Effect of additives on solution properties of ethylene oxide–propylene oxide statistical copolymers

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In this paper, the effect of different additives on the solubility and intrinsic viscosity $[\eta]$ of ethylene oxide–propylene oxide statistical copolymers in water is studied. In the case of mineral additives, the order of 'salting out' is the same as for ethylene oxide homopolymer. If one excepts the case of sodium iodide, the variations of the viscosimetric expansion can be plotted on the same curve as a function of reduced temperature for different salts. Organic additives have an increasing or decreasing effect on the lower critical temperature (*LCST'*) of the copolymers according to their polarity. The relation between the variations of $[\eta]$ and *LCST'* is much more complex than for mineral additives since $[\eta]$ at a given temperature depends on the free energy of mixing of the two solvents.

(Keywords: ethylene oxide–propylene oxide copolymers; mineral salts and organic additives in aqueous solutions; lower critical solution temperature; intrinsic viscosity; partial specific volume)

INTRODUCTION

In the previous paper we have discussed some results dealing with the conformational and thermodynamic properties of aqueous solutions of ethylene oxide–propylene oxide (EO–PO) statistical copolymers and we have focused our attention on the influence of their hydrophobicity[1].

It is well known that the lower critical solution temperature (*LCST'*) of aqueous solutions of poly(ethylene oxide) (PEO) is lowered by addition of inorganic salts[2–4] but there is a lack of available information dealing with the effect of organic compounds[5]. We have undertaken a systematic study of the influence of different mineral salts and water-soluble organic compounds such as alcohols, diols and amides on different properties of EO–PO aqueous solutions: *LCST'*, intrinsic viscosity and apparent specific volume.

Moreover, the industrial use of these polymer solutions (for instance, as cooling fluids or stiffening agents) can be limited by different problems:

(i) Water freezing or separation and crystallization of some additives such as borax (generally added as anticorrosive agent) during storage at low temperature. It is then necessary to know the laws of variation of water freezing temperature as a function of the concentration of the different solutes and the solubility limits of the anticorrosive agent under the same conditions.

(ii) Polymer rejection, after the use of the solutions, which could be resolved by addition of inorganic salts.

The main purpose of this paper is to present some experimental data whose knowledge is required for prediction of the effectiveness of these solutions in various possible applications. Moreover, we give a number of results important to interpreting properties of water–polymer–additive systems that present a *LCST'* behaviour. The previous paper was more particularly devoted to a more fundamental discussion on the observed behaviours.

We will successively give results obtained with the ternary systems: (a) water–copolymer–inorganic salt; and (b) water–copolymer–organic additive.

EXPERIMENTAL

Copolymer samples

The four copolymer samples (A, B, C, D) used in this work were kindly supplied by Servimetal, France, and have already been carefully characterized by ^1H and ^{13}C n.m.r., elemental analysis, gel chromatography, light scattering and viscosimetry at room temperature[1]. Their characteristics are given in *Table 1*.

Methods

Cloud-point measurements. Cloud points were obtained with a Mettler FP81 turbidimeter. The solutions were introduced in glass tubes (1 mm inner diameter and 79 mm length), which are illuminated by a white light source, placed in an oven and heated at a given heating rate (2°C min^{-1} in our case). The cloud point is

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Table 1 Copolymer characteristics

Sample	Y^a	$10^{-4} M_w{}^a$	I^a	$[\eta]^a$
A	0.193	3.2	1.47	38.5
B	0.263	3.6	1.15	32.6
C	0.194	3.1	1.18	34.3
D	0.121	3.0	1.20	37.5

[a] Y = molar fraction of PO units; M_w = weight-average molecular weight from light scattering measurements; I = polydispersity index from gel chromatography; $[\eta]$ = intrinsic viscosity ($cm^3\ g^{-1}$) measured at 25°C

automatically determined as the temperature at which the light scattering at 90° abruptly jumps.

Viscosimetry. The viscosity was determined with an automatic viscosimeter of the Gramain–Libeyre type thermostated at ± 0.1°C. It was equipped with a capillary of 0.7 mm i.d.[6]. Since the copolymer molecular weights are rather low, their solutions have a Newtonian behaviour and the high shear rate in the capillary viscosimeter does not perturb the measurement.

In the case of ternary and binary systems, intrinsic viscosity $[\eta]$ was obtained by the classical method by extrapolating to zero concentration the values of reduced viscosity, η_{red}:

$$\eta_{red} = (\eta - \eta_0)/\eta_0 c_p \qquad (1)$$

where η and η_0 are the viscosity of the ternary solution and of the binary solvent water–salt or water–organic compound, respectively, and c_p is the polymer concentration (in $g\ cm^{-3}$).

Density measurements. Density measurements were performed with a densimeter (Anton Paar DMA 02) of the Kratky type equipped with a home-built cell allowing one to obtain the liquid density with an accuracy of $5 \times 10^{-5}\ g\ cm^{-3}$ (ref. 7).

The apparatus is thermostated at ± 0.005°C. The apparent specific volume Φ_2 is calculated from the slope of the linear variation of specific volume of the ternary water–polymer–additive solution, v_{123}, as a function of the w/w polymer concentration:

$$\Phi_2 = v_{13} - dv_{123}/dw_2 \qquad (2)$$

where v_{13} is the specific volume of the binary water–additive system. As for viscosimetric measurements, the binary solutions are prepared first, a weighted quantity of polymer is then dissolved in them at 25°C by gentle stirring and the homogeneous solution is then diluted by the binary solutions. We used polymer concentrations between 0.25% and 40% w/w.

