Depression of the critical temperature in PMMA–cosolvent systems

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A theoretical expression is developed to calculate the critical line of a polymer–mixed solvent system, at the limit of decreasing proportion of one of the solvents. This expression is written in terms of binary interaction parameters, and provides a criterion to predict whether or not the liquid mixture is expected to be a cosolvent of the polymer. The expression should be useful to describe powerful cosolvent systems, and it is applied to calculate the depression of the critical line in the system PMMA–acetonitrile +chlorobutane. Experimental cloud point data are determined on this system and the results are compared with the theory. Other cosolvents of PMMA are discussed.

INTRODUCTION

In polymer–cosolvent systems, the phase separation temperature (T_p) of the polymer dissolved in either single liquid is higher than in certain compositions of the liquid mixture. Mixing of the two liquids produces a depression of this temperature, with respect to its value in the single liquid solutions. In the case of PMMA, several powerful cosolvent mixtures have been reported recently[1]. In such powerful cosolvents, a small proportion of liquid 2, added to the polymer–liquid 1 solution, is enough to produce a large decrease in T_p. Because of this steep decrease in T_p, the region of liquid mixture compositions accessible to phase separation determinations is, in some systems, that in which the mixture is very rich in liquid 1. A coefficient expressing quantitatively the cosolvent power of these mixtures is $(dT_p/dx)_0$, where x is the mole fraction of liquid 2 in the solvent mixture, and subscript zero means $x \to 0$. Large negative values of $(dT_p/dx)_0$ are the characteristic feature of the powerful cosolvent systems reported[1].

From the theoretical point of view, the critical temperature (T_c) of the system, is easier to study than T_p for an arbitary polymer–solvent concentration. T_c is the value of T_p corresponding to the critical concentration. In the present paper, we develope a theoretical expression to calculate $(dT_c/dx)_0$, in polymer–mixed solvent systems. This derivative expresses the initial slope of the critical line as a function of solvent composition. The theoretical expression developed for $(dT_c/dx)_0$ is written in terms of the interaction parameters for the binary systems. As an application of this theoretical expression it is used to calculate $(dT_c/dx)_0$ in the powerful cosolvents reported recently[1].

To compare these theoretical $(dT_c/dx)_0$'s with experimental, we have determined $(dT_c/dx)_0$ in PMMA–acetonitrile (AcN) + 1-chloro-*n*-butane (ClBu), by measuring T_p as a function of polymer concentration (c) and liquid mixture composition (x). For the remaining systems, we use the previously reported $(dT_p/dx)_0$ directly to compare with the theory.

EXPERIMENTAL

Polymer sample

The sample used is a monodisperse PMMA standard, polymerized according to the method of Löhr and Schulz[2], which has been supplied by Dr. T. G. Croucher, from Polymer Laboratories Ltd. (Shrewsbury, England). This polymer shows no crystallinity and its tacticity determined by n.m.r. is: 44% syndio, 51% hetero (triad content). Its molecular weight, as specified by the supplier, is: $M_n = 125\,000$; $M_w/M_n \lesssim 1.1$.

Solvents

Freshly distilled Carlo Erba RPE products were used.

Determination of T_p

Capillary tubes, filled with polymer solutions, are placed in a water bath and the temperature slowly decreased. The phase separation temperature (T_p) in each tube is taken when a copper wire, placed directly behind the tube, blurrs (as observed with the naked eye).

To obtain the data in *Figure 1* we start with the polymer dissolved in one of the single solvents and gradually add small amounts of the second solvent using a calibrated dispenser. Before each addition, we take a sample of the solution and fill a capillary tube. The material for these transfer operations is kept inside a warm oven to prevent precipitation.

