn/d\phi_1)] \qquad (1)$$

where M^* is the apparent molecular weight measured in the mixed solvent, ϕ_1 is the volume fraction of methylcyclohexane, component (1) in the solvent, n is the refractive index, and $(dn/d\phi_1)$ for the present system is 0.071.

The results are summarized in Table I and λ^*, plotted as a function of ϕ_1 is shown in Figure 2. The sigmoidal dependence of λ^* on ϕ_1, which appears to be characteristic of cosolvent systems,[1,3,8] is observed here and one can deduce that in the composition range ϕ_1 = 0.3-0.55, methyl-

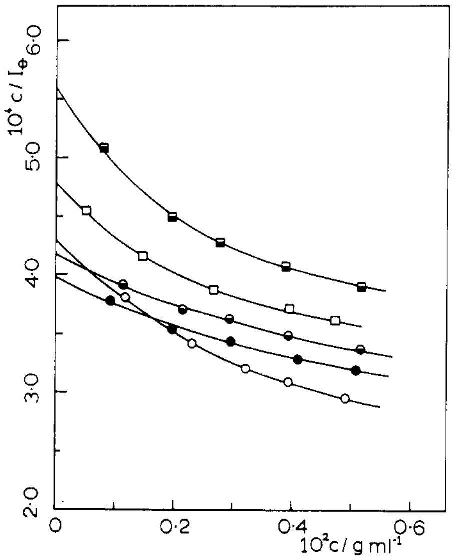

Figure 1. Light-scattering behavior of polystyrene M_w = 1.56 × 10^5 at 298 K in the mixed-solvent methylcyclohexane–diethyl ether: ϕ_1 = 0.30 (○); ϕ_1 = 0.35 (●); ϕ_1 = 0.40 (◒); ϕ_1 = 0.50 (□); ϕ_1 = 0.60 (◼). All data are measured at an angle of θ = 90°.

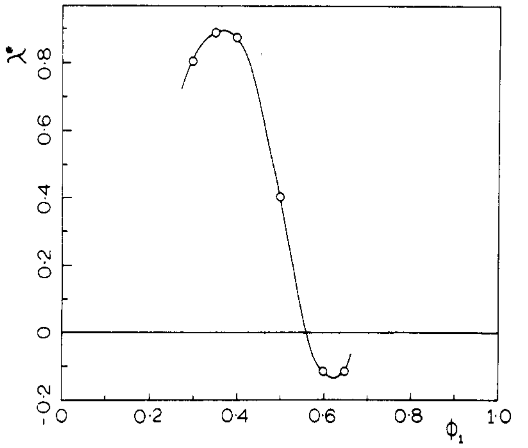

Figure 2. Selective adsorption parameter λ^* plotted as a function of the volume fraction of methylcyclohexane (ϕ_1) at 298 K.

Table I
Refractive Index Increments, Apparent Molecular Weights, Selective Adsorption Parameters, and Corrected Second Virial Coefficients for the Quasi-Ternary System Methylcyclohexane–Diethyl Ether–Polystyrene

ϕ_1	(dn/dc), cm^3 g^{-1}	10^{-5} M_w*	λ*	$10^3 A_2$, cm^3 g^{-2} mol
0.30	0.215	2.40	+0.800	−3.86
0.35	0.220	2.47	+0.890	−2.24
0.40	0.215	2.47	+0.870	−1.53
0.50	0.225	1.94	+0.401	−0.80
0.60	0.240	1.49	−0.113	−2.54
0.65	0.245	1.32	−0.115	−2.73

Table II
Expansion Data and Reduced Parameters for Methylcyclohexane

T (K)	V_1 (cm^3)	10^3 α (K^{-1})	$\tilde{V}_1$	V_1* (cm^3)	T_1* (K)
273	1.2731	1.053	1.2405	1.0263	4890
283	1.2867	1.077	1.2525	1.0273	4906
293	1.3008	1.101	1.2644	1.0288	4929
303	1.3154	1.124	1.2762	1.0307	4956
313	1.3304	1.145	1.2879	1.0330	4987
323	1.3459	1.166	1.2994	1.0357	5024
333	1.3618	1.186	1.3108	1.0389	5064
343	1.3781	1.204	1.3220	1.0425	5107
353	1.3950	1.222	1.3330	1.0465	5153
363	1.4123	1.240	1.3438	1.0509	5203
373	1.4300	1.257	1.3545	1.0558	5255

cyclohexane is preferentially adsorbed by the polymer from the bulk solution, while ether is preferentially adsorbed when the mixed-solvent composition lies above ϕ_1 = 0.55.

