Polymer–cosolvent systems: 6. Phase behaviour of polystyrene in binary mixed solvents of acetone with n-alkanes–examples of 'classic cosolvency'

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The demixing behaviour of polystyrene fractions in binary combinations of acetone (1) and a series of n-alkanes (2) containing up to twenty carbon atoms has been established and the data presented as phase contour diagrams. Each binary liquid system exhibits the characteristics of classic cosolvency and the maximum molecular weight of polymer that may be dissolved is *ca.* 10^6 gmol^{-1} in combinations of acetone and tridecane. The shapes of the phase contour diagrams can be related to the solvent behaviour of the n-alkane used towards polystyrene, although cosolvent action is not a simple linear function of the mixture composition.

Keywords Cosolvency; binary solvent mixtures; polystyrene; acetone; n-alkanes; critical solution temperatures; phase diagrams

INTRODUCTION

In part 5 of this series[1] the demixing behaviour of polystyrene in n-hexane, n-heptane and n-octane is described. The three alkanes are all poor solvents for the polymer, dissolving only molecular weights below *ca.* 9100 g mol^{-1}. In this paper the demixing behaviour of polystyrene (3) dissolved in a number of binary solvent mixtures prepared from acetone(1) and a series of n-alkanes (2) is described and in which a strong cosolvent effect can be demonstrated.

The mechanism of cosolvency, and hence the ability to predict potential cosolvent pairs, is still a matter of some debate. The simplistic approach of using a solvent mixture with an average solubility parameter (δ) closer to (or equal to) that of the polymer than the δ parameters of the separate components implies that cosolvent mixtures will only be formed when $\delta_1 < \delta_3 < \delta_2$[2,3]. This has been shown not to be a necessary criterion for cosolvency to occur, and systems where both δ_1 and δ_2 are greater and smaller than δ_3 have been reported[4,5]. Cosolvency has also been explained in terms of associated structures which can occur in simple solvent systems but which are broken in cosolvent mixtures[6-8]. A more general criterion for cosolvency, however, is suggested from the observation that the excess free energy of mixing ΔG_M^E of known cosolvent binary liquid systems is positive[3,5,9], implying that the 1–2 liquid contacts are not particularly favoured energetically. In cosolvent systems where the two separate components are themselves poor solvents for the polymer, the 1–3 and 2–3 contacts are not particularly favourable either, and the possibility of '1–2–3' contacts which are conducive to solution has been suggested[5]. ΔG_M^E has been determined for a number of acetone + n-alkane (hexane to hexadecane) systems and values in the range +900 to +1200 J mol^{-1} reported[10-12], the mixtures thus deviate significantly from ideality, and indeed show only limited miscibility just below room temperature[13]. On this basis binary mixtures of acetone and n-alkanes reported here were expected to show a cosolvent effect.

EXPERIMENTAL

The polystyrene samples used were narrow fractions obtained from either the Pressure Chemical Co. or from Dow Physical Research Labs. The solvents were dried and distilled prior to use or, in the case of hexadecane and eicosane, were recrystallized. Solvent mixtures were made up by volume or by weight as necessary. Precipitation temperatures (T_p) were measured as described previously[3] at a polymer volume fraction (with respect to total solvent) of $\phi_3 = 0.04$. This concentration is close to the critical concentration for polystyrene at both the upper critical solution temperature (*UCST*) and the lower critical solution temperature (*LCST*) in n-hexane, n-heptane and n-octane.[1]

The demixing temperatures of n-alkanes in acetone were also determined as the onset of observable turbidity on cooling.

RESULTS AND DISCUSSION

The demixing behaviour of polystyrene in n-alkane/acetone mixtures is shown in *Figures 1* and *2*. Each figure is a 'phase-contour' diagram in which the precipitation temperatures (in both the *UCST* and *LCST* regions) at various experimental volume fractions of the mixed solvent (ϕ_1^{exp}) have been joined for each polystyrene

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fraction studied. The vertical separation at any composition gives the miscibility range for $\phi_3 = 0.04$. The $\phi_1^{exp} - T$ plane bounded by any contour indicates the region of complete miscibility of polystyrene of a particular molecular weight, again at $\phi_3 = 0.04$. However, since the *UCST* and *LCST* are to be found at temperatures close to this polymer concentration, the contours provide an adequate guide to the *minimum* regions of *complete* miscibility of polystyrene in the various acetone/n-alkane mixed solvents.