RESULTS

The experimental results of T_p are shown in *Figure 1*. They have been obtained starting with solutions of different polymer concentrations, c, and following the procedure described in the Experimental Section for the addition of cosolvent. As seen in *Figure 1*, the decrease of T_p is linear over the range of x studied. Therefore, the cosolvent power is described by a single coefficient – the initial slope $(dT_p/dx)_0$. To determine $(dT_p/dx)_0$, the data in *Figure 1*

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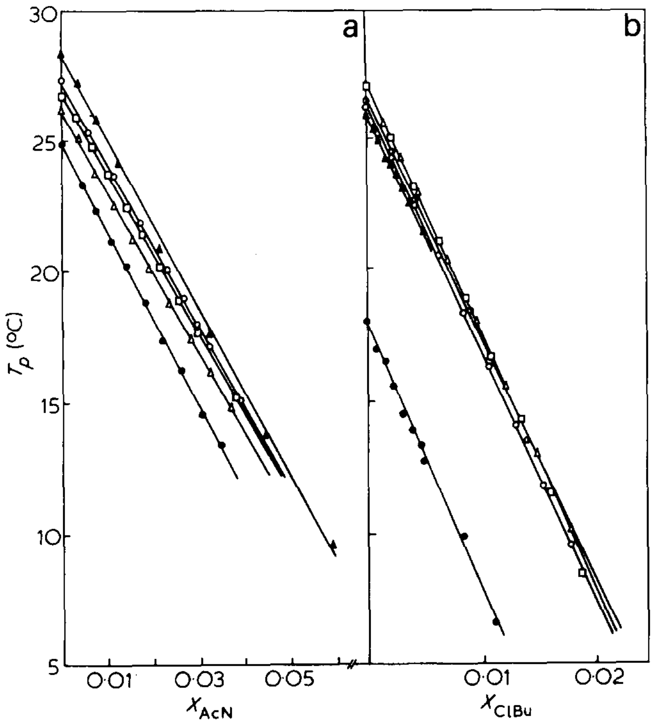

Figure 1 Phase separation temperature (T_p), as a function of solvent mixture composition, determined on the system PMMA–acetonitrile + chlorobutane, at several polymer concentrations, c (x 10^2/g cm^3): (a): c = ▲, 12.2; ○, 9.17; □, 7.14; △, 4.36; ●, 2.13. (b): c = ○, 9.47; ◐, 8.22; △, 5.89; □, 3.69; ▲, 2.17; ●, 0.442

Table 1 $(dT_p/dx)_0$ determined on the cosolvent system PMMA–acetonitrile + 1-chlorobutane, at several polymer concentrations, c

Solvent 1	Solvent 2	$c \cdot 10^2$ (g cm^{-3})	$(dT_p/dx)_0$ $\cdot 10^{-2}$ (K)
Acetonitrile	Chlorobutane	0.442	−9.9
"	"	2.17	−9.3
"	"	3.69	−9.6
"	"	5.89	−9.6
"	"	8.22	−9.2
"	"	9.47	−9.4
Chlorobutane	Acetonitrile	2.13	−3.3
"	"	4.36	−3.1
"	"	7.14	−3.1
"	"	9.17	−3.1
"	"	12.2	−3.3

have been fitted to a linear regression for each polymer concentration. The results obtained are shown in *Table 1*. It is seen that $(dT_p/dx)_0$ is practically independent of polymer concentration.

The T_p's of this system are plotted in *Figure 2* in the form of cloud point curves. The points shown in this *Figure* are calculated values obtained from the linear fit of T_p vs. x. The cloud point curve, corresponding to the single solvent ClBu, shows an irregular shape and lacks a threshold in the polymer concentration range studied. Irregularities in the cloud point curve of PMMA in ClBu, and difficulties in obtaining reproducible results, have been reported[3]. This was attributed to association of the polymer[3], the importance of which, in cosolvency, has been discussed in our previous report[1].

THEORY

In this section we shall develop a theoretical expression which could describe cosolvency quantitatively, by calculating the decrease in critical temperature of the system (T_c) generated by a small addition of the cosolvent $(dT_c/dx)_0$.