An estimate of the apparent second virial coefficient A_2* was made by measuring the initial slopes of the curves in Figure 1. These were corrected for the effects of preferential solvation using[7]

$$A_2 = A_2^*(M^*/M) \tag{2}$$

The plot of A_2 *vs.* ϕ_1 in Figure 6a, illustrates that in spite of the poor quality of the solvent mixture at this temperature, the system appears to display synergism and the composition of the mixture exhibiting maximum polymer solubility is in the region of ϕ_1 = 0.40–0.50. This is in reasonable agreement with the selective adsorption curve where λ^* = 0 occurs at ϕ_1 = 0.55 which is considered to represent the composition of the best solvent mixture.

Critical Solution Temperatures. The data presented above only provided a limited picture of the cosolvency. Considerably more information can be obtained by measuring the ucst and lcst as a function of both chain length and solvent composition and thereby constructing[2] a phase contour diagram for the system. In Figure 3 the critical solution temperatures are plotted against ϕ_1 for four fractions of polystyrene to produce a series of contour diagrams denoting the polymer solubility under various conditions. Of the two liquids in the mixture, ether is usually regarded as a nonsolvent for polystyrene, but it can dissolve the polymer if the molecular weight is low enough. This is shown in Figure 3 for sample M_w = 2.04 × 10^4, which is soluble in all compositions of the mixed solvent at 300 K, but even for this sample, the enhanced solubility in the mixed solvent is evidenced by the concave curvature of the cst–ϕ_1 lines. It is also interesting to note that the lcst of this fraction in pure ether is only 316 K. As M_w increases, ether becomes a nonsolvent so that the contour lines no longer touch the ϕ_1 = 0 axis and the cosolvent effect becomes more pronounced.

The first component in the mixture, methylcyclohexane, is a conventional Θ solvent for polystyrene at higher temperatures (Θ_u = 345 K). This results in the solubility loops always being open on the ϕ_1 = 1.0 axis, in contrast to systems composed of two nonsolvent.[2]

As each contour line formed defines the limits of solubility for polystyrene, of a given molecular weight, in the mixed solvent, extrapolation of this data to M_w = ∞ should allow construction of a contour line representing theta or pseudoideal conditions. This will comprise both upper and lower Θ temperatures for the corresponding solvent compositions in the system. This is shown as the broken line in Figure 3, bounding an area of compositions and temperatures in which any polystyrene fraction will be soluble. The curve was constructed by plotting reciprocal critical solution temperatures against $r^{-1/2}$, where r is the chain length of the polymer, for a number of solvent compositions and extrapolating to r = ∞. Typical curves are shown in Figure 4 and it can be seen that as the solvent quality deteriorates, the plots become increasingly curved until eventually the hyperbolic form representing restricted solubility is obtained. This increasing curvature of the lines means that the data cannot be adequately described by the simple Shultz–Flory equation[9]

