

Location of three critical phase boundaries in poly(acrylic acid)–dioxane solutions

J. M. G. Cowie* and B. Swinyard

Department of Chemistry, University of Stirling, Stirling FK9 4LA, UK

(Received 2 June 1989; revised 23 October 1989; accepted 26 October 1989)

The phase behaviour of poly(acrylic acid)–dioxane solutions has been studied over a wide range of solution concentration and temperature. Three distinct phase boundaries have been observed on increasing the temperature from ambient where homogeneous solutions are obtained. Phase separation occurs, below the boiling point of dioxane, when the solutions are heated and this first cloud-point curve has been called a quasi-lower critical solution temperature (*LCST*) boundary. Further heating of the two-phase system in sealed tubes leads to redissolution of the polymer and the location of an upper critical solution temperature (*UCST*) for the solution. If the temperature is allowed to rise further, phase separation again takes place at an *LCST* that is due to free-volume differences in the solution.

The heats of dilution and laser Raman spectra of the poly(acrylic acid) solutions and those of a model compound, propionic acid, dissolved in dioxane have been examined below the quasi-*LCST*. Evidence for hydrogen bonding between the solvent and the carboxylic groups in the polymer has been found.

It is suggested that the ability of dioxane to dissolve the polymer at ambient temperatures but not at higher temperatures below the solvent boiling point is a result of a changing balance between specific, polar, polymer–solvent interactions and normal, non-polar, dispersion forces, the ratio of which alters with changing temperature.

(Keywords: polyacrylic acid; quasi-lower critical solution temperature; phase equilibria; heats of dilution)

INTRODUCTION

The observation of a lower critical solution temperature (*LCST*) in non-polar polymer solutions, where phase separation occurs on raising the temperature, is now a well established phenomenon and can be explained by modern theories of polymer solutions developed by Prigogine¹, Patterson² and Flory³. These theories show that differences in the thermal expansion (or free volume) of the two components can lead to phase separation at elevated temperatures, which is often quite close to the gas–liquid critical temperature of the solvent, and that the process is entropically controlled. There are, however, a number of systems in which phase separation occurs on heating but where the phase separation temperature is well below the critical point and is usually below the boiling point of the solvent. The majority of these are aqueous solutions of polar polymers. In a few cases, such as poly(oxyethylene)^{4,5} and poly(vinyl alcohol)⁶ dissolved in water, after phase separating at a lower temperature these systems redissolve on further heating to form a closed loop of immiscibility, exhibiting both an upper critical solution temperature (*UCST*) and an *LCST*⁷. In these aqueous solutions, where both the heat of dilution and the excess entropy of dilution are generally negative, phase separation on heating has been explained by hydrophobic effects^{8,9}. It is postulated that addition of a hydrophobic molecule to water increases the ordering of the water molecules in the vicinity of the solute, and that this hydrophobic hydration gives rise to the negative entropy of dilution. When there are polar groups on the

polymer capable of hydrogen bonding with the solvent, then the thermodynamic properties of the solution are governed by the ratio of the polar interactions to the apolar contacts. As the temperature is increased, the constraints imposed on the water molecules hydrating the polymer decrease, thereby allowing the hydrophobic interactions to increase, leading eventually to phase separation. The driving force for this lower critical phase separation is again regarded as being entropic as with the *LCST* in non-polar systems, but has different origins. Thus one ought to distinguish between these two types of *LCST* as it should be theoretically possible to locate both in polar solutions. The *LCST*, which is caused by differences in free volume, is now regarded as a feature common to all polymer solutions, whereas the *LCST* arising from specific solvent–polymer interactions, other than van der Waals interactions, will probably be confined to polar systems. As the underlying cause of phase separation in the latter case is different and present only in certain polar systems we shall call it a quasi-*LCST*.

While the presence of a quasi-*LCST* is most commonly observed in aqueous solutions, there are a few examples in which this phenomenon has been observed for polar polymers dissolved in non-aqueous polar solvents. Systems for which this has been reported include poly(methacrylonitrile) in butanone¹⁰, poly(acrylic acid) in dioxane^{11–14} and poly(2-vinylpyridine) in chloroform/hexane mixtures¹⁵.

