Polymer–cosolvent systems: 7. The application of free volume theory to the classical cosolvent systems formed from polystyrene in acetone and n-alkanes

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The Prigogine–Patterson theory of polymer solutions has been applied to the cosolvent systems formed from mixtures of acetone (1) with n-alkanes (2). The necessary reduction parameters were calculated taking due account of acetone/alkane interactions as characterized by the Flory X_{12} parameter. The effect of relatively increased free volume differences in the solvent mixtures is counteracted by a marked decrease in the enthalpy term which brings about an overall decrease in the polymer/solvent interaction parameter (χ). It is suggested that cosolvency is predominantly enthalpic in origin and a possible mechanism is postulated.

INTRODUCTION

The free volume approach to polymer solution thermodynamics can, at least semi-quantitatively, account for critical solution behaviour. In particular, the Prigogine theory, in the form adopted by Patterson, has been used by us[1-3] and others[4,5] to describe the phase behaviour of polymers dissolved in both good and in poor solvents. The theory can also be applied to mixed solvents by treating the mixture as a single fluid with empirically determined reduction parameters[6]. However, in the absence of the necessary information (expansion and compressibility coefficients) on the mixed solvent, simple volume fraction averaged values of the reduction parameters can also give satisfactory results[7]. In the preceding two papers in this series[8] the phase behaviour of polystyrene (3) in n-alkanes and, in particular, in mixtures of acetone (1) with n-alkanes (2) has been described, and a cosolvent effect demonstrated. The necessary properties of all the single liquids are available and we have chosen to employ the Flory prescriptions[9] in order to estimate the acetone/alkane mixed solvent reduction parameters necessary for the application of the theory. The relevant equations are, for the pressure reduction parameter

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12} \qquad (1)$$

for the temperature reduction parameter

$$T^* = p^* / \{ (\phi_1 p_1^* / T_1^*) + (\phi_2 p_2^* / T_2^*) \} \qquad (2)$$

and for the core volume

$$V^* = x_1 V_1^* + x_2 V_2^* \qquad (3)$$

where the unsubscripted symbols refer to the mixed solvent. The segment fraction is defined by

$$\phi_1 = 1 - \phi_2 = x_1 V_1^* / (x_1 V_1^* + x_2 V_2^*) \qquad (4)$$

and the site fraction by

$$\theta_2 = 1 - \theta_1 = \phi_2 / \left(\phi_1 \frac{S_1}{S_2} + \phi_2 \right) \qquad (5)$$

x_i is the mole fraction and S_i the ratio of the surface area to the core volume of the solvent molecules. The ratio S_1/S_2 is a measure of the surface sites available for interaction with neighbouring molecules and, for our purposes, acetone is treated as a sphere of volume V_1^* and the n-alkanes as right cylinders with a diameter of 5 Å and having volumes equal to V_2^*.

In order to calculate p^* and T^* the value of X_{12}, the Flory interaction parameter which takes account of the energy differences between like and unlike contacts, must be established. X_{12} may be evaluated from either experimental heat of mixing or volume of mixing data[9,10] and a particularly simple method has been outlined by Howell et al.[11] using only a single value of the excess heat of mixing (H^E) at $x_1 = x_2 = 0.5$. The heats of mixing have been experimentally determined for acetone with the n-alkanes pentane, hexane, decane and hexadecane[12,13] and the values of X_{12} which fit the H^E data at $x_1 = 0.5$ are listed in *Table 1* along with the other equation of state parameters for the single solvents and for polystyrene. The magnitude of X_{12} for the acetone/alkane interaction is seen to be dependent on the alkane chain length[†] and

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[†] A dependence on chain length was also employed by Orwoll and Flory[14] to account for the thermodynamic properties of binary mixtures of n-alkanes. The magnitude of X_{12} might reasonably be expected to be temperature dependent also and the use of the values shown in *Table 1* to estimate mixed solvent behaviour at higher temperatures is an unavoidable approximation. It should not, however, affect the conclusions reached.