Cryoscopic measurements. We have constructed for this study a simple cryometer, which is made of a double-walled glass cell (25 mm inner diameter and 150 mm height). This cell is cooled by a Haake F3 circulating cryostat (-60°C to $+20$°C) and is filled by the solution at mid-height. A probe of a Hewlett-Packard quartz thermometer ($\pm 2 \times 10^{-4}$ °C) is placed at the centre of the liquid.

The initial temperature of liquid and cryostat was 25°C. At zero time, the cryostat temperature was -10°C and the liquid temperature was registered as a function of time. The freezing point is the cryoscopic plateau temperature. The apparatus has previously been calibrated with solutions of sodium chloride of concentrations ranging between 0 and 20% w/w. We have obtained for the cryoscopic constant $K = 1.86$°C mol^{-1}, near that given in the literature[8].

Study of borax solubility. We have performed some visual observations of the crystallization of borax at low temperature. The ternary or quaternary solutions are in a 25 cm^3 vessel which is kept in a cryostat at given temperature for 10 h and a deposit of well formed crystallites can be observed.

EXPERIMENTAL RESULTS

Ternary systems water–copolymer–salt

Variation of LCST'. We have previously shown[1] that EO–PO copolymers in pure water present the same type of solubility diagram as the homopolymer PEO, and the shape of a typical curve (such as that reproduced in *Figure 1*) can approximately be predicted from the Flory–Huggins theory. The critical temperature *LCST'* is a linear decreasing function of the molar fraction of PO in the copolymer.

Addition of salts generally lowers *LCST'* without significantly changing the critical concentration and the shape of the demixing curve. The same observation was made by Saeki *et al.* for PEO in the presence of NaCl[4]. We have generally measured the variation of the cloud point as a function of salt concentration, c_s, at constant $c_p = 4\%$ w/w.

In *Figure 2a* we give the variations of *LCST' versus* c_s for sample A and in the presence of KI, NaCl, Na_3PO_4, Na_2CO_3 and borax ($Na_2B_4O_7$). In *Figure 2b*, we compare the effects of KI and Na_2CO_3 for the three other copolymer samples. We have also plotted the results of Bailey and Callard[2] for PEO. The order of the salting out of the sodium salts compared at equal molar salt concentration seems to be approximately the same for the copolymers as for PEO, as already given by these authors (borax effect has never been investigated):

$$KI < NaCl < Na_2CO_3 < Na_3PO_4 < Na_2B_4O_7$$

This order is reminiscent of the classical 'Hofmeister series' for proteins. It has been shown that this order can