In our derivation the starting point is the interaction parameter for the ternary system, χ, in the approximation which treats the solvent mixture as a single liquid of mean properties. The usual expression for such a single-liquid χ is due to Scott[4], and contains the simplification of considering the two liquids to be of equal molar volume. Chen[5] extended Scott's formula to include solvents of any molar volume and arrived at:

$$\chi = (1-x)\chi_{13} + x\chi_{23} - (1-x)x\frac{V_2}{V_m}\chi_{12} \tag{1}$$

where χ_{ij}'s are binary interaction parameters, subscript 3 denotes polymer, and V_i, V_m, are molar volumes of component i and solvent mixture, respectively. Chen's derivation includes the assumption that there is no coupling between interaction parameter and combinatorial terms, in the chemical potential. However, such non-coupling assumption is not needed, because equation (1) derives directly from the Flory–Huggins chemical potential. Another formula for χ was derived by Dondos and Benoit[6], by comparing the interaction parameter with the total swelling function of intrinsic viscosity, but their expression reduces, also, to equation (1) (assuming additivity of volumes).

χ is a function of two variables – solvent composition, x, and temperature, T (through the χ_{ij}'s). We can write $\chi = \chi(T,x)$, and apply the chain rule of partial derivatives to obtain:

$$(\delta T/\delta x)_\chi = -(\delta\chi/\delta x)_T/(\delta\chi/\delta T)_x \tag{2}$$

At the critical point of the system, χ has a constant value, χ_c, which, according to Flory–Huggins theory, can be calculated from the degree of polymerization (r):

$$\chi_c = \frac{1}{2}(1 + r^{-1/2})^2 \tag{3}$$

To obtain $(dT_c/dx)_0$, we use equation (2). Firstly we calculate the derivatives on the right hand side of this

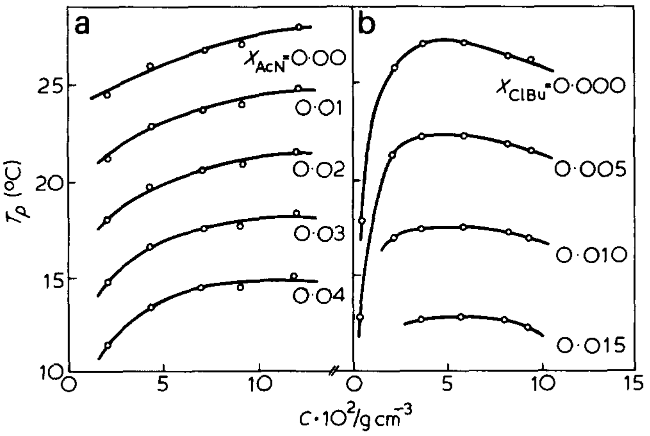

Figure 2 Cloud point curves, for the system PMMA–acetonitrile + chlorobutane, obtained from the data in *Figure 1*

equation by using equation (1) for χ. Then, we particularize equation (2) to the critical point ($\chi=\chi_c$), and get $\mathrm{d}T_c/\mathrm{d}x$. Finally, going to the limit $x \to 0$, we obtain:

$$(\mathrm{d}T_c/\mathrm{d}x)_0=(\chi_{23}-\chi_{13}-\frac{V_2}{V_1}\chi_{12})/(-\mathrm{d}\chi_{13}/\mathrm{d}T) \qquad (4)$$

All the magnitudes in the right hand side of equation (4) are to be evaluated at the critical temperature correspoding to $x=0$, i.e. T_{c1}, the value of T_c for the polymer–single solvent 1 system*.

Using equation (4) we discuss the conditions which lead to the existence of cosolvency in a given system. When T_{c1} is a UCST (as is the case in our phase separation studies), $-\mathrm{d}\chi_{13}/\mathrm{d}T>0$, and $(\mathrm{d}T_c/\mathrm{d}x)_0$ has the same sign as the numerator of equation (4). Choosing solvent 1 such that $T_{c2}>T_{c1}$, then $(\mathrm{d}T_c/\mathrm{d}x)_0<0$ guarantees that the system is a cosolvent one. Since $\chi_{23}-\chi_{13}>0$, at T_{c1}, the numerator in equation (4) is negative (cosolvent system) if the unfavourable interaction between the two liquids is large enough to compensate for their different affinity towards the polymer, i.e. if $(V_2/V_1)\chi_{12}>\chi_{23}-\chi_{13}$. The interaction parameter χ_{12} is related to the excess Gibbs function of the solvent mixture (G^E), so that equation (4) gives a more detailed criterion for cosolvency than the simple one of $G^E>0$, first suggested on intuitive grounds. The information needed to predict $(\mathrm{d}T_c/\mathrm{d}x)_0$ from equation (4) includes the binary interaction parameters of the polymer in each one of the two solvents as a function of temperature, and also χ_{12} (G^E) for the liquid mixture.