this behaviour fits more closely to a quadratic rather than linear change. The values in brackets in the last column of *Table 1* have been interpolated and extrapolated on the basis of a least squares quadratic fit to the four experimentally based values. Using these, and equations (1)–(5), p^*, T^* and V^* can be evaluated at any chosen composition of the acetone (1)+n-alkane (2) cosolvent mixtures described in part 6 of this series[8] leading to the corresponding values of c, where

$$c = \frac{p^* V^*}{RT^*} \qquad (6)$$

is one-third of the external degrees of freedom of the solvent mixture. The free volume difference between polystyrene (3) and the solvent mixture is then given by $c\tau^2$ where

$$\tau = (1 - T^*/T_3^*)^{\frac{1}{3}} \qquad (7)$$

The parameter v^2, which characterizes contact energy differences in the Prigogine–Patterson Theory, may be obtained at any cosolvent mixture composition if it is assumed that the T_p values on the phase contour diagrams (*Figures 1* and *2* of part 6 of this series[8]) can be identified with the respective critical solution temperatures. The T_p data are then extrapolated as previously described[8] to yield the coalescence points of the upper and lower critical solution temperatures where, under these conditions, the Patterson expression pertaining to critical conditions[4,8] reduces to

$$2cv^2 = 0.75c\tau^2 + 0.25(1 + r_\infty^{-1/2})^2 \pm$$

$$(0.75c\tau^2(1 + r_\infty^{-1/2})^2)^{1/2} \qquad (8)$$

Here r_∞ is the coalescence value of r defined as V_3^*/V^*. The values of v^2 thus derived, and of $c\tau^2$, are plotted for each of the cosolvent systems against composition in *Figures 1* and *2*.

DISCUSSION

$c\tau^2$ and v^2 (or cv^2) quantify the entropic (χ_{ms}^S) and enthalpic (χ_{ms}^H) contributions to χ_{ms}, the interaction parameter of the polymer with the solvent mixture, and govern the temperatures of demixing in the LCST and UCST regions respectively. If $c\tau^2$ and v^2 were linear functions of solvent

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‡ T_3^* is the polystyrene temperature reduction parameter.

composition then both critical solution temperatures would be similarly linearly related to solvent composition and cosolvent behaviour thus absent. As can be seen in *Figures 1* and *2* these two parameters deviate appreciably from linear or 'ideal' behaviour in opposite directions, and it is convenient to discuss the behaviour of each in turn.
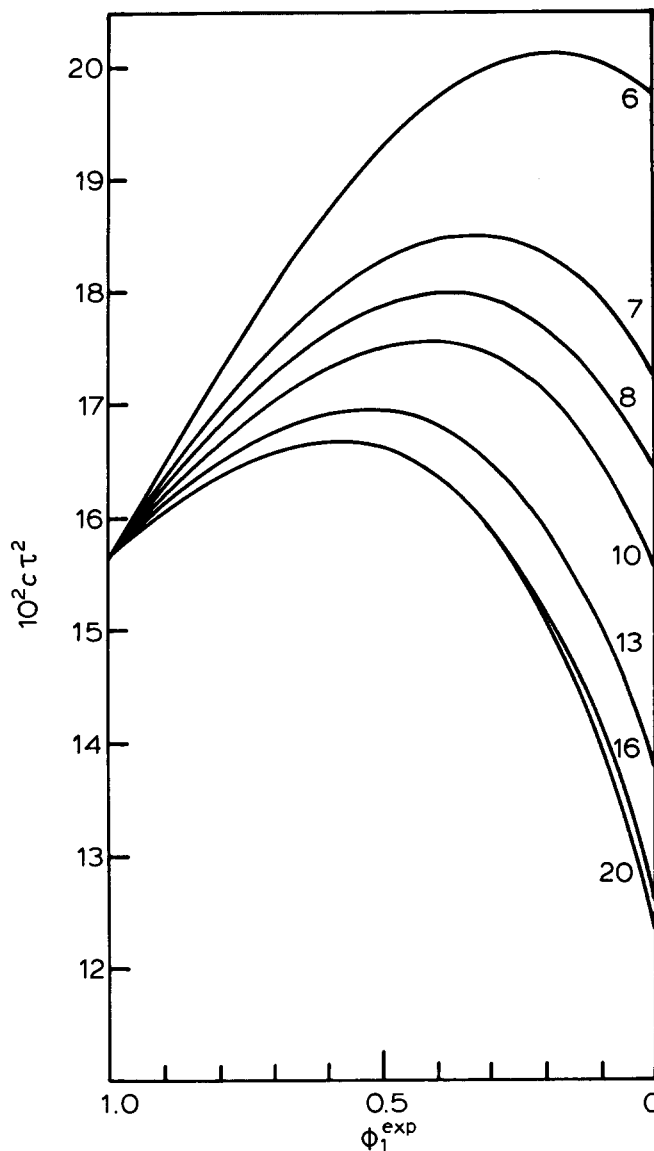