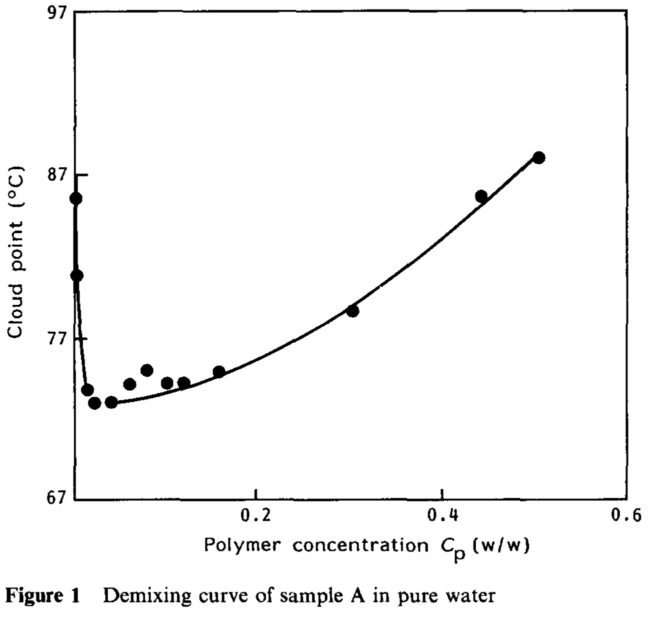

Figure 1 Demixing curve of sample A in pure water

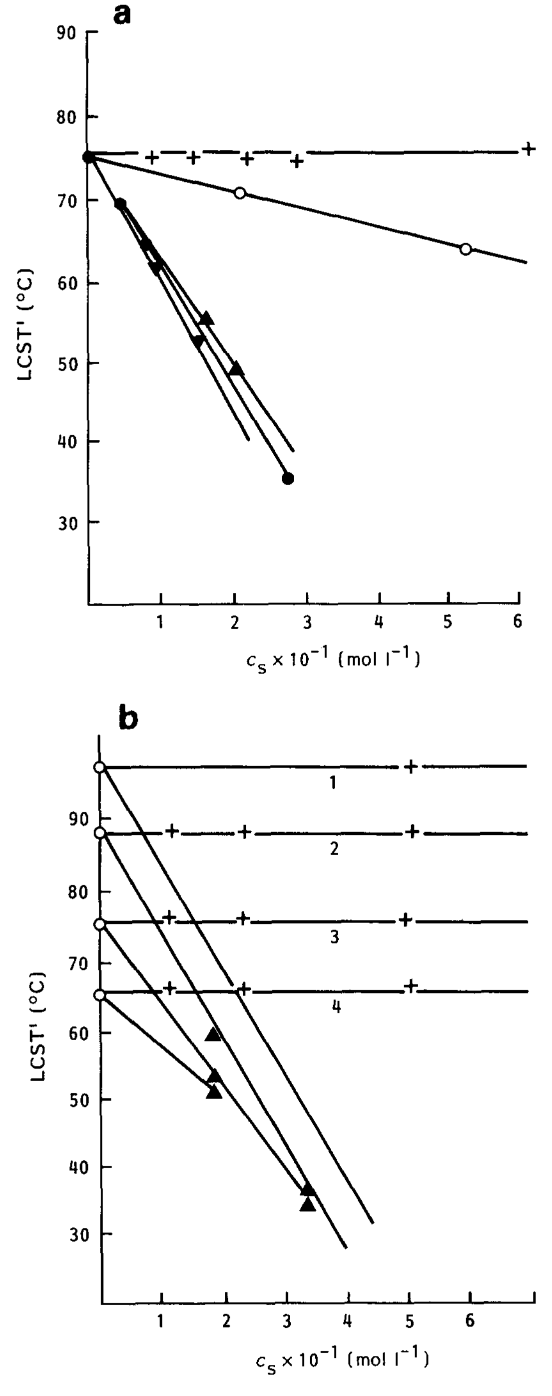

Figure 2 *LCST'* dependence on salt concentration. (a) Sample A with KI (+), NaCl (○), Na_3PO_4 (●), Na_2CO_3 (▲), $Na_2B_4O_7$ (▼). (b) PEO (1) and samples B (2), C (3) and D (4) with KI (+) and Na_2CO_3 (▲)

be changed on the basis of ionic strength, which could be the driving factor if one assumes the neutral salts have an increasing effect on the activity coefficient of the neutral polymer solute[2]. For an ionic strength of 1, for sample A, one finds *LCST'* reductions of 49, 45, 43, 20 and 0°C for $Na_2B_4O_7$, Na_2CO_3, Na_3PO_4, NaCl and KI respectively. This order reveals that borax is the most efficient 'salting out' salt. Nevertheless, we have not taken into account the size of borate ion or its association into polyions, which makes the comparison difficult.

As shown in *Figure 2b*, for the same Na_2CO_3 concentration, *LCST'* depression is a decreasing function of the PO fraction in the copolymer, *Y*.

In *Table 2*, we give the values of $\Delta LCST'/\Delta c_s$ and $\Delta LCST'/LCST'\Delta c_s$. Both sets of values decrease on increasing *Y*. One can observe that $\Delta LCST'/\Delta c_s$ is a quite linear function of *Y*. We have recently shown that *LCST* also varies linearly with *Y* in the absence of salt:

$$LCST'_{c_s=0} = LCST'_{\substack{c_s=0\\ Y=0}} - AY \qquad (3)$$

This result suggests a simple approximate law of *LCST'* *versus* *Y* and c_s:

$$LCST'(Y, c_s) = LCST'_{\substack{c_s=0\\ Y=0}} - Bc_s - (A + Cc_s)Y \qquad (4)$$

where *B* and *C* are constants depending on the salt and $A = 154$.

From the demixing curves, it is theoretically possible to know the concentration of the two phases in equilibrium above *LCST'*. This could be useful practical information, if one wants easily to determine the conditions that could allow elimination of the polymer from the aged solution (rejection problem). We have measured the polymer and salt concentrations of the polymer-poor phase in the case of water–sample A–Na_2CO_3 system at a given temperature, 28°C, and for different initial values of c_s. These c_s values, 3.5, 4.0, 4.5, 5.0, 5.5%, correspond to *LCST'* equal to 27, 22, 17, 12 and 7°C respectively. From curves analogous to that drawn in *Figure 1*, we have obtained an order of magnitude of c_p in the polymer-poor phase (see curve 1 of *Figure 3*). By comparison with experimental results, one can see that such a method underestimates c_p; however, the differences are not very high. *Figure 3* also shows that salt is almost totally excluded from the

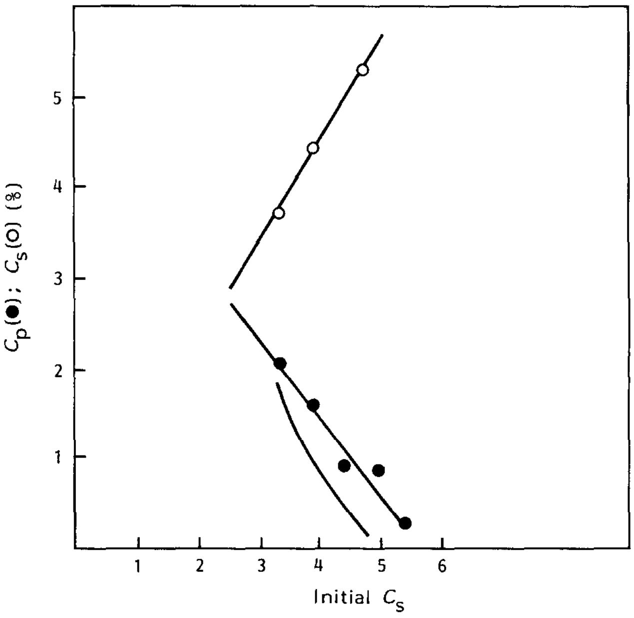

Figure 3 Concentration of polymer and salt in the polymer-poor phase *versus* initial salt concentration (sample A plus Na_2CO_3, 28°C); initial polymer concentration = 4%