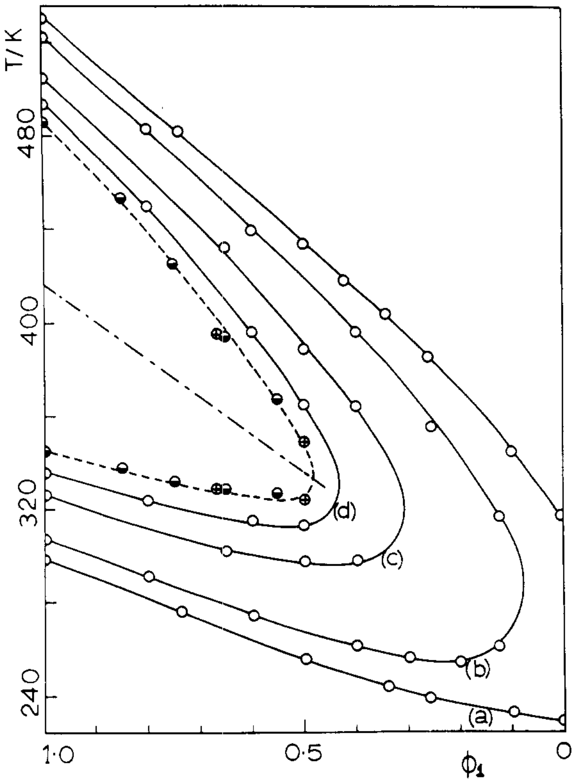

Figure 3. Critical solution temperatures for polystyrene fractions in the mixed-solvent methylcyclohexane–diethyl ether: (a) M_w = 2.04 × 10⁴; (b) M_w = 3.70 × 10⁴; (c) M_w = 1.56 × 10⁵; (d) M_w = 6.70 × 10⁵. ◒ represents theta conditions obtained by extrapolation (see text and Figure 4); ⊕ represents A_2 = 0 defined by light scattering (see Figure 6b), — - — - is the rectilinear diameter of the single-phase region.

$$1/T_c = (1/\Theta)\{1 + (1/\psi_1)[(1/r^{1/2}) + (1/2r)]\} \qquad (3)$$

and the extrapolations become less reliable as the solvent becomes poorer.

The accuracy of the experimentally extrapolated Θ points was verified from measurements of the slopes of C/I_{90} *vs.* C plots as a function of temperature for the two solvent compositions ϕ_1 = 0.5 and 0.667. All glass light-scattering cells, which were flame sealed under vacuum, were used to ensure a constant solution composition at elevated temperatures. This is illustrated in Figure 6b and the temperatures at which the slopes were zero compare favorably with the curve extrapolated from phase-separation data.

The Prigogine theory of corresponding states, in the form developed by Patterson and his coworkers, and the essentially equivalent approach of Flory, provide a more elaborate basis for treatment of such data.[5,6] According to Patterson, the equation relating to critical conditions is

$$\frac{C_1\nu^2}{1 - \tilde{V}^{-1/3}} + \frac{C_1\tau^2}{2[(4/3)\tilde{V}^{-1/3} - 1]} = \frac{1}{2(1 + r^{-1/2})^2} \qquad (4)$$

which predicts curvature in a plot of cst *vs.* $r^{-1/2}$. Here C_1 is a measure of the number of external degrees of freedom of the solvent molecule, τ is a measure of the difference in free volume of the components and ν represents the difference in the chemical nature of the components.[5] The reduced volume of the solvent $\tilde{V}_1$ can be calculated from the expansion coefficient α using

$$\tilde{V}_1 = \left[\frac{\alpha_1 T}{3(1 + \alpha_1 T)} + 1\right]^3 \qquad (5)$$

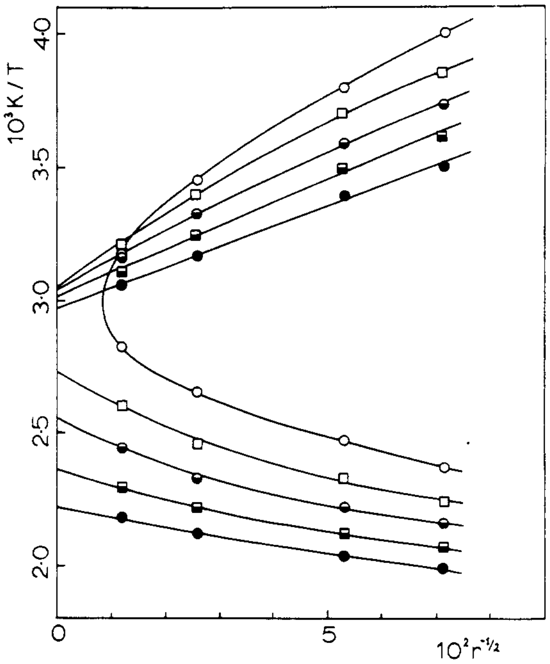

Figure 4. Sections from Figure 3 at constant ϕ_1; r is the degree of polymerization: ϕ_1 = 0.85 (●); ϕ_1 = 0.75 (⬓); ϕ_1 = 0.65 (◒); ϕ_1 = 0.55 (□); ϕ_1 = 0.45 (○).