The *LCST* originating from free-volume differences is normally observed well above the boiling point of the liquid; consequently its experimental detection in aqueous systems (where the critical point of water is 647 K) may be difficult because of the potentially high temperatures involved, at which the polymer may degrade. This would

* To whom correspondence should be addressed at present address: Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK

not necessarily be the case for polar organic solvents with lower gas-liquid critical points, and it was decided to examine the phase behaviour of poly(acrylic acid) in 1,4-dioxane more closely.

EXPERIMENTAL DETAILS

Materials

Poly(acrylic acid) samples were obtained from Poly-science as aqueous solutions, with the exception of PAA20 and PAA17, which were supplied by Allied Colloids and ICI Mond Division, respectively. The polymers were isolated either by freeze-drying the aqueous solutions or by casting and drying films.

Molecular-weight measurements

Number-average molecular weights (M_n) were determined either by vapour-pressure osmometry at 328 K (samples PAA2, PAA5, PAA17, PAA20) or by membrane osmometry (samples PAA50, PAA90, PAA150, PAA300), using dry 1,4-dioxane as solvent. The values are collected in Table 1.

Solvents

1,4-Dioxane was refluxed for 2 h over calcium hydride followed by fractional distillation. The purified solvent was then stored over sodium wire prior to use and the water content, as determined by the Karl-Fisher method, gave consistent results of less than 0.1% water from different batches of solvent dried in this way.

Phase boundary measurements

Polymer solutions, of various concentrations, were prepared *in situ* in glass tubes (3 mm i.d.) using 0.3 cm³ of dry dioxane. The polymer was introduced into the tubes as strips of thin film and weighed, then solvent was added.

The tubes were sealed under vacuum, taking care to leave a vapour space above the solution. The tubes were then heated in a water bath for temperatures up to 353 K, and in a silicone oil bath for higher temperatures, at a rate of approximately 0.5 K min⁻¹. Phase separation was observed visually and this could be assisted by watching for the 'blurring' of the image of a copper wire placed behind each tube. After initial phase separation had taken place, heating was continued with agitation of the tubes to assist any redissolution process. Phase separation temperatures were also observed, during cooling cycles.

Critical-point determination

Critical points at the quasi-LCST phase boundary were determined for several samples using the phase volume ratio method described by Koningsveld¹⁶. Several concentrations of polymer solution were prepared in

sealed tubes as for the phase separation studies and immersed in a thermostatted bath controlled for several different temperatures (T) above the temperature of the phase separation boundary (T_p). The solutions precipitate at these temperatures and the two phases were then allowed to separate completely; this usually took between 1 and 2 h. The relative volumes of each were then estimated from the heights of the dilute (l_d) and the concentrated (l_c) phases and the ratio $r = (l_d/l_c)$ was then plotted as a function of $(T - T_p)$ for each concentration studied. The critical concentration C^* can then be determined for the conditions $r = 1$ and $(T - T_p) = 0$. For concentrations above and below the critical concentration, the value of r tends to infinity and zero respectively as $(T - T_p)$ tends towards zero.

Microcalorimetry

The heats of dilution (ΔH_d) of poly(acrylic acid) and a model compound, propionic acid, were measured in 1,4-dioxane using an LKB 10700-2 batch calorimeter. The heat of dilution is related to the final volume fraction ϕ_2 of solute when Δn moles of solvent are added to a solution of initial solute volume fraction ϕ_1 , i.e. $\Delta H_d = RT\chi_H\phi_1\phi_2\Delta n$, where χ_H is the enthalpy component of the interaction parameter χ ; then χ_H is equivalent to κ_1 the enthalpy of dilution parameter pertaining to the Flory-Krigbaum dilute-solution theory.

Laser Raman spectroscopy

Spectra were measured using a Spex Ramalog RSM spectrometer using a coherent CR6 argon-ion laser (514.5 nm). Solutions of PAA17 and PAA50 (concentrations 3.29%) in dioxane were contained in thin-walled capillary cells and were studied in the temperature range 295–353 K. Propionic acid solutions in dioxane were examined at solution concentrations of 20%.