Table 2 Absolute and relative increment of *LCST'* for samples B, C and D with Na_2CO_3

Sample	D	C	B
$\Delta LCST'/\Delta c_s$	151	120	90
$\Delta LCST'/LCST'\Delta c_s$	0.42	0.34	0.26

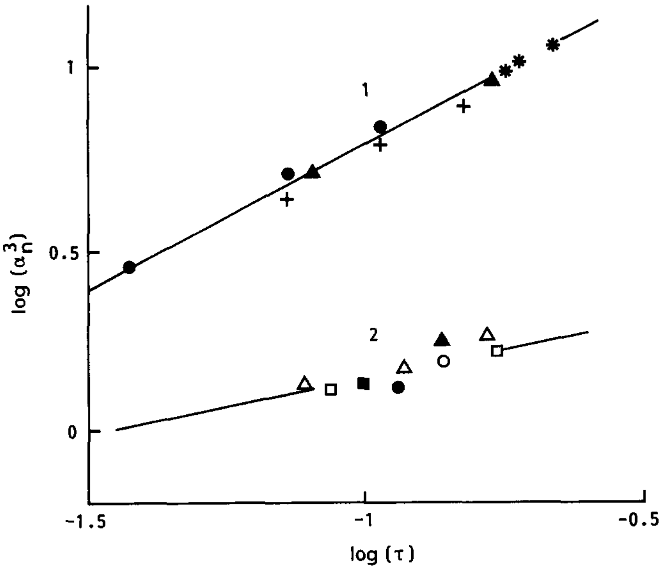

Figure 4 Logarithmic plot of viscosimetric expansion as a function of reduced temperature. (1) PEO from ref. 2 with KBr (∗), KF (+), K_2SO_4 (▲) and $MgSO_4$ (●). (2) Our copolymers: sample D plus Na_2CO_3 (○), sample C plus Na_2CO_3 (□), sample B plus Na_3PO_4 (△), sample A plus Na_2CO_3 (■), sample A plus Na_3PO_4 (▲)

polymer-rich phase. Moreover, from demixing curves one can also predict, at 28°C and for $c_s = 5.5\%$, a polymer concentration of 50% for the polymer-rich phase; this corresponds to a volume approximately 12.5 times lower than the solution volume before phase separation, if the initial c_p value is 4%. We have measured a volume ratio of 12 in good agreement with this prediction.

Then, with a polymer of this order of molecular weight, one can separate the solution in two phases, one containing all salt and the other one containing all the polymer, by heating 20°C above *LCST'*. Moreover, the effectiveness of the separation can be approached by simply considering the demixing curves, which are easily available.

Viscosity. As expected, we have observed that most salts reduce $[\eta]$ measured at 25°C. In the case of PEO, Bailey and Callard[2] have shown that the salts have the same order of effectiveness in reducing $[\eta]$ measured at 30°C as in lowering *LCST'*. They were even able to obtain a single line by plotting *LCST' versus* $[\eta]_{T=30°C}$ for five salts.

Such a result can be understood by considering the Flory theory[9] or the more recent 'blob' theory[10,11] dealing with the problem of polymer expansion. At a given molecular weight, polymer expansion must be a function of the reduced temperature:

$$\tau = 1 - \theta/T \qquad (5)$$

where θ is the theta temperature of Flory[9]. Many expressions have been established for binary polymer–solvent systems which present demixing by cooling (*UCST*) and when $T > \theta$, θ being the value of *UCST* for an infinite molecular weight. In the previous work[1], where we assumed that these theories are also applicable to the case of systems that present *LCST'* behaviour, we have calculated the τ dependences of the viscosimetric expansion for EO–PO copolymers as well as for PEO and our results show that they are quite similar to those obtained for other systems (polystyrene–cyclohexane for instance) and $T >$ *UCST*.

If the ternary systems water–polymer–salt can be simply considered as binary systems whose θ value varies with c_s, one expects that the viscosimetric expansion coefficient $\alpha_n = [\eta]/[\eta]_0$ varies as:

$$\alpha_n \propto N^{0.3}\tau^{0.6} \qquad (6)$$

in the asymptotic region (N being the polymerization degree). In *Figure 4*, we compare the variations of α_n^3 as a function of τ obtained from our measurements performed at 25°C in the presence of sodium carbonate and phosphate and as deduced for PEO in the presence of different salts from Bailey and Callard's results[2]. For PEO, all the experimental points are gathered on the same straight line whatever the nature of the added salt. The same dependence can also be observed for our four polymers of different compositions and with Na_2CO_3 and Na_3PO_4. The orders of magnitude of expansion and slope of the logarithmic plot of *Figure 4* are different from that given for PEO. This is simply due to the difference of sample molecular weights: the molecular weight of the PEO sample (probably 7×10^6) studied by Bailey and Callard[2] was much higher than that of our copolymers (see *Table 1*). In the first case the asymptotic limit is reached and the experimental exponent of the law of α_n *versus* τ, 0.64, is very near that predicted by theories. It appears that in a first approximation and in most cases, one can consider the ternary systems water–polymer–salt under *LCST'* in the general framework of the theories developed for binary systems above *UCST*.