Literature values[10,11] of C_1 and T_1^*, the temperature reduction parameter, for ether and methylcyclohexane were used to calculate the corresponding values of $C_1\tau^2$ and $C_1\nu^2$ for the mixtures, using a linear interpolation of the form $\bar{x} = \phi_1 x_1 + \phi_2 x_2$, where x_i the parameter for the pure solvent. T_i^* calculated for the mixtures in this way differs only slightly from that estimated using Patterson's approximate relation[5] for mixtures of homologues. The results for the single and mixed-solvent systems were disappointing, however, as can be seen in Figure 5a–c where neither a good data fit nor close correlation with the absolute values of the critical temperatures, were obtained.

Estimation of T_i^* for the mixtures using an interpolation procedure was verified by using a more direct method. The expansion coefficients of methylcyclohexane and the two solvent mixtures were measured by dilatometer over the temperature range 293–373 K. The specific volume V (cm³ g⁻¹) can be expressed by the relations

$$V = 1.273 + 1.341 \times 10^{-3}\,T + 2.282 \times 10^{-6}\,T^2$$

for methylcyclohexane

$$V = 1.297 + 1.575 \times 10^{-3}\,T + 2.953 \times 10^{-6}\,T^2$$

for ϕ_1 = 0.667 and

$$V = 1.312 + 1.659 \times 10^{-3}\,T + 3.550 \times 10^{-6}\,T^2$$

for ϕ_1 = 0.50. Here the temperature T is in degrees centigrade. The expansion coefficient $\alpha = 1/V(\mathrm{d}V/\mathrm{d}T)$ was calculated for each liquid and binary mixture and $\tilde{V}$ follows from eq 5. Each τ was derived from the expressions

$$\tilde{T}_i^{-1} = T_i^*/T = \tilde{V}_i^{4/3}/(\tilde{V}_i^{1/3} - 1) \qquad (6)$$

and

$$\tau = 1 - (T_1^*/T_2^*) \qquad (7)$$

using a value of the characteristic reduction parameter T_2^* for polystyrene of 7205.[11] Here $\tilde{T}$ is the reduced temperature.

The data for methylcyclohexane are given in Table II and show that, contrary to the theoretical expectation,

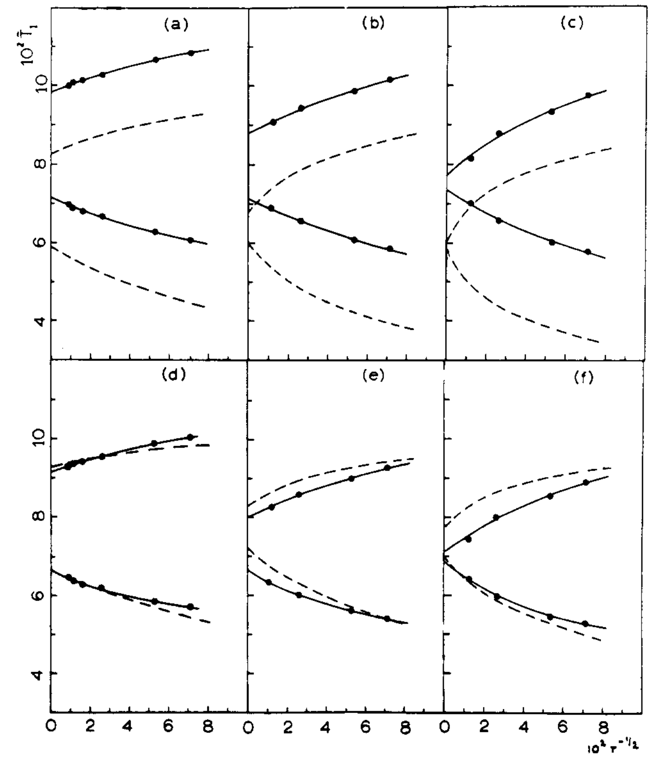

Figure 5. Plots of $r^{-1/2}$ *vs.* the reduced critical solution temperature $\tilde{T}_1$ for $\phi_1 = 1.0$ (a and d), $\phi_1 = 0.667$ (b and e) and $\phi_1 = 0.5$ (c and f). a–c are calculated using literature and interpolated values of T_1^*; d–f are calculated using values of T_1^* derived from experimentally determined expansion coefficients. See Tables III and IV for parameters used.