RESULTS

Phase equilibria

Phase separation temperatures were determined for each sample over a wide range of concentrations of up to 40% (wt/vol). No phase separation could be located in solutions of sample PAA2. For the other samples studied, three phase separation boundaries were located with increasing temperature, with the exception of sample PAA5, which displayed only one lower critical phase boundary as shown in Figure 1a. The phase diagrams for the remaining samples are drawn in Figures 1b-f, showing that the gross features are common to each sample. When the temperature is increased from ambient, a quasi-LCST is located close to or below the boiling point of dioxane (374 K), and if the minimum phase separation temperature T_{pm} of this lower critical cloud-point curve is taken as a reference then the quasi-LCST is seen to decrease generally with increasing molecular weight of the polymer.

Critical concentrations C^* for the quasi-LCST boundaries were determined by the Koningsveld phase volume ratio method and these values of T_c are listed for comparison with T_{pm} in Table 2. Generally T_c is higher than T_{pm} , which may reflect the sample polydispersity, and it also shows less evidence of any dependence on sample molecular weight.

On increasing the temperature further, the polymer

Table 1 Number-average molecular weights for poly(acrylic acid) samples

Sample	$10^{-4}M_n$ (v.p.o.)	Sample	$10^{-4}M_n$ (osmotic pressure)
PAA2	0.164	PAA50	2.57
PAA5	0.291	PAA90	10.50
PAA17	0.970	PAA150	15.80
PAA20	1.600	PAA300	26.20