However, in *Table 3* we have reported the $[\eta]$ and *LCST'* values for samples B to D measured in the presence of KI. One notes a surprising behaviour since addition of KI has a significant lowering effect on $[\eta]$ measured at 25°C while it does not modify *LCST'*. We have no satisfactory explanation for this unexpected result.

Density. Results of density measurements are given in *Figure 5* where the apparent specific volume Φ_2 is plotted *versus* concentration of different additives, inorganic salts or organic compounds. It is interesting to note that Φ_2 decreases when the added salt (Na_2CO_3 or Na_3PO_4) has a lowering effect on *LCST'* while it remains constant with addition of KI, which does not affect phase separation behaviour. We will again find the same correlation with organic additives.

The Φ_2 decrease probably reflects an enhancing of the

Table 3 Parameters of the systems water–copolymer–KI

Sample	[KI] (10^{-1} mol l^{-1})	$[\eta]$ (cm^3 g^{-1})	*LCST'* (°C)
B	0	32.6	66
	1.27	29.9	66.7
	2.54	29.0	67
	5.08	26.5	66.7
C	0	34.3	75.1
	1.27	32.9	75.5
	2.54	30.6	75.8
	5.08	27.2	75.6
D	0	37.5	87.2
	1.27	29.9	87.9
	5.08	29.1	87.7

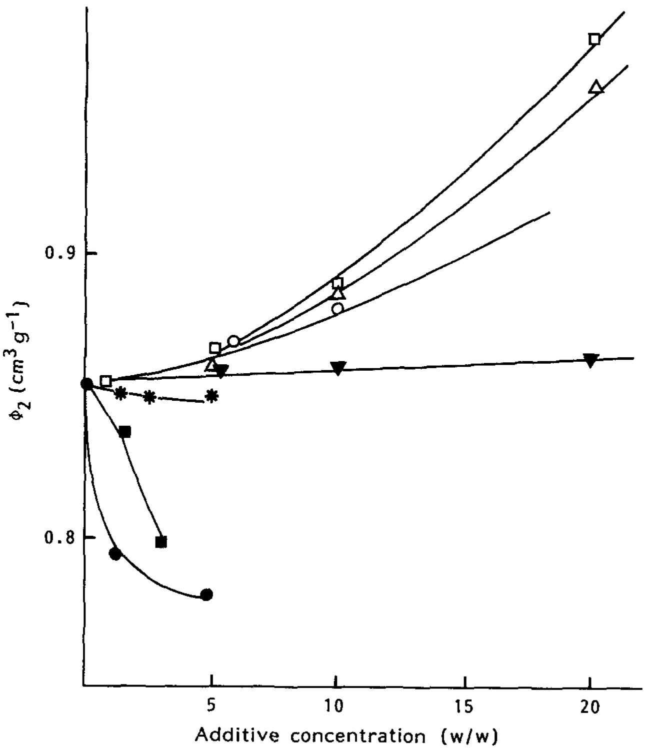

Figure 5 Dependence of the apparent specific volume of sample A with concentration of different additives: Na_2CO_3 (■); Na_3PO_4 (●); KI (*); formamide (□); acetamide (○); ethylene glycol (Δ); 1,3-butanediol (▼)

water structure in the near-vicinity of the polymer molecules and probably corresponds to excess entropy lowering, which induces phase separation at a temperature lower than in pure water. The case of KI is probably particular: its addition does not significantly change the hydration around the polymer and consequently the excess entropy and *LCST'*. However the viscosity lowering perhaps means that KI has some influence on the excess enthalpy at least at room temperature.

Cryoscopy. This study has been performed with borax as salt because it has the greatest 'salting out' effect measured by the *LCST'* lowering and it is commonly used as an anticorrosive agent.

In *Figure 6*, we have plotted the cryoscopic lowering for the two binary systems water–polymer (sample A) (curve A) and water–borax (curve B) and for the ternary system water–polymer–borax for a constant ratio borax/polymer (curve C).

As shown by curve A, the variation of the cryoscopic lowering *versus* c_p in the first system presents the curvature expected for a polymer solution, with a departure from linearity due to the polymer–polymer interaction terms. For the aqueous borax solutions, the curve is linear but its slope is approximately 5 times higher than that calculated from the chemical formula of the compound. In fact, it has been shown that borax dissolves in water by dissociating into smaller species such as BO_2^-, HBO_2^-, BO_4^{2-} and $B(OH)_3$, and some polymeric species have also been identified[12,13].

The ternary system presents two behaviours according to the concentration range:

(i) At low concentration, $c_p < 10\%$ and $c_s < 1.9\%$, the cryoscopic lowering, ΔT_f, increases and is slightly higher than that calculated on the basis of simple additivity of the effects of polymer and salt. It is not surprising that polymer–borax interactions induce a departure from ideality.