Figure 1 Plots of the free volume parameter $(c\tau^2)$, in each of the binary solvent systems+polystyrene, against the experimental volume fraction of acetone (ϕ_1^{exp}). The number of carbon atoms in the n-alkane component of each mixture is indicated

Table 1 Equation of state parameters for the pure compounds used in calculations

	T^*/K	$p^*/J\,cm^{-3}$	$V^*/cm^3\,mol^{-1}$	$V/cm^3\,mol^{-1}$	$10^{-8}S/cm^{-1}$	c	$H^E/J\,mol^{-1}$	$X_{12}/J\,cm^{-3}$
n-pentane[a]	4170	421	85.38	115.13	1.08	1.04	1450[e]	84.7
n-hexane[a]	4420	448	99.48	130.61	1.04	1.21	1560[e]	85.0
n-heptane[a]	4670	431	113.65	146.45	1.01	1.26	–	(85.9)
n-octane[a]	4850	431	127.89	162.63	0.99	1.37	–	(86.7)
n-decane[a]	5130	447	156.1	194.9	0.95	1.64	1980[f]	89.1
n-tridecane[a]	5430	435	198.3	243.6	0.92	1.91	–	(93.6)
n-hexadecane[a]	5680	448	241.1	292.8	0.90	2.29	2380[f]	99.9
n-eicosane[a]	5860	459	298.0	354.0	0.88	2.81	–	(111.2)
acetone[b,c]	4355	597	55.54	73.98	1.07	0.91$_6$	–	–
polystyrene[d]	7420	–	84.33	–	–	–	–	–

Equation of state data calculated from:– [a]ref. 17 at 293K; [b]ref. 18, [c]ref. 19 and [d]ref. 20 at 298K. Excess heat of mixing for equimolar amounts of acetone and alkane at [e]293K and [f]298K, taken from refs. 12 and 13 respectively
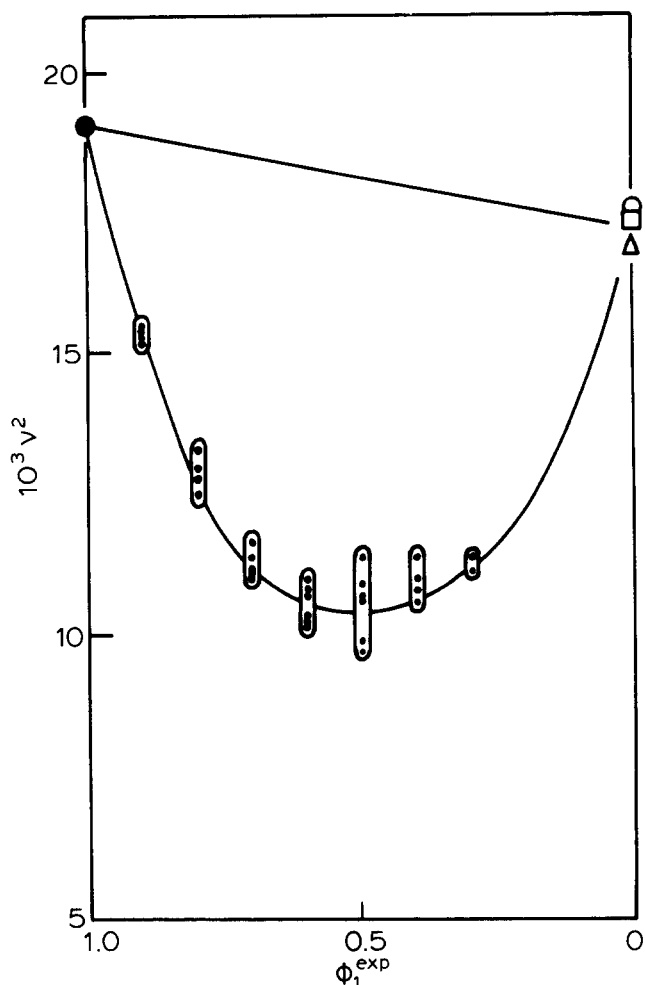
Figure 2 Interaction parameter v^2 vs. ϕ_1^{exp} in the binary solvent systems+ polystyrene. v^2 values calculated at each value of ϕ_1^{exp} show no correlation with n-alkane chain length. $\bullet = v^2$ for polystyrene in acetone[7], and in hexane ($\bigcirc$), heptane ($\square$) and octane ($\triangle$)[8]