T_i^* is not a constant. This suggests that as the choice of T_i^* is now completely arbitrary, and as most literature values appear to refer to ambient temperature (298 K), selection of T_i^* at a more appropriate reference temperature may lead to improved agreement between theory and experiment. A reference temperature lying between the ucst and lcst would seem to be an appropriate choice and a value of 373 K was chosen. The selection was governed by the fact that this led to T_i^* values giving the best fit to the data.

The values of T_i^* measured at a reference temperature of 298 K are shown in Table III. In the first column the literature values of T_i^* for the single solvents are given and the corresponding interpolated values for the mixtures. Column 4 contains T_i^* calculated from the experimental expansion data, and it can be seen that the values for the mixtures are very similar to the interpolated T_i^*. In Table IV, the data are listed for a reference temperature of 373 K; interpolated data (column 1) for the mixed solvents, are again almost identical with those derived from direct experimental measurement. Two facts emerge; the choice of a new T_i^* improves the correlation in the polystyrene–methylcyclohexane systems immensely (see Figure 5d) and a direct experimental measurement of expansion data for mixed solvents leads to values of T_i^* which are almost identical with those derived using simple interpolation procedures. The absolute values of the critical temperatures predicted by the new parameters are now in better agreement with experiment (see Figure 5e,f).

Polystyrene–Methylcyclohexane. Reciprocal critical solution temperatures, measured in methylcyclohexane alone, were essentially linear with respect to $r^{-1/2}$ and could be treated using eq 3. The parameters derived for the binary system are $\Theta_u = 344$ K, $\psi_{1u} = 0.45$; $\Theta_L = 484$ K, $\psi_{1L} = -0.79$. The expected change of sign for ψ_1, on passing from upper to lower critical conditions, is found. The Θ temperatures are identical with those reported recently by Kuwahara *et al.*[11] although our values of ψ_1 are about 15% lower. The discrepancy is caused by different definitions of r. Kuwahara uses the ratio of the molar volumes at a fixed temperature whereas we have used the degree of polymerization.

Table III
System Parameters at 298 K

ϕ_1	T_1^*/K	$10^3\ C_1\nu^2$	$C_1\tau^2$	T_1^*/K (Expt)
1.00	4870	18.0	0.120	4940
0.667	4599[a]	13.8	0.148	4595
0.50	4463[a]	11.3	0.163	4480
0.00	4056	5.5	0.229	4105

[a] Linear interpolation; C_1(ether) = 1.11; C_1(methylcyclohexane) = 1.14.

Table IV
Systems Parameters at 373 K

ϕ_1	T_1^*/K	T_1^*/K	$10^3\ C_1\nu^2$	$C_1\tau^2$
1.00	5255	5255	26.9	0.084
0.667	4962[a]	4954	22.1	0.110
0.50	4828[a]	4828	19.4	0.122
0.00	4405			

[a] Interpolated.

Discussion

The ternary system studied here is composed of polystyrene dissolved in mixtures of a nonsolvent ether and a Θ solvent methylcyclohexane. At temperatures well below the Θ temperature for the polystyrene–methylcyclohexane system, a cosolvent effect is observed when ether is added. The effect is chain length dependent, but even for infinitely large molecular weight polymer, complete solution is obtained in the composition range, $\phi_1 = 0.48$–1.0 at $T = 345$ K, and cosolvency, observed within these limits is manifest in a lowering of the precipitation temperatures down to a minimum of 324 K at $\phi_1 = 0.54$. Shorter chain lengths can be dissolved in a wider composition range and at lower temperatures.

The mechanism of cosolvency is still open to discussion. The original explanation was based on the idea that the optimum cosolvent mixture would be one with a cohesive energy matching that of the polymer, but the use of the Scatchard mixing rule does not lead to a mixture with a δ value closer to the polymer than either solvent for this system. Thus one cannot discuss the enhanced solubility of the polymer in those simple terms. Attempts have been made to elaborate on the original Hildebrand approach, most notably by Hansen[12] who has formulated a three-dimensional solubility parameter. The Hildebrand δ is subdivided into contributions from hydrogen bonding, permanent dipole–dipole interactions, and a dispersion component. From this, one can define a sphere of solubility with a given radius which is characteristic of the polymer. The Hansen approach predicts ether is a nonsolvent and that methylcyclohexane lies just inside the solubility sphere. Calculation of the solubility behavior of mixtures indicates that the polymer will only dissolve in binary compositions between $\phi_1 = 0.7$ and 1.0. The method is relatively unsatisfactory, except perhaps as a qualitative guide for such systems, in that it does not predict any cosolvent action.