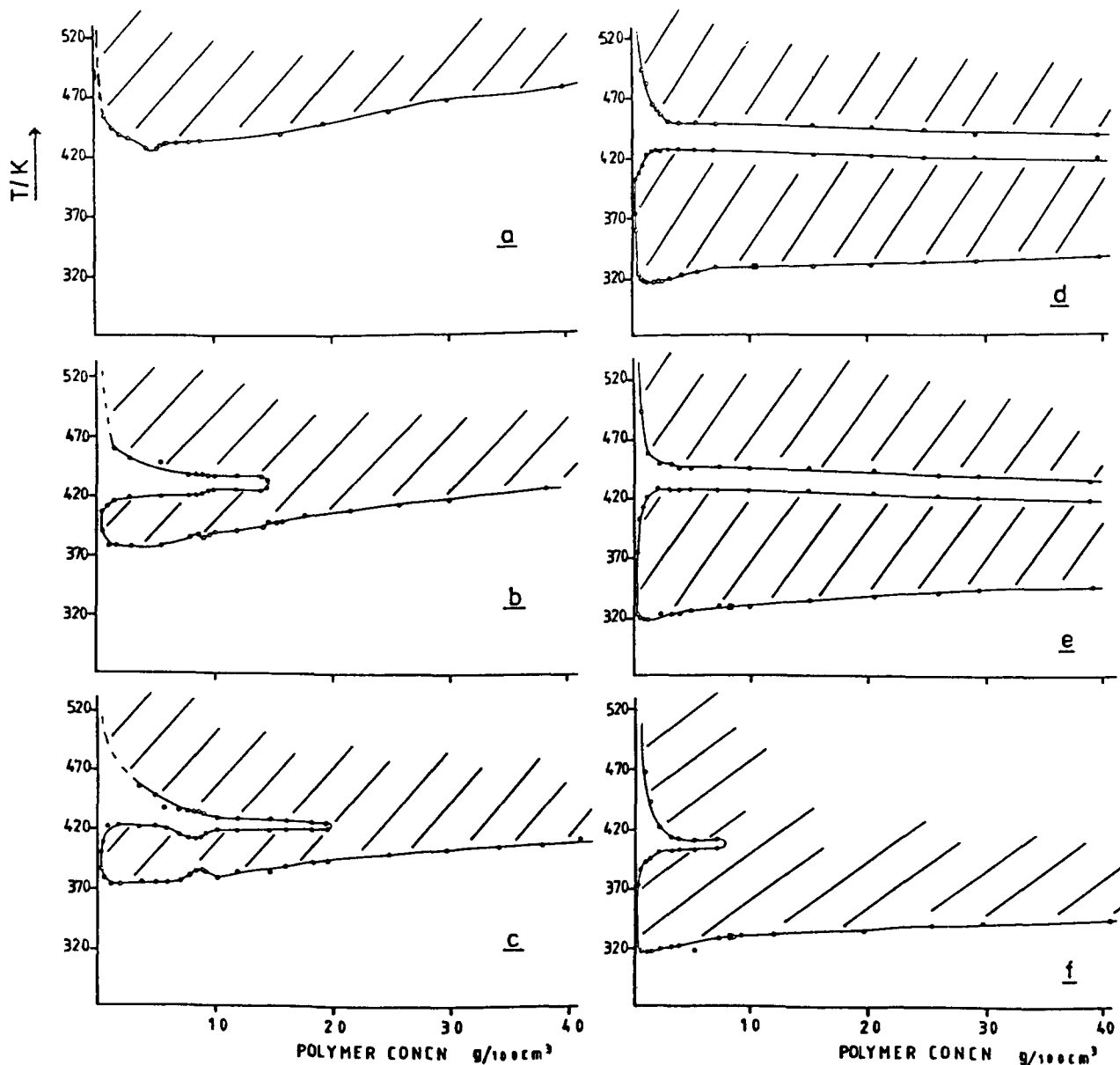


Figure 1 Phase boundaries for poly(acrylic acid) samples in dry dioxane: (a) PAA5; (b) PAA17; (c) PAA20; (d) PAA50; (e) PAA90; (f) PAA150

Table 2 Phase separation temperatures at the minimum (T_{pm}) of the quasi-LCST cloud-point curve, and at the critical concentration (T_c). Also values of the UCST and LCST at solution concentration of approximately 2%

Sample	Quasi-LCST		Critical concentration C^* , (g/100 cm ³)	UCST (K)	LCST (K)	ΔT
	T_{pm} (K)	T_c (K)				
PAA5	427	—	—	—	—	—
PAA17	378	—	—	417	456	39
PAA20	374	—	—	422	456	34
PAA50	319	331	10.51	426	458	32
PAA90	319	330	8.28	427	450	23
PAA150	318	329	8.23	401	421	20
PAA300	303	308	7.02	379	394	15

redissolves and passes through an upper critical phase boundary, at temperatures near to the boiling point of the solvent. This is followed by a region of miscibility before the solution again undergoes phase separation. This latter phase separation point has all the characteristics of a conventional LCST observed in a non-polar system. It is difficult to be precise about the critical

temperatures for these upper and lower critical boundaries, and an arbitrary solution concentration of 2% was used to derive the temperatures collected in Table 2. From these data the LCST values show the expected trend with molecular weight, but this is not the case for the UCST values. The latter increase with M_n as expected up to $M_n \sim 10^5$ but then decrease for samples with higher

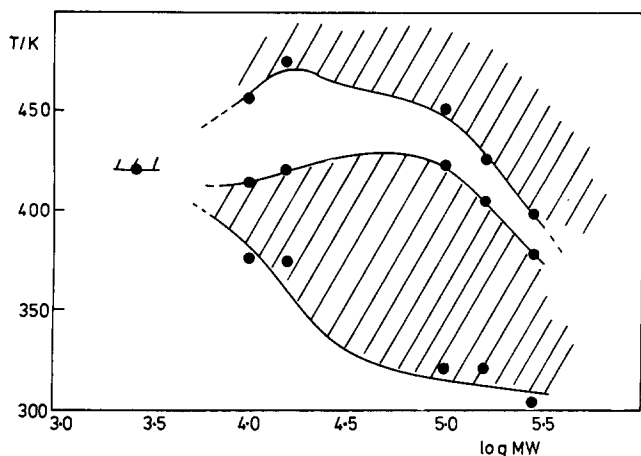


Figure 2 Lower, upper and quasi-lower solution temperatures as a function of molecular weight showing the general phase boundary trends. Shaded areas are two-phase regions