Comparing equation (4) with the criterion for cosolvency implicit in Scott's work[4], the condition under which a polymer, dissolved in a mixture of two non-solvents, would have two plait points, at a given temperature, as derived by Scott is:

$$\chi_{13}+\chi_{23}-1<\chi_{12} \qquad (5)$$

This condition was derived for $r=\infty$ and $V_2=V_1$. If we particularize equation (4) to this case ($\chi_{13}=\chi_c=1/2$ for $r=\infty$, the system is cosolvent when the numerator of equation (4) obeys:

$$\chi_{23}-\frac{1}{2}<\chi_{12} \qquad (6)$$

Applying Scott's condition (equation (5) above) to the neighbourhood of temperature T_{c1}, where $\chi_{13}=1/2$, we also get equation (6). Therefore, both criteria for cosolvency are identical. Equation (4) has the advantage that it can be applied to any value of r, not necessarily ∞, and that it holds also for solvent pairs having unequal molar volumes. More importantly, equation (4) represents not only a criterion to predict whether a given system should be cosolvent or not, but also provides a way to calculate the magnitude of such cosolvency, as expressed by the measurable coefficient $(\mathrm{d}T_c/\mathrm{d}x)_0$. We now apply this equation to calculate the strong cosolvent effect of the system PMMA–AcN + ClBu, studied here, and of others reported previously.

COMPARISON WITH EXPERIMENT

Experimental values of T_c are taken as the threshold temperatures in the cloud point curves of *Figure 2*. For ternary systems, threshold and critical temperatures are not identical. However, critical line and measured binodal edge are in good agreement[7]. The differences between threshold and critical temperatures, in the closely related system PMMA–*sec*-BuOH + ClBu, are negligible. Besides, the precise location of the critical point does not matter very much for the determination of $\mathrm{d}T_c/\mathrm{d}x$, because as we have seen in *Table 1*, this slope is practically independent of polymer concentration.

The cloud point curve of PMMA in pure AcN clearly shows a maximum, but in pure ClBu the maximum is not reached at the polymer concentrations studied. The anomalous phase separation behaviour of PMMA in ClBu may be responsible for the lack of a clear maximum, as discussed above. As T_c, we take the highest T_p determined in the cloud point curves because the critical composition should be very close to that point. Wolf and Blaum[7] determined the critical point in ClBu to be located at 16.5 wt% polymer, using a sample of the same characteristics as ours, but with a lower molecular weight of 56500. With our polymer, the critical point should be at a smaller concentration. The experimental values determined for $(\mathrm{d}T_c/\mathrm{d}x)_0$ in the system PMMA–AcN + ClBu are shown in *Table 2*. We now calculate the theoretical value of $(\mathrm{d}T_c/\mathrm{d}x)_0$ for this system, using equation (4).

As an approximation to the binary interaction parameters required, χ_{ij}, we use the expression given by regular solution theory:

$$\chi_{ij}=\frac{V_i}{RT}(\delta_i-\delta_j)^2+\beta \qquad (7)$$

where δ is the solubility parameter (cohesive energy density) and the value $\beta=0.34$ has been found adequate for many polymer-solvent pairs[8]. Using the same δ values as in ref 1* we obtain for $(\mathrm{d}T_c/\mathrm{d}x)_0$ the results shown in *Table 2* (column A).