All of the acetone (1) + n-alkane (2) systems show the characteristics of 'classic' cosolvency, as found for the system acetone + ether + polystyrene[3], in that miscibility ranges are dramatically increased at intermediate compositions of the solvent mixture. Taking acetone (1) + n-hexane (2) as an example, *Figure 1* shows that polystyrene 20400 is not completely miscible with acetone and even

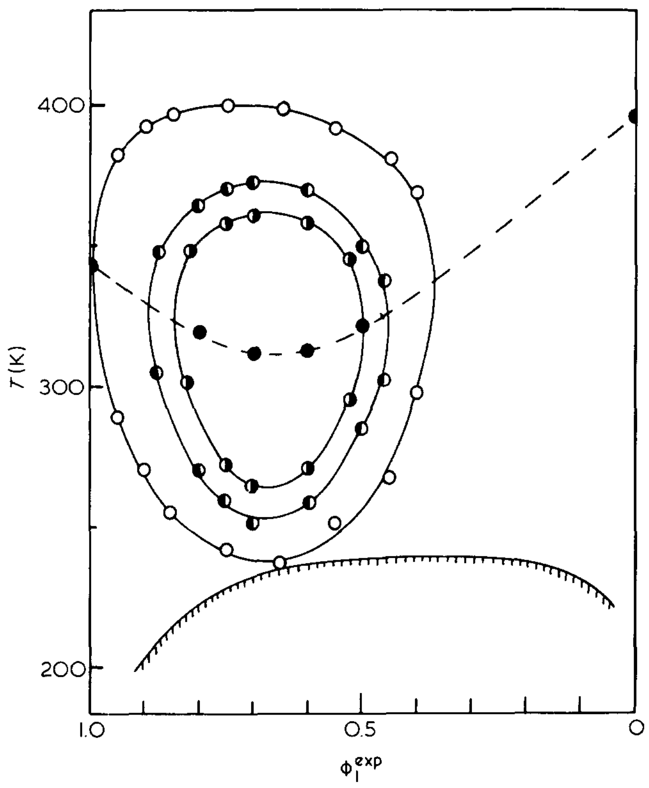

Figure 1 Phase contour diagram for polystyrene in the binary solvent mixture acetone (1) + n-hexane (2). Precipitation temperatures for polystyrene molecular weights (g mol^{-1}); 20400 –○–, 37000 –◐– and 51000 –◑–. Phase separation boundary for acetone (1) + n-hexane (2); ⫽⫽⫽ Coalescence points —●—