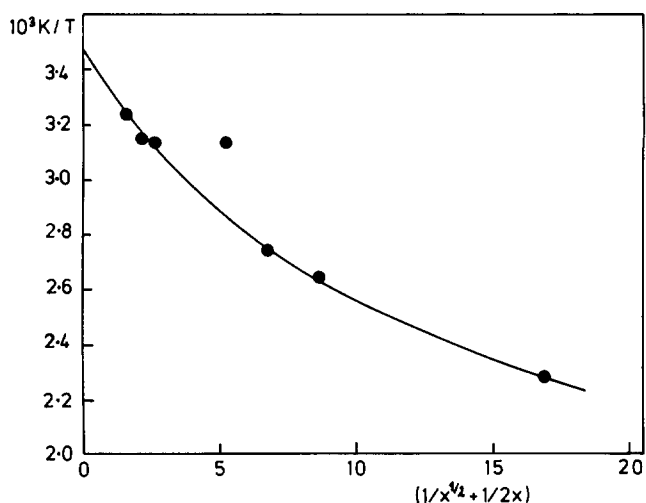


Figure 3 Schultz-Flory plot of quasi-LCSTs for poly(acrylic acid)-dioxane solutions, using equation (1)

molecular weights. Comparison of the change in the miscibility range, ΔT , between these two boundaries shows that this decreases with rise in M_n , as might be expected.

The concentration range over which the upper miscibility region extends also varies with the sample: for PAA17, PAA20, PAA150 and PAA300 it is limited to concentrations $< 20\%$, whereas for PAA50 and PAA90 there was no closing of the miscibility range, which remained open up to $\sim 40\%$ concentration. It is not obvious why these differences should be observed. The only apparent trend in this region was an increase in the miscibility range on moving from PAA17 to PAA90, but a decrease was noted thereafter for PAA150 and PAA300. These general features are summarized in *Figure 2*.

Lower theta temperature

Stable solutions were obtained at temperatures below the quasi-LCST boundaries. A theta temperature of $\theta = 303$ K was reported¹¹ for poly(acrylic acid) in dioxane (containing $\sim 2\%$ water) and it is of interest to determine whether a theta temperature might exist for the system when the dioxane is dry.

Phase separation temperatures T_{pm} were extrapolated

according to the Flory-Krigbaum equation:

$$\frac{1}{T_{pm}} = \frac{1}{\theta} \left[1 + \frac{1}{\psi_1} \left(\frac{1}{x^{1/2}} + \frac{1}{2x} \right) \right] \quad (1)$$

where x is the degree of polymerization and ψ_1 is the entropy of dilution parameter. If the values of T_{pm} for the quasi-LCST boundary are used in equation (1), the data extrapolate to $\theta = 290$ K and give a limiting value of $\psi_1 = -0.26$ (see *Figure 3*). This plot has a pronounced curvature, which places some doubt on the validity of applying equation (1) to polar systems. The original derivation was based on the solution behaviour of non-polar polymer solutions at the UCST and may not apply to the polar solutions studied here. The same procedure has not been applied to the other critical boundaries because of the uncertainty concerning the appropriate phase separation temperature to use. The entropy of dilution parameter is seen to be negative at the quasi-LCST but, as relatively little is understood about this region, an attempt was made to obtain more information on the thermodynamic characteristics of the solutions by measuring heats of dilution.

Heats of dilution

The solubility of a polymer in a liquid is governed by the free energy of mixing, determined by the interplay of the enthalpy and entropy contributions. The heat of mixing of a polymer in a solvent is difficult to measure accurately and the enthalpy of dilution is more commonly estimated. This is expressed conveniently as the integral heat of dilution ΔH_d where:

$$\Delta H_d = RT\phi_1\phi_2 \Delta n\chi_H \quad (2)$$

Here ϕ_1 and ϕ_2 are the volume fractions of the polymer in solution before and after dilution respectively, Δn is the number of moles of solvent added and χ_H is the apparent enthalpy parameter defined by:

$$\chi_H = \chi_1 + \chi_2\phi + \chi_3\phi^2 \quad (3)$$

or by the approximation:

$$\chi_H = \chi_1 + \chi_2(\phi_1 + \phi_2)/2 \quad (4)$$

If there is no concentration dependence of χ_H then it is equivalent to the Flory enthalpy of dilution parameter κ_1 and:

$$(\chi - 0.5) = \kappa_1 - \psi_1 \quad (5)$$

where χ is the interaction parameter characterizing near-neighbour interactions.