LCST demixing results from a large free volume or expansion difference between a dissolved polymer and its solvent. In the Prigogine–Patterson theory the relative expansions of polymer and solvent are quantified by their respective temperature reduction parameters. Numerically close T^* values indicate small free volume differences and, in the absence of other effects, relatively high *LCST* demixing behaviour. The distinct positive deviation of $c\tau^2$ in each of the cosolvent systems implies the opposite effect i.e. a greater free volume difference between polymer and mixed solvent than would be obtained by simple compositional averaging of the free volume differences in the single solvents. The behaviour shown in *Figure 1* is a consequence of the X_{12} values characterizing the interactions in the binary mixtures being large and positive and it can be generally concluded that polymers dissolved in binary mixtures which form with an appreciably positive H^E (and this will normally include mixtures with positive free energies of mixing) will exhibit miscibility ranges at lower temperatures than might be expected from interpolation of the single solvent demixing behaviour. This is reflected in the loci of maximum cosolvent action shown in *Figures 1* and *2* of part 6 of this series[8]. Cosolvent behaviour, defined by an increase in *LCST* and lowering of *UCST* values, in such mixtures does not originate from favourable free volume effects and must therefore be a result of a more favourable enthalpic contribution which can outweigh the above. This conclusion is substantiated by the large negative deviation of the v^2 values in acetone (1)+n-alkane (2) mixtures from ideal linear behaviour which can be seen in *Figure 2*.

Energetically unfavourable contact interactions are characterised by large values of v^2 with low values indicating favourable contacts, and in the limit of like–like interactions v^2 assumes the value zero. In the present case the relatively lower v^2 of the solvent mixtures do not represent any simple averaging of the acetone (1)+polystyrene (3) and the n-alkane (2)+polystyrene (3) values,
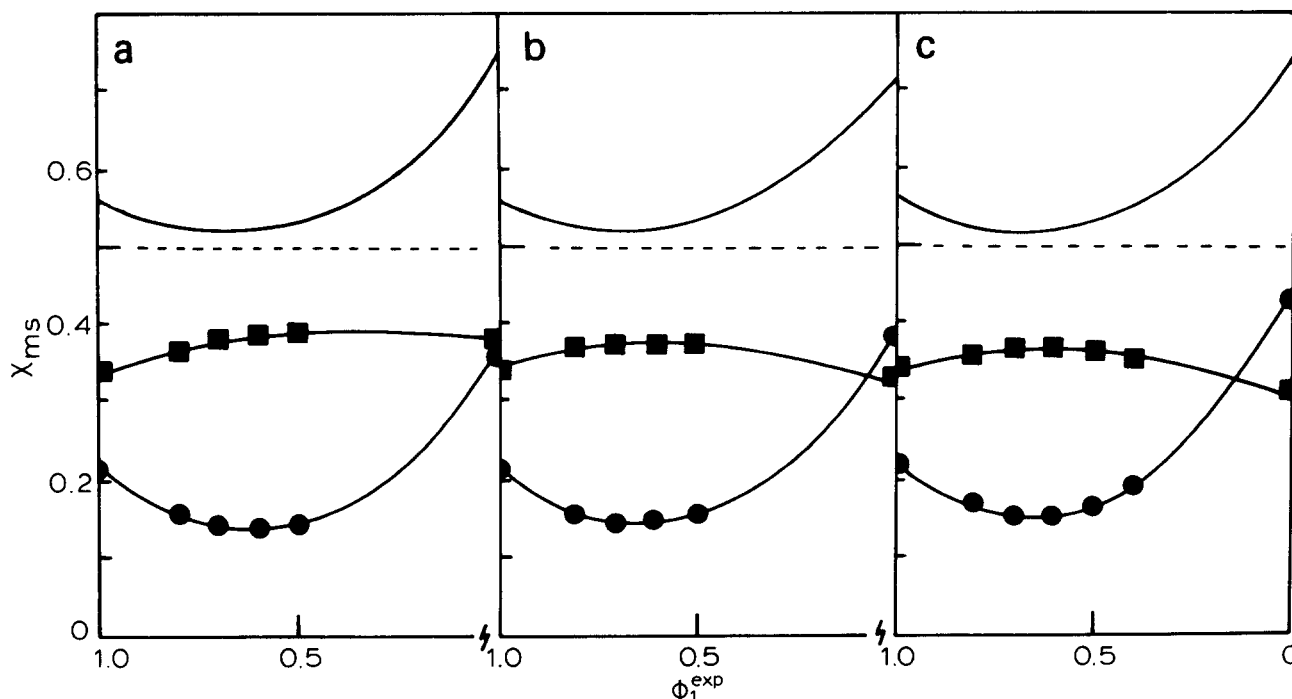