Table 2 Comparison between theoretical and experimental values of $(\mathrm{d}T_c/\mathrm{d}x)_0$, for the cosolvent system PMMA–acetonitrile + chlorobutane

		$(\mathrm{d}T_c/\mathrm{d}x)_0 . 10^{-2}$ (K)				
		Theory				
Solvent 1	Solvent 2	A	B	C	D	Experiment
AcN	ClBu	−14.5	+1.2	−11.8	−9.4	−9.4
ClBu	AcN	−11.2	−2.2	−6.6	−4.6	−3.2

A: Equation 4
B: Equation 10
C: Equation 4 using three dimensional ($\delta_d, \delta_p, \delta_h$) parameters
D: Equation 4 using two dimensional (δ_v, δ_h) parameters

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* In the limit $r\to\infty$, $T_c=\theta$, and equation (4) gives the decrease in θ temperature caused by the cosolvent: $(\mathrm{d}\theta/\mathrm{d}x)_0$. For finite molecular weights, χ_c is not strictly a constant, when $V_1 \neq V_2$, because r varies with solvent composition. However for high enough molecular weights, this variation should be of negligible influence in the narrow region of x where $(\mathrm{d}T_c/\mathrm{d}x)_0$ is determined.

* Tabulated at 25°C, while χ_{ij} has to be calculated at T_{c1} and at T_{c2}. However, both T_{c1} and T_{c2} are very close to 25°C in this system (26.9 and 28.4°C in AcN and ClBu, respectively)

Theory correctly predicts: (a) the negative sign of $(\mathrm{d}T_c/\mathrm{d}x)_0$; (b) its relative magnitude at both ends of solvent composition (that $-(\mathrm{d}T_c/\mathrm{d}x)_0$ is larger when solvent 1 is AcN). However, it fails in the absolute magnitude of $(\mathrm{d}T_c/\mathrm{d}x)_0$. In both cases, theory predicts a value larger than the experimental one, and overestimates the cosolvent effect in this system. A similar overestimate was obtained by other means in the case of the cosolvent pair *sec*-BuOH (1)+ClBu (2)[7].

Our theoretical expression uses a single-liquid interaction parameter. Some part of the theoretical overestimation of cosolvency could be attributed to this single-liquid approximation, because its effect is to exaggerate the solvation of the macromolecule over the one predicted by treating the system as a truly ternary one.

In order to check whether the agreement with experiment can be improved by avoiding the single-liquid approximation, we have again worked out the derivation of $(\mathrm{d}T_c/\mathrm{d}x)_0$ but starting with a more general χ which takes into account selective solvation and describes the system as a truly ternary one. Such an interaction parameter is obtained as follows: χ can be defined in terms of the total swelling function (Y) by:

$$\chi = \frac{1}{2} - \frac{V_m}{V_1} Y \tag{8}$$

Instead of using the single-liquid version of Y, we take the complete expression, first derived by Schultz and Flory[9], with the result (assuming additivity of volumes):

$$\chi = (1-x)\chi_{13} + x\chi_{23} - (1-x)x\frac{V_2}{V_m}\left\{\chi_{12} - \frac{[l-1+\chi_{13}-l\chi_{23}+(\varphi_1-\varphi_2)\chi_{12}]^2}{2(l\varphi_1+\varphi_2-2\chi_{12}\varphi_1\varphi_2)}\right\} \tag{9}$$

where $l = V_1/V_2$, and φ_i is volume fraction in the solvent mixture. Applying equation (2) with χ given by equation (9), we finally obtain:

$$\left(\frac{\mathrm{d}T_c}{\mathrm{d}x}\right)_0 = (-d\chi_{13}/\mathrm{d}T)^{-1}\left\{\chi_{23} - \chi_{13} - \frac{V_2}{V_1}\left[\chi_{12} - \frac{V_2}{2V_1}(l-1+\chi_{13}+\chi_{12}-l\chi_{23})^2\right]\right\} \tag{10}$$

This can be considered as an extension of equation (4). It avoids the single liquid approximation and takes into account the influence of selective solvation.

We now calculate $(\mathrm{d}T_c/\mathrm{d}x)_0$, according to equation (10) using the same δ parameters as before (for the χ_{ij}'s). The result is shown in *Table 2* (column B), showing that the single-liquid approximation gives a better description of the system. It predicts qualitatively the cosolvency observed (negative values of $(\mathrm{d}T_c/\mathrm{d}x)_0$ at both ends of the solvent composition range), while the full equation for a truly ternary system does not (one of the $(\mathrm{d}T_c/\mathrm{d}x)_0$ values is positive). Using the single liquid approximation to describe the solvent power of a mixed solvent, the effect of short-range forces, acting between the polymer segments and the solvent coating adjacent to them, may be cancelled out by the effect of the mean potential acting throughout the polymer region. The net result is that the solvent power is well approximated by simple average of the individual solvents[10].