(ii) Above this concentration, ΔT_f becomes a decreasing function of c_p and the curve tends to join again that of polymer. This suggests that another type of demixing takes place at low temperature and more precisely that borax precipitation occurs. This hypothesis has been verified by some visual observations of solutions kept at different temperatures for at least 10 h. Big crystals of borax can be observed in the bottom of the vessel and we have been able to determine the variation of the borax melting point, T_{cB}, as a function of polymer concentration for two borax concentrations. *Figure 7* shows that polymer has an increasing effect on T_{cB}. This result means that polymer excludes borax from solution and explains the cryoscopic results. The strong interactions between

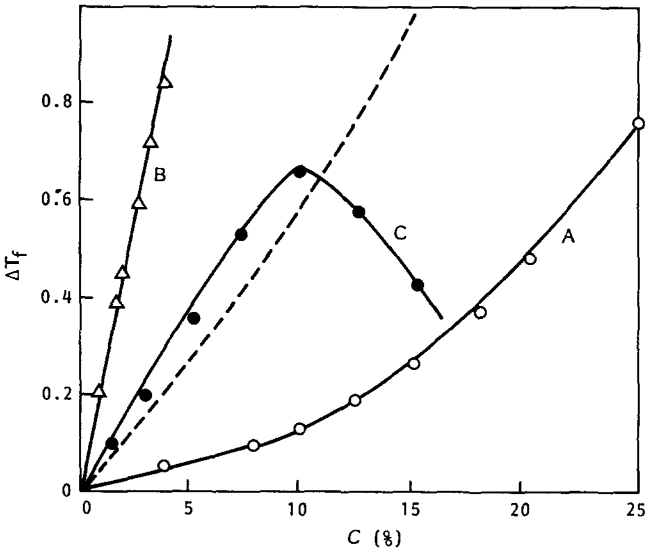

Figure 6 Cryoscopic lowering for water–sample A (A), water–borax (B) and water–sample A–borax (C); the abscissa indicates the concentrations of polymer or borax for binary systems and the polymer concentration in the ternary system, the borax/polymer being maintained constant and equal to 19%

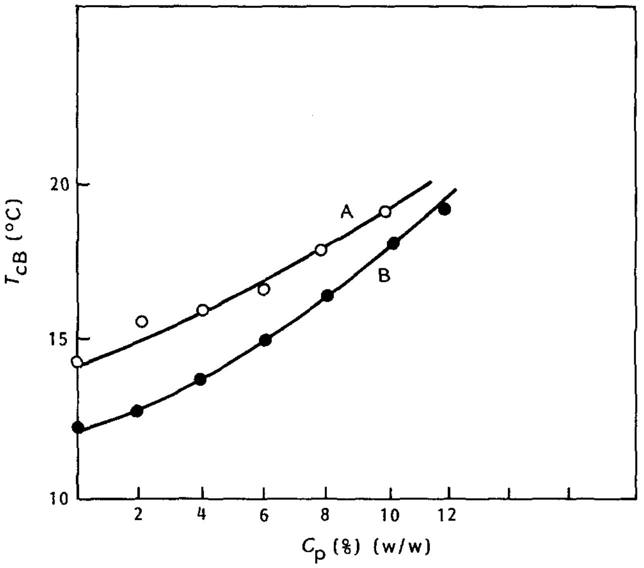

Figure 7 Melting temperature of borax in aqueous solutions as a function of concentration of sample A: (A) borax 4% and (B) borax 5%

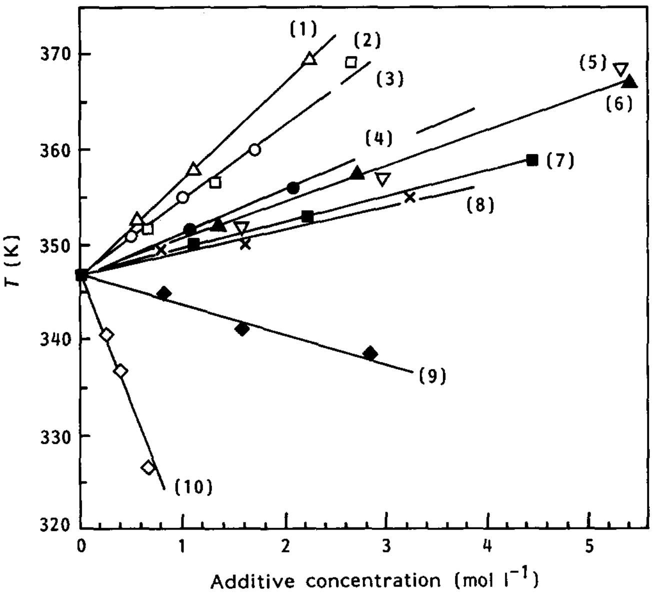

Figure 8 Variations of sample A *LCST'* with different organic additives: 1,3-butanediol (1); propylene glycol (2); acetamide (3); n-propanol (4); methanol (5); urea (6); formamide (7); ethylene glycol (8); ethanol (9); n-butanol (10)

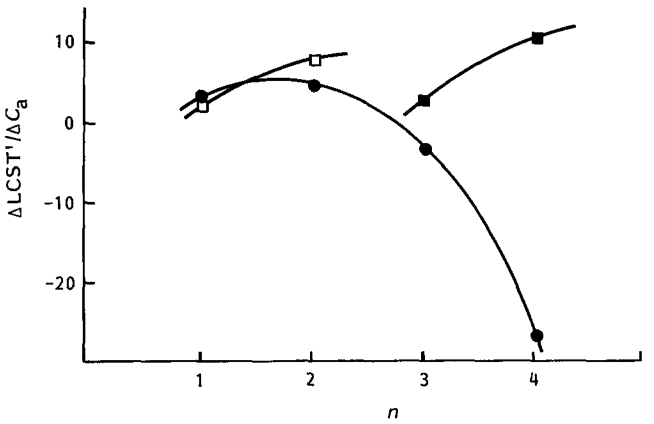

Figure 9 $\Delta LCST'/\Delta c_a$ for alcohols (●), amides (■) and diols (□) as a function of their carbon number n, in the case of sample A

borax and these copolymers are also probably the origin of the high 'salting-out effect'.