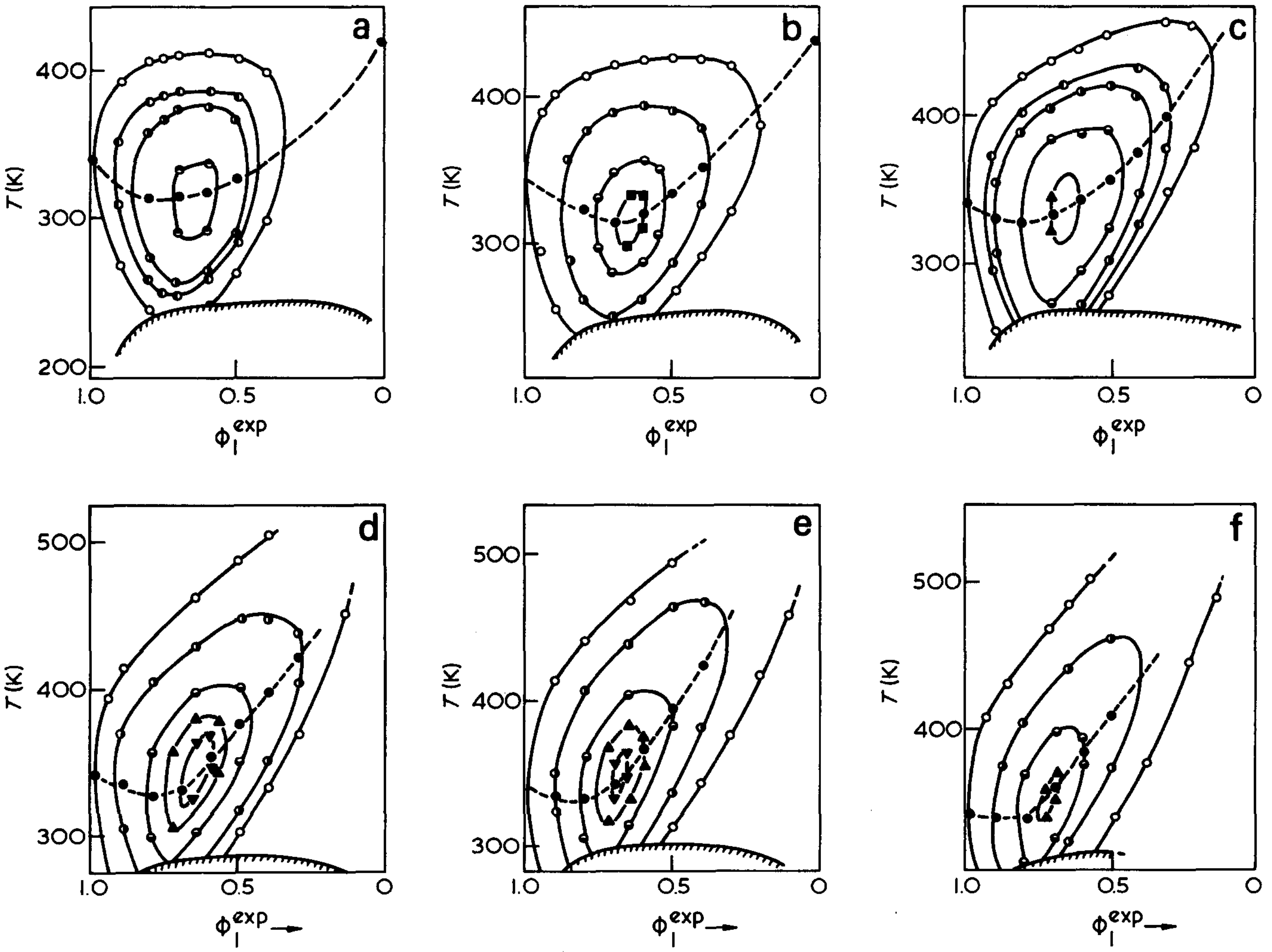

Figure 2 Phase contour diagrams for polystyrene in acetone (1) + n-alkane (2) binary solvent mixtures. n-alkane is (a) heptane, (b) octane, (c) decane, (d) tridecane, (e) hexadecane and (f) eicosane. Polystyrene molecular weights (g mol^{-1}); 20400 –○–, 110000 –◓–, 153000 –◒–, 267000 –■–, 390000 –▲– and 670000 –▼–. Coalescence points ---●---. Acetone + n-alkane phase boundary indicated ⫽⫽⫽

less so with n-hexane, but, for $\phi_1^{exp} \simeq 0.65$, this molecular weight now has a large miscibility range of ~ 160K. At the same solvent composition, polystyrene 51 000 can be dissolved. As the n-alkane component of the solvent mixture becomes longer there is a corresponding enhancement of cosolvent action. The cosolvent loops increase in size and the maximum molecular weight that the system is capable of dissolving also rises. The solvent composition at which this occurs stays remarkably constant at $\phi_1^{exp} \simeq 0.65$ although there is a marked distortion of the phase contour diagrams towards $\phi_1^{exp} = 0$ and higher temperatures.