The use of excess thermodynamic functions to act as a guide to cosolvency appears to be a much sounder approach and our previous results support the suggestion

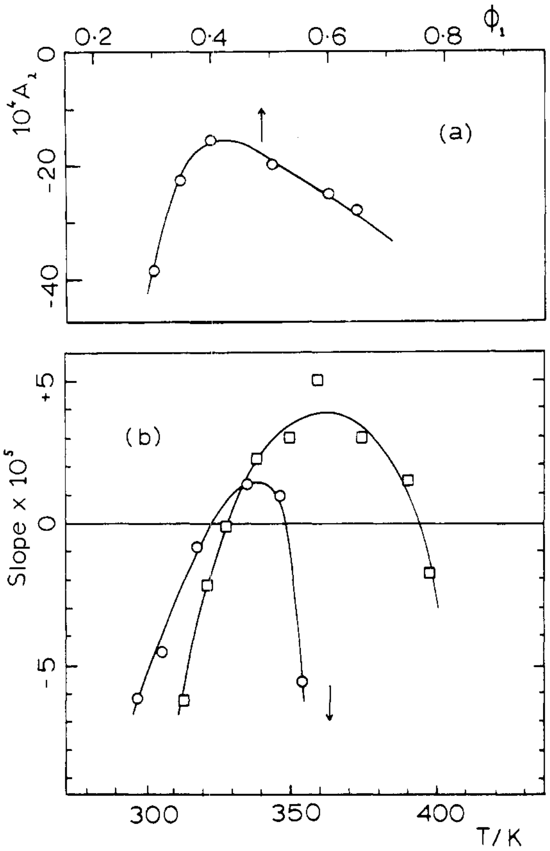

Figure 6. (a) A_2 *vs.* ϕ_1 for polystyrene fraction $M_w = 1.56 \times 10^5$ at 298 K; (b) slope of C/I_θ *vs.* C plots as a function of temperature for $\phi_1 = 0.50$ (○) and $\phi_1 = 0.667$ (□). All data measured at an angle $\theta = 90°$.

that cosolvent pairs possess a positive excess free energy of mixing $\Delta G_M{}^E$. A value of $\Delta G_M{}^E = +200$ J mol^{-1} at $\phi_1 = 0.5$ was estimated from the Rayleigh scattering of this binary liquid pair which is in keeping with this proposal. When $\Delta G_M{}^E$ is positive 1–2 liquid contacts are not particularly favored energetically. In a cosolvent system neither 1–3 nor 2–3 contacts are favorable either, but one can postulate the formation of 1–2–3 contacts on dissolution of the polymer in the mixtures which lower the free energy of the system. This type of explanation is consistent with the observed selective adsorption behavior. For the fraction $M = 1.56 \times 10^5$, λ^* is zero at $\phi_1 = 0.57$, and the maximum A_2 occurs at $\phi_1 = 0.40$–0.45. The small discrepancy between ϕ_1 values is to be expected if the molar volumes of the components differ[13] and one can say that a ϕ_1 of 0.5–0.57 represents the optimum composition of the best cosolvent mixture for the polymer. This mixture is the one in which the maximum number of 1–2–3 contacts can form. In this context one should probably consider that the so-called 1–2–3 contact is representative of a polymer chain and its immediate solvent environment as a whole rather than necessarily depicting isolated contacts involving a segment of each of the three species. Selective adsorption is then a consequence of the drive by the polymer to maintain the optimum solvent environment which will ensure maximum compatibility among the species. Thus for mixtures in the composition region $\phi_1 = 0.2$–0.57, methylcyclohexane is preferentially adsorbed, whereas ether is selectively adsorbed in the range $\phi_1 = 0.57$–0.7.