From a practical point of view, these sets of experiments show that the domains of complete miscibility of both compounds in the phase diagram are reduced. If one extrapolates the measurements of *LCST'* and T_{fB} one can expect that, for c_p and c_s above 10%, there is no longer a temperature range where both compounds are simultaneously soluble.

Ternary systems water–polymer–organic additives

Variations of LCST'. *Figure 8* shows that organic additives can have a lowering or increasing effect on *LCST'* of sample A. To try to establish a polarity scale of such effects, in *Figure 9* we have plotted $\Delta LCST'/\Delta c_a$ (c_a being the additive concentration) as a function of the carbon number of the additive molecule. One can see that for alcohols, this relative increment of *LCST'* passes through a maximum for ethanol, $n = n' = 2$. We have not performed measurements for amides or diols of higher molecular weight, but it seems that this carbon number for the maximum is shifted towards higher values when the polarity of the compounds increases. Much more systematic studies should be necessary to explain such results, which probably result from a balance between the enthalpic effects of polymer–additive and water–additive interactions and the entropic structuring effect of the hydrophobic part of the additives, both effects depending on the length of hydrocarbon chain, the nature of the polar group and the isomerism of the additives[14].

Two other pieces of information could be added:

(i) We have studied the effect of n-propanol in an extended concentration range and we have observed a behaviour inversion for $c_a = 20\%$ (see *Figure 10*).

(ii) We have compared the influence of acetamide, the most efficient compound for increasing *LCST'* of sample A, on the solubility of the other copolymers B, C and D. In the three cases, acetamide enhances solubility but the relative effect on *LCST'* becomes more important on decreasing *Y*, a result similar to that obtained with salts ($\Delta LCST'/\Delta c_a = 6.61$, 7.99 and 9.63°C mol^{-1} and $\Delta LCST'/LCST'\,\Delta c_a = 0.100$, 0.105 and 0.111 mol^{-1} for D, C and B respectively).

Viscosity. We have measured the intrinsic viscosity of sample A in binary solvents at 25°C and we have again taken the representation that Bailey and Callard[2] used for PEO–water–salt systems. We have simply plotted in *Figure 11 LCST'* as a function of $[\eta]$ measured at 25°C. One can see that the phenomena are much more complicated than in the case of inorganic additives. From the same point of view, when *LCST'* increases one would expect $[\eta]$ to increase. This is generally true if one excepts the case of acetamide (see *Figure 12* for copolymers B, C and D), but all the curves corresponding to the different additives are significantly separated. When additives have a lowering effect on *LCST'*, a correlated $[\eta]$ decrease could be expected, while the inverse variation is obtained (see for instance the case of n-butanol). However, one remarks that, in such a representation, the order of the curves follows the order of polarity at least for alcohols (see *Figure 11*).

One could assume that with organic compounds the

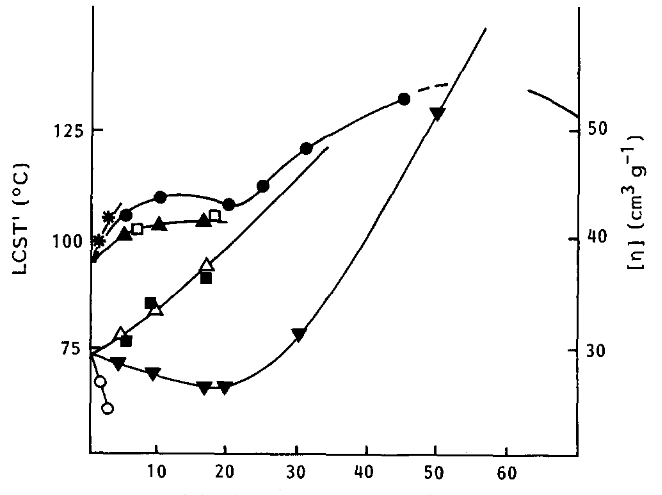

Figure 10 Variations of *LCST'* and $[\eta]$ for sample A at 25°C as a function of concentration of different additives: methanol (■, ▲); ethanol (△, □); n-propanol (▼, ●); and n-butanol (○, ∗)

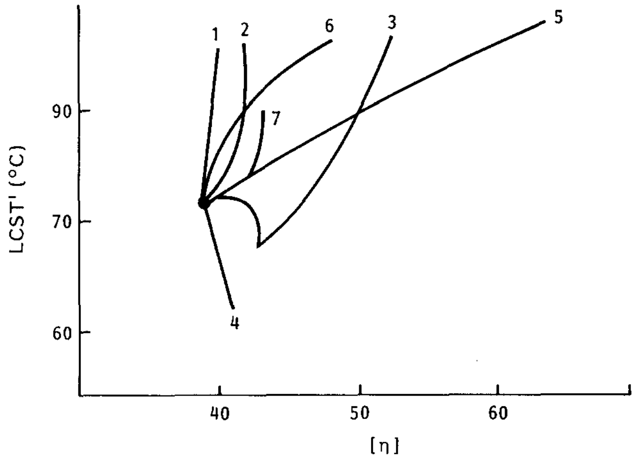

Figure 11 Plots of *LCST' versus* $[\eta]$ at 25°C for sample A with: methanol (1); ethanol (2); n-propanol (3); n-butanol (4); propylene glycol (5); 1,3-butanediol (6); and formamide (7)