The system which we study here is composed of polar molecules and may show the influence of specific interactions between groups. In regular solution theory, the importance of dipolar and specific interactions is taken into account by decomposing the δ parameter into dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) components. In our previous report on cosolvents of PMMA[1], it was shown that the existence of asymmetric cosolvent pairs (AcN + BuOH, for example) could only be explained by using such a separation of contributions. This leads to a three dimensional representation of δ. An alternative two dimensional representation in which dispersion and dipolar contributions are considered together ($\delta_v^2 = \delta_d^2 + \delta_p^2$), and only δ_h is taken separately, was shown to give also an explanation for the existence of the asymmetric cosolvent pairs. In these systems, the consideration of δ_h as an independent contribution is important. We look, then, for improved agreement between the calculated and experimental $(\mathrm{d}T_c/\mathrm{d}x)_0$ by using the two or three dimensional representation of δ, together with the single liquid treatment of χ. That is, we use equations (4) and (7), with $(\delta_i-\delta_j)^2$ given either by:

$$(\delta_i-\delta_j)^2 = (\delta_i-\delta_j)_d^2 + (\delta_i-\delta_j)_p^2 + (\delta_i-\delta_j)_h^2 \tag{11}$$

or by:

$$(\delta_i-\delta_j)^2 = (\delta_i-\delta_j)_v + (\delta_i-\delta_j)_h^2 \tag{12}$$

The results calculated for $(\mathrm{d}T_c/\mathrm{d}x)_0$ using δ_d, δ_p, δ_h, and δ_v values, taken from ref 1, are shown in *Table 2* as columns C and D. Both types of calculation give a better description of experiment than the previous one. The two dimensional (δ_v, δ_h) representation is best and produces an excellent fit of the experimental results*. We may conclude that in this system, when combined with the (δ_v, δ_h) representation of the χ_{ij}'s, the single liquid approximation to χ gives a good theoretical description of the depression in critical temperature, $(\mathrm{d}T_c/\mathrm{d}x)_0$, provoked by the addition of cosolvent.

We shall now verify whether this conclusion applies to the other powerful cosolvents of PMMA reported previously[1]. For them we have only $(\mathrm{d}T_p/\mathrm{d}x)_0$ values determined at a single concentration. They are now compared with the theoretical $(\mathrm{d}T_c/\mathrm{d}c)_0$ calculated from equation (4), (7) and (12) with δ_v and δ_h from ref 1. The results for this comparison are contained in *Table 3*. The calculated values are of the same magnitude as the experimental ones (around -10^3K). In view of the large cosolvent effect observed in these systems the theoretical predictions seem to be satisfactory. However, the detailed agreement is not perfect, with differences between theory and experiment as large as $\simeq 60\%$. The use of a one-dimensional δ value, instead of δ_v and δ_h, does not produce any improvement, except in the case of the cosolvent pair AcN + CCl_4 for which the value of $(\mathrm{d}T_c/\mathrm{d}x)_0$ calculated,

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* Another point in favour of the (δ_v, δ_h) representation is that it gives the best description of the experimental G^E for the binary solvent mixture AcN + ClBu

Table 3 Comparison between theory and experiment in other cosolvents of PMMA previously reported (ref 1)

		Experiment	Theory
Solvent 1	Solvent 2	$(dT_p/dx)_0$ ($\times 10^{-2}$ K)	$(dT_c/dx)_0$ ($\times 10^{-2}$ K)
AcN	AmAc	−11.1	−18.0
"	ClBu	−9.4	−9.4
"	CCl_4	−12.3	−7.2
"	BuOH	−7.6	−12.5
ClBu	AcN	−3.2	−4.6
"	BuOH	−17.0	−14.0

using single δ values for each component, is -12.6×10^2K, in excellent agreement with experiment. Obviously, CCl_4 has no hydrogen bonding contribution and, in this case, the separation of δ_h seems not to be adequate.

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