The effectiveness of a cosolvent mixture may be quantified by the miscibility range of a chosen polymer fraction. However, in this series of mixtures acetone/n-alkane demixing occurs and this truncates an increasingly large part of each phase contour diagram. The systems are compared, therefore, on the basis of the phase separation behaviour at $\phi_1^{exp} = 0.65$, and this is shown in *Figuee 3* where the T_p values are plotted as a function of $r^{-1/2}$. r is defined, as before[1], by the ratio of the hard core volumes of the polymer and solvent V_3^*/V^*, where $V^* = x_1 V_1^* + x_2 V_2^*$ is the hard core volume of the mixture at $\phi_1^{exp} = 0.65$ with x_1 and x_2 the corresponding mole fractions. The limiting molecular weight ($\bar{M}_n^{lim}$) which each solvent mixture is capable of dissolving is taken to be the point at which the precipitation temperatures, associated with upper and lower critical solution behaviour, coincide. *Figure 4* is a plot of log $\bar{M}_n^{lim}$ against the length of the hydrocarbon component of the cosolvent mixture, from which it can be seen that a maximum in cosolvent action occurs in a mixture of acetone + tridecane. The cosolvent effect of this combination is comparable with mixtures of acetone and diethyl ether[3], as measured by the fact that polystyrene of $\sim 10^6$ g mol^{-1} can be dissolved at the appropriate compositions of the respective solvent mixtures.

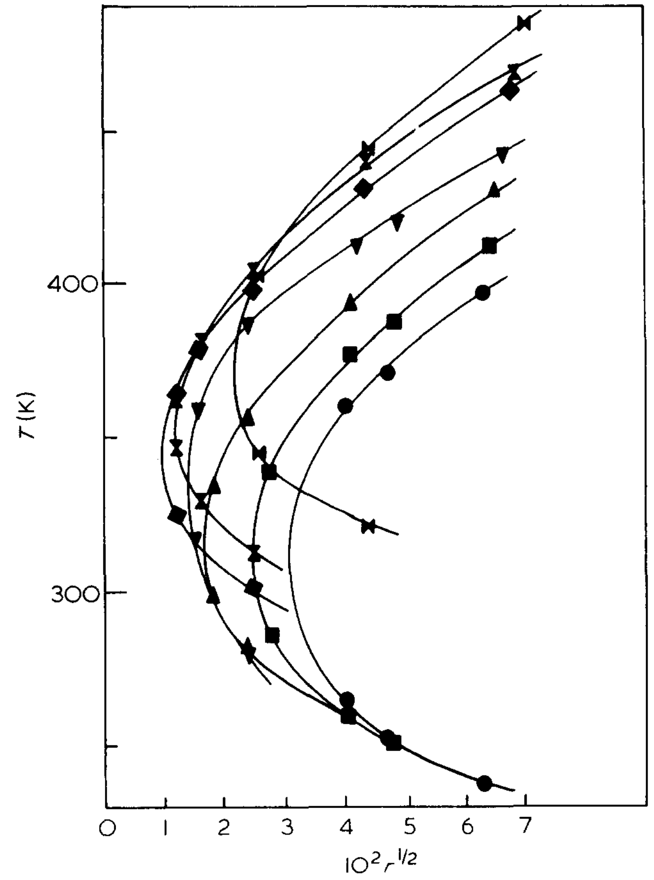

Figure 3 Plots of precipitation temperature vs. $r^{-1/2}$ for the cosolvent systems at an acetone (1) volume fraction of 0.65 where the n-alkane (2) component is; –●– hexane, –■– heptane, –▲– octane, –▼– decane, –◆– tridecane, –⧗– hexadecane and –⋈– eicosane