Although the cosolvent effect is not as pronounced as has been observed previously, there does exist a range of temperatures and compositions which define conditions for solubility for polystyrene of all chain lengths. This region of complete polymer–solvent compatibility is bounded by both upper and lower critical temperatures, and a variation in the polymer–solvent interaction parameter χ_1 should be observed with χ_1 decreasing from the limit of 0.5 as the temperature increases, followed by an increase to 0.5 again. This behavior is reflected in the A_2 *vs.* T curves which have been measured for two mixed-solvent compositions. The maximum value of A_2 lies very close to the rectilinear diameter of the one-phase region, which can be used to define the locus for conditions of maximum solubility (see Figure 6).

The ability of the Prigogine–Flory[5,6] theory to predict the critical temperatures bounding the single-phase region for the binary system polystyrene–methylcyclohexane was not wholly successful when $T_i{}^*$ values selected from the literature were used to calculate the curves. The shape and spread of the curves (Figure 5a) could be reproduced, but not the absolute value of T_c. The application of the binary theory to ternary systems was equally unsuccessful when literature data, for which $T_i{}^*$ was calculated at room temperature, were used with a simple interpolation procedure to obtain $T_i{}^*$ for the mixtures. The calculated curves were skewed in the upper critical region relative to the experimental points, and as expected, required a temperature shift to obtain coincidence of theory and experiment, see Figure 5b,c. A much improved theoretical and experimental correlation was obtained when a higher reference temperature was selected at which to recalculate $\tilde{V}_1$, and so τ. This was done directly for the liquid mixtures without resorting to any interpolation procedures, but the values of $T_i{}^*$ obtained, were almost identical with those calculated by interpolation at this new reference temperature. This suggests that, in spite of differences between the solvent molecules, the assumption that the liquid mixture can be treated as a single solvent in the context of the Flory–Prigogine theory is a reasonable one.

The data in Table II show that one weakness of the present theory lies in the evaluation of $T_i{}^*$. This is in agreement with the findings of other workers.[14,15] Consequently, selection of $T_i{}^*$ is largely arbitrary and as the critical regions are widely separated and normally situated above ambient temperatures, it was decided to select values of $T_i{}^*$ lying between the upper and lower critical temperatures for the quasi-binary and quasi-ternary systems examined here. The choice of $T_i{}^*$ at a reference temperature of 373 K led to remarkably good agreement between theory and experiment on an absolute basis. Not only did the theoretical chain-length dependence match the experimental results, but the prediction of the absolute value of T_c was also good. Thus the curves as drawn in Figure 5d–f required no temperature-shift factor to bring about coincidence of the data. Of course, the agreement is to some extent fortuitous as the choice of reference temperature is essentially arbitrary and in this case governed by the "best-fit" criterion. However, we believe the selection of the new reference temperature to be more realistic, lying as it does between the two extreme critical conditions. Before one could present justification for the choice of reference temperature, considerably more data would have to be gathered from other systems for comparison. Regretably, the weakness in the theory which leads to a variable $T_i{}^*$, may make the search for a temperature selection rule rather futile.

One can conclude from the results presented here that, within the framework of the Prigogine–Flory theory, quasi-ternary systems can be dealt with moderately well, if the binary liquid mixture is treated as a single liquid. The experimental measurements of the expansion coefficients for binary liquid mixtures show that simple interpolation procedures are quite adequate to calculate the parameters required to describe this system. This may not be generally true and could depend on the magnitude of the liquid–liquid interactions. In the light of these observations it was decided not to extend the theory at this time to encompass ternary systems as such.

Further work is in progress to establish the validity of the various points raised in this study.

Acknowledgment. The authors thank the S. R. C. for financial support during this work, in the form of a fellowship to I. J. M.

References and Notes

(1) J. M. G. Cowie and J. T. McCrindle, *Eur. Polym. J.*, **8**, 1185 (1972).

(2) J. M. G. Cowie and I. J. McEwen, *J. Chem. Soc., Faraday Trans 1*, **70**, 171 (1974).

(3) J. M. G. Cowie and J. T: McCrindle, *Eur. Polym. J.*, **8**, 1325 (1972).

(4) A. Dondos and D. Patterson, *J. Polym. Sci., Part A2*, **7**, 209 (1969).

(5) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969); D. Patterson, *J. Polym. Sci., Part C*, **16**, 3379 (1968).

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

(7) J. M. G. Cowie, *Pure Appl. Chem.*, **23**, 355 (1970).

(8) Z. Tuzar and M. Bohdanecky, *Collect Czech. Chem. Commun.*, **34**, 289 (1969).