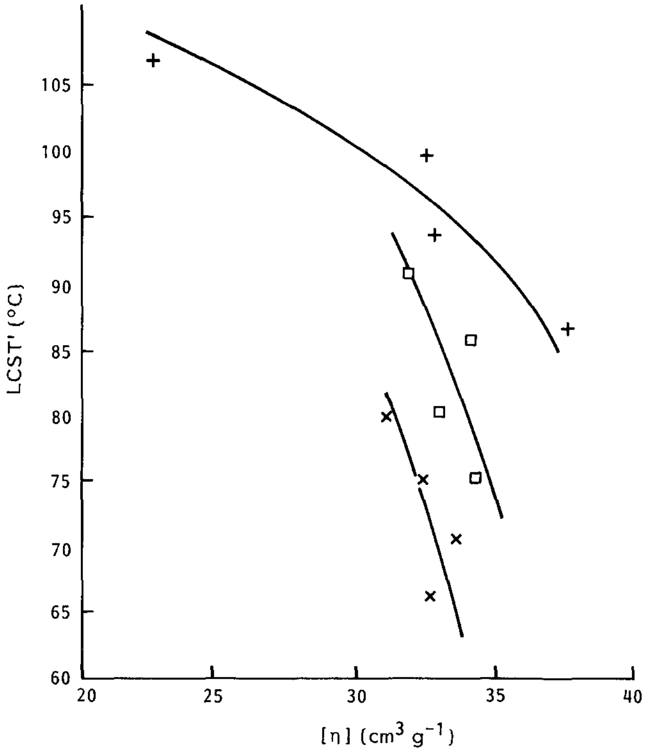

Figure 12 Variations of *LCST' versus* $[\eta]$ at 25°C for samples B (×), C (□) and D (+) in acetamide

strong interactions between the two solvents affects the intrinsic viscosity at 25°C and that such an effect does not allow this simple correlation between *LCST'* and $[\eta]$, which gives satisfactory results with salts (if one excepts the case of KI) and can be justified by theories.

This hypothesis is justified by the results of *Figure 10*, where we have plotted the variations of *LCST'* and $[\eta]$ measured at 25°C for sample A in the presence of methanol, ethanol, n-propanol and n-butanol. If one adds to this information that $[\eta]_a$ of sample A in the pure additives is respectively 31.13, 30.5, 29.4 and 29 $cm^3\,g^{-1}$, one can conclude that these systems are characterized by a large excess of viscosity $[\Delta\eta]$ with respect to the mean values $[\eta]$ calculated from intrinsic viscosities in each pure solvent:

$$[\eta] = \Phi_a[\eta]_a + (1 - \Phi_a)[\eta]_w \tag{7}$$

where Φ_a is the volume fraction of additive and $[\eta]_w$ is the intrinsic viscosity in water. It is obvious that this viscosity excess is an increasing function of n. It has been shown by Schultz and Flory[15] that the dimensions of a polymer chain in a mixed solvent, solvent 1 and solvent 2[14], depend on the interaction parameter χ_{12} between two solvent molecules:

$$\chi_{12} = G^E/x_1(1 - x_1)RT \tag{8}$$

where x_1 is the molar fraction of solvent 1 in the mixture and G^E is the free energy of mixing. When $\chi_{12} > 0$, $[\Delta\eta]$ must be positive and if $\chi_{12} < 0$, $[\Delta\eta]$ must be negative. This qualitative approach has been well verified on different non-polar systems[15,16] and more recently for polyacrylamide in water–methanol[17]. It also explains the sign of $[\Delta\eta]$ and the fact that $[\Delta\eta]$ depends on n. The values of G^E taken in ref. 14 are: 250.4, 780.4, 1586 and 2352 $cal\,mol^{-1}$ for methanol, ethanol, n-propanol and n-butanol respectively.

In the case of n-propanol we have studied the phase separation and viscosity in a more extended range of c_a (see *Figure 10*). An interesting observation can be made: a minimum of *LCST'* for 20% propanol corresponds to a singular point in the viscosity curve, which presents a maximum around 10%. In fact it is known that the excess heat of mixing ΔH^E of water–n-propanol shows a complex dependence on concentration. Thus it has been found that in mixtures of low alcohol content, $\Delta H^E < 0$, but as the mole fraction of alcohol increases, ΔH^E goes through a minimum at 10%, and at high concentration it also goes through an endothermic maximum, an inflection point appearing for 20%. The correlation is perhaps not fortuitous.

The apparent inconsistency between *LCST'* and the $[\eta]$ values at room temperature is well explained by the effects of the water–additives interactions and their variations with temperature. It should be useful to carry out measurements of $[\eta]$ of PEO or of this type of copolymer in a more extended temperature range and one can predict some changes in the values of $[\Delta\eta]$.

Density. Figure 5 shows that solvents which increase *LCST'* tend to increase the Φ_2 values also.

CONCLUSIONS

We give a set of experimental results on the solubility of EO–PO copolymers in water in the presence of different additives. We have discussed the possible relation existing between the lower critical solution temperature *LCST'* and the viscosity measured at room temperature. Some behaviour laws have been established which allow one to predict their properties. More fundamental interpretations should require further experimental information.

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