Figure 3 χ_{ms}^H (—●—) and χ_{ms}^S (—■—) vs. ϕ_1^{exp} for the three binary solvent systems acetone+hexane (a), +heptane (b), +octane (c). The full curve represents $\chi_{ms}=\chi_{ms}^H+\chi_{ms}^S$ and the broken line indicates $\chi_{ms}=0.5$. All data calculated at 320K

and this must arise from more subtle effects at the molecular level. A possible mechanism that can be envisaged is one in which a cosolvent mixture provides a polymer with an increased *number* of potential interaction sites compared with those available separately in the two single solvents. In a poor solvent a certain number of polymer–solvent contacts must be made to promote solution and these compete with polymer–polymer contacts which provide the drive towards demixing. If, in a solvent mixture, additional contacts are then available through interaction with the second component—even though these are energetically no more favourable than the first single solvent contacts—a cosolvent action will be achieved. This picture assumes that a polymer presents a number of different potential contact sites or surfaces, each of which can interact most effectively with an appropriate solvent molecule (or part of a solvent molecule) such that the combined (1–3) and (2–3) contacts lead to enhanced solvation of the chain. Both the shape of a solvent molecule and the nature of the various surface sites it may possess must be regarded as important factors when comparing solvents. The former has been considered by Delmas[16] and the latter will be the subject of a future contribution. At present it is suggested that large cosolvent effects will most likely occur in combinations of poor solvents, each component of which interacts favourably with sets of different sites on the polymer chain. Cosolvency will thus be found when the components are dissimilar in polarity, or possess functional groups of differing chemical natures and/or polarity.

Returning to the v^2-composition behaviour shown in *Figure 2*, it can be seen that all of the binary mixtures may be adequately described by a single curve over the whole range of study and that this extrapolates sensibly to the v^2 values already established for polystyrene dissolved in hexane, heptane and octane. Direct estimates of v^2 for solutions of polystyrene in the higher alkanes from demixing behaviour are unobtainable because of the elevated temperatures involved. Nevertheless it is obvious from the data in *Figure 2* that the values of v^2 at intermediate compositions of the binary mixtures are up to *ca.* 50% less than those in the single solvents and, in terms of the Patterson–Prigogine theory, imply that cosolvency results from a much reduced *enthalpic* contribution to χ_{ms}. A previously published analysis of the cosolvent system acetone (1) + diethyl ether (2) + polystyrene (3)[7] also yields v^2 values which deviate in precisely the same manner as those in *Figure 1*, substantiating the proposed origin of cosolvency, since in this system also the solvents mix with a positive H^E.

The isothermal (320K) variations of both χ_{ms}^H and χ_{ms}^S in the cosolvents acetone (1) with hexane (2), heptane (2) and octane (2) are shown in *Figure 3*. The data were calculated from the appropriate values of $c\tau^2$ in *Figure 1* and of v^2 in *Figure 2*, using equations (1) and (7) of part 5 of this series[8]. Cosolvency is characterized by a minimum in χ_{ms} at intermediate compositions of a binary mixture. *Figure 3* implies that this results from a purely enthalpic effect, namely a minimum in the χ_{ms}^H-composition curves which is sufficient to counteract the unfavourable free volume effect mentioned earlier and which leads to the shallow maxima in χ_{ms}^S.