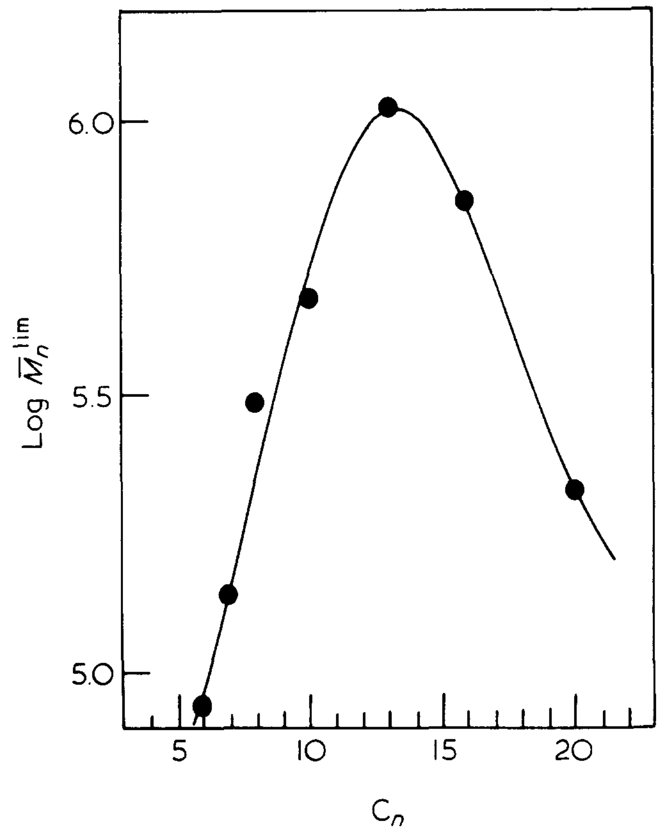

Figure 4 Plot of the log of the limiting molecular weight ($\bar{M}_n^{lim}$) vs. number of carbon atoms per alkane (C_n) for each of the cosolvent systems at volume fraction of acetone (1) = 0.65

A qualitative rationalisation of the maximum in cosolvent action, and of the distortion of the phase diagrams with increasing n-alkane chain length, can be given with reference to the data presented in the preceding paper. It was shown that the temperatures at which the n-alkanes exhibit their maximum interaction with polystyrene are a function of the chain length of the solvent molecule. The demixing of polystyrene in acetone (1) + n-alkane (2) combinations as $\phi_1^{exp} \rightarrow 0$ must become increasingly dominated by the n-alkane/polystyrene interactions, which dictate the position of the miscibility ranges on the temperature scale, and thus causes the progressive change in the shape of the cosolvent loops. The improvement in cosolvent action as registered in *Figure 4* will, in part, also be a result of any change in the n-alkane/polystyrene interaction. It is reasonable to suppose that any improvement in the solvating power of one component in such a series of mixtures will result in that mixture itself becoming a better solvent. The application of free volume theory[1] indicates that the compatibility of the n-alkanes with polystyrene achieves a maximum around n-nonane. The cosolvent action of this series of mixtures also shows a maximum, albeit at a different n-alkane chain length, in this case tridecane. Non-coincidence is not unexpected since the influence of n-alkane/acetone interactions will be present in the mixed solvents and, in fact, may be the overriding factor in determining the extent of cosolvent action. The effect of such interactions will be examined in the next paper in this series[14], in which the cosolvency exhibited by this series of binary liquid systems will be interpreted in terms of the free volume theory of polymer solutions.

By using the same extrapolation procedure mentioned earlier to determine $\bar{M}_n^{\text{lim}}$ at $\phi_1^{\text{exp}} = 0.65$ the temperatures at which the upper and lower T_p's coalesce were established at other mixed solvent compositions. These are indicated on *Figures 1* and *2* and are joined to describe a 'locus' of maximum cosolvent action for each mixture. The coalescence temperatures for polystyrene in hexane, heptane and octane are taken from the preceding paper and that of polystyrene in acetone from previous work[3]. The extrapolations of the loci in the diagrams for acetone (1)+decane (2) to acetone (1)+eicosane (2) indicate rapidly increasing temperatures of maximum interaction of polystyrene with these higher alkanes and confirm the trend suggested earlier[1]. It is interesting to note that the loci do not, even approximately, follow a linear interpolation between the temperatures of maximum interaction in the single solvents, and similar non-linearity occurs in the acetone+ether cosolvent system[3] and others[15]. In solvent mixtures formed from one good and one poor solvent, linear behaviour is much more closely followed[5,15].

Because of polymer degradation at higher temperatures it did not prove possible to describe the phase contour diagrams over the complete range of ϕ_1^{exp} for the longer n-alkane+acetone mixtures. However, the demixing behaviour of polystyrene as depicted in *Figures 1* and *2* unquestionably shows that a considerable cosolvent effect exists and that the maximum cosolvent action is always found at compositions which are closer to the better solvent of the pair (acetone). The temperature at which any cosolvent mixture is most effective is lower than would be predicted from linear interpolation of the behaviour of polystyrene in the two components separately. In the following paper an analysis in terms of free volume theory is presented, and the behaviour of the characteristic parameters employed by the theory is examined in the cosolvent mixtures.

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