(9) A. R. Shultz and P. J. Flory, *J. Amer. Chem. Soc.*, **74**, 4760 (1952).

(10) K. S. Siow, G. Delmas, and D. Patterson, *Macromolecules*, **5**, 29 (1972).

(11) N. Kuwahara, S. Saeki, S. Konno, and M. Kaneko, *Macromolecules*, **6**, 246 (1973).

(12) C. M. Hansen, *Chem. Technol.*, **2**, 547 (1972).

(13) A. Zivny, J. Pouchly, and K. Solc, *Collect. Czech. Chem. Commun.*, **32**, 2753 (1967).

(14) P. J. Flory and H. Hocker, *Trans. Faraday Soc.*, **67**, 2258 (1971).

(15) H. Hocker and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2270 (1971).

Computer Graphics in the Solution of the Chain Deformation Problem

Steven D. Stellman

Department of Biochemical Sciences, Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08540. *Received July 2, 1973*

ABSTRACT: Gō and Scheraga have given a general solution for determining the possible conformations of a section of a flexible polymeric chain between two fixed bonds (if the bonds coincide, the problem is equivalent to ring closure). Often, the fixed bonds are related by symmetry, such as that imposed by helicity or folding of antiparallel chains. A technique is shown for obtaining solutions using interactive computer graphics, whereby a plausible chain conformation or fold is approximated manually and completed by mathematical minimization. The procedure allows rapid, repetitive exploration of multiple solutions, and has many options for changing constraints. As an example, the backbone conformation of GpC, a dinucleoside phosphate, is used as a starting model, and gives upon minimization a set of backbone angles in the range of 11-fold helical RNA.

The chain deformation problem and the mathematically equivalent ring closure problem are of great importance in studies of biopolymers.[1] The problem arises whenever the geometrical relationship of two monomeric units to each other is known, for example, through a postulated hydrogen-bonding scheme, or by symmetry, and it is required to find the coordinates of atoms along or connected to the backbone chain between the fixed units.

A simple method of solution would obviously be of benefit in building models for chain folding of tRNA[2] or proteins,[3] and indeed any case where the groups (nucleotide bases or amino acids) on either side of the fold region are fixed with respect to each other.

In this paper we demonstrate a simple yet effective method for determining possible conformations of backbone atoms between fixed base units of a helical polynucleotide chain. The method is perfectly general and could be applied to any other polymeric system, such as a protein. While we have exploited the method specifically in our model building work with computer graphics, the mathematics are perfectly adaptable to nongraphical systems. However, computer graphics has unique advantages in the applications for which our model-building programs were developed.

Conformations of Polynucleotides

The backbone chain of a helical polynucleotide such as DNA contains many bonds about which semihindered or free rotation can occur. Consequently, a large (perhaps infinite) number of conformations exists which satisfy reasonable stereochemistry.

If the helix pitch and unit cell length in the fiber axis direction are determined for fibers of this polymer through X-ray fiber diffraction, then the cylindrical coordinates of the base and backbone atoms are usually obtained by manually building wire models consistent with these data, ruling out those models which are stereochemically impossible, and refining the remaining models through a least-squares procedure.[4,5]

The deformation problem enters the situation because, given the absolute orientation of, say, one base with respect to the fiber axis, the coordinates of the next and every succeeding base are uniquely fixed by helical symmetry. The problem is then to find possible conformations of the sugar–phosphate backbone which fit in between two adjacent bases and which are stereochemically acceptable (in terms of near-standard bond lengths and bond angles).

Digital computers have long been used to generate the accurate coordinates of such models from initial data measured on stiff-wire models, and to refine the models against observed X-ray diffraction data.[6] Recently, computers employing interactive three-dimensional graphics have been used to generate complete models themselves.[7] An obvious advantage of this procedure is to circumvent the hazards of real models, such as gravitational collapse, inflexible bond lengths and bond angles, and poorly measurable dihedral angles. Fast calculation of interatomic overlaps is also possible.[8]

In the following section we describe a method for constructing such models directly comparable with X-ray diffraction data. Given the screw and fiber axis length as initial conditions, and allowing the orientation of the base with respect to the fiber axis and its distance therefrom as adjustable parameters, the deformation problem is solved