Similar conclusions may be reached from an examination of *Figure 4* which again shows the variations in χ_{ms}^H and χ_{ms}^S for the binary solvent mixtures, but here calculated at the coalescence temperatures of the upper and
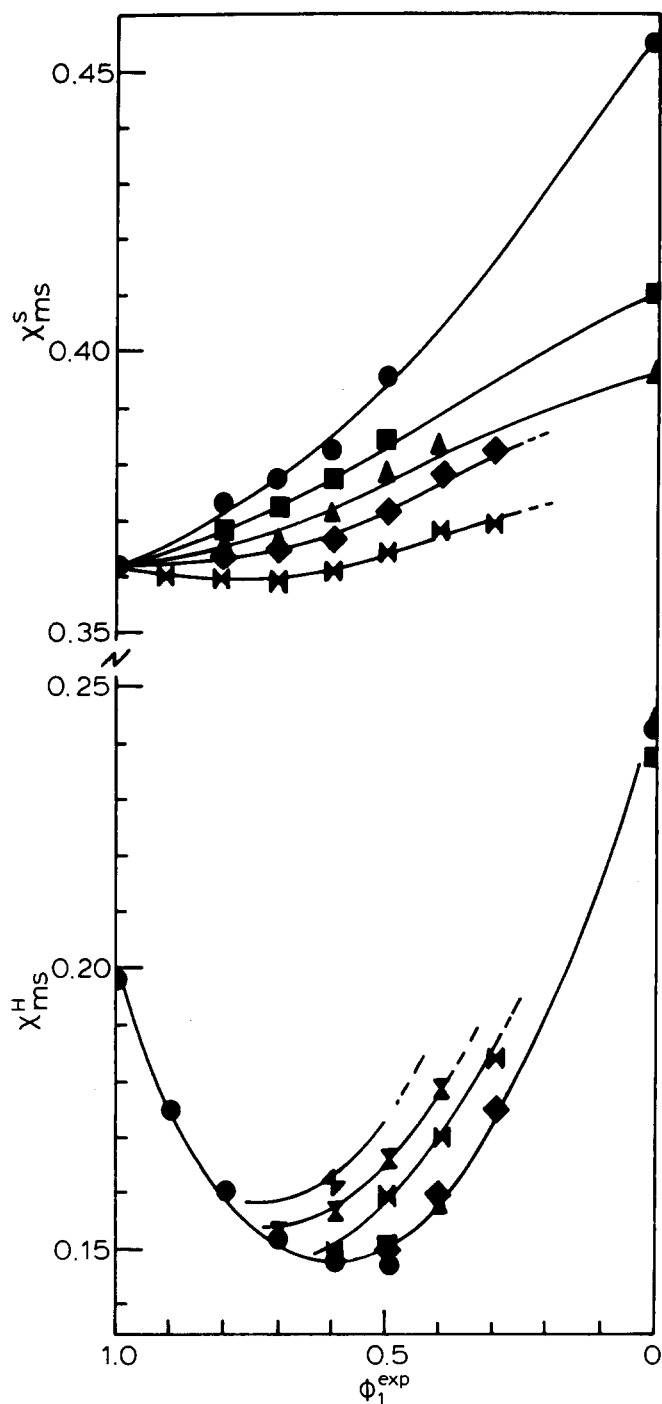

Figure 4 χ_{ms}^H and χ_{ms}^S vs. ϕ_1^{exp} along the loci of maximum cosolvent action in binary mixtures of acetone+ (−●−) hexane, (−■−) heptane, (−▲−) octane, (−◆−) decane, (−⋈−) tridecane, (−✕−) hexadecane, and (−✦−) eicosane. The χ_{ms}^S curves for hexadecane and eicosane are almost identical to that for tridecane. The values of χ_{ms}^H for heptane, octane and decane at $\phi_1^{exp}>0.5$ are coincident with those of hexane

lower T_p values. *Figure 4* thus presents the changes in these terms along the loci of maximum cosolvent action. In all cases χ_{ms}^S changes smoothly along shallow, approximately sigmoidal, curves and decreases as the n-alkane component of the mixture increases in size. χ_{ms}^S at intermediate compositions now shows a slight negative deviation from linear behaviour in acetone rich compositions. As in the isothermal case, χ_{ms}^H passes through pronounced minima. Although at $\phi_1^{exp} \geqslant 0.75$ a single curve adequately describes all the alkane/acetone mixtures, for the longer

alkanes it is clear that the enthalpic contribution becomes solvent mixture dependent and extrapolation suggests that binary alkane/polystyrene interactions become much less favourable after n-nonane, in close accord with previous predictions[8]. The loci of maximum of cosolvent effect, therefore, pass through temperatures such that the unfavourable free volume effects are minimised, and indeed cosolvency under these conditions is a result of a decrease in both χ_{ms}^H and χ_{ms}^S (albeit small) with respect to their respective single solvent values. It is also as a result of a balance between enthalpic and entropic contributions that the most effective cosolvent action occurs with mixtures of acetone with tridecane, rather than might be inferred from the calculation[8] that the 'best' alkane/polystyrene interaction occurs with nonane. The origin of this lies with the binary acetone/alkane interactions, characterised by X_{12}, which dictate the relative magnitudes of the entropic effects in the binary and single solvents respectively.

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