Propionic acid-dioxane solutions

A model compound was studied first and propionic acid was selected as a suitable analogue for poly(acrylic acid). The heat of mixing for propionic acid with dioxane has been determined by Wilhelm *et al.*¹⁷, who showed that it was endothermic at 298 K over the complete range of concentration. This was confirmed in the present work, during which it was also found that for measurements made at 304, 308 and 312 K the heat of mixing became less endothermic with rise in temperature. The heats of dilution and the corresponding χ_H were estimated at 298 K and the results are summarized in *Figures 4a* and *4b*. The heat of dilution is endothermic and χ_H is a linear function of $(\phi_1 + \phi_2)/2$ with a negative slope and intercept $\chi_1 = +6.5$.

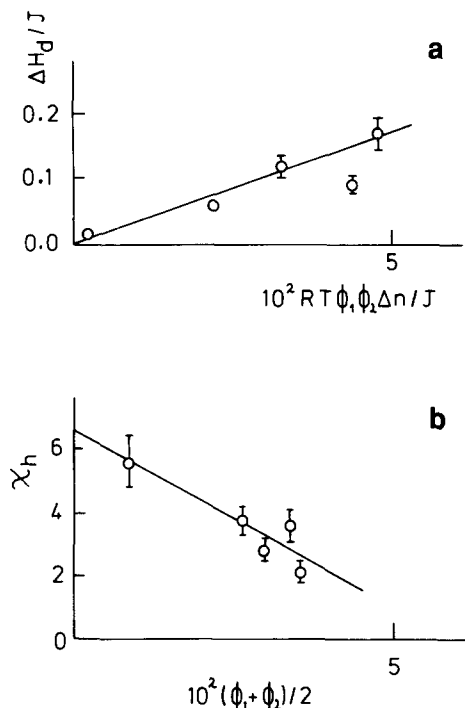


Figure 4 (a) Enthalpy of dilution plotted according to equation (2) for propionic acid mixed with dioxane. (b) Corresponding χ_H values treated according to equation (4)

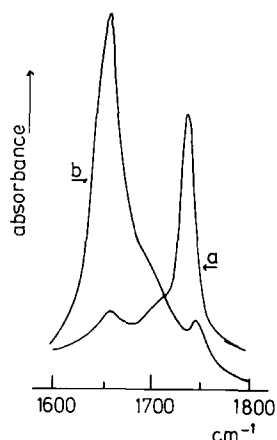


Figure 5 Raman spectra for (a) propionic acid mixed with dioxane (20% w/v solution of the acid) and (b) pure propionic acid

The Raman spectrum of pure liquid propionic acid was measured, and shows a symmetrical carbonyl stretching frequency peak at 1659 cm^{-1} , which has been interpreted as being due to a hydrogen-bonded dimeric species¹⁸.

When the acid is diluted with dioxane at 298 K a new peak appears at 1740 cm^{-1} arising from a non-hydrogen-bonded species¹⁹ while the peak at 1659 cm^{-1} weakens, as shown in Figure 5. As the temperature is increased, the intensity of the peak due to the dimeric species diminishes steadily, indicating further disruption of the hydrogen-bonded species to form free molecules. Thus dilution of the propionic acid with dioxane breaks up the hydrogen-bonded dimers in the acid, resulting in an endothermic heat of mixing and dilution. The observed decrease in the heat of mixing with increasing temperature must then be due to the reduction in the concentration of acid dimers as the temperature is raised.

Poly(acrylic acid)-dioxane

The heats of dilution (ΔH_d) and the corresponding χ_H parameters determined for PAA150 in dioxane are shown in Figures 6a and 6b to provide some indication of the errors in the data. Similar plots for PAA50 are presented in Figures 7a and 7b, where for clarity only the smoothed curves through the data obtained at several temperatures are drawn to illustrate the trends. The heat of dilution is endothermic at all the temperatures studied but there is no consistent trend in ΔH_d observable with change in temperature. Extrapolation of χ_H to infinite dilution gave similar values for both PAA50 and PAA150, reflecting the similarities in phase behaviour. The plots were curved, however, indicating a more complex concentration dependence of the χ_H parameter than for the propionic acid.

The laser Raman spectrum was more difficult to measure because of local overheating tendencies during the measurements, but four peaks could be identified for PAA50 in dioxane at 1639 , 1658 , 1690 and 1730 cm^{-1} . Using the interpretations for propionic acid and poly(methacrylic acid)²⁰, the 1658 and 1639 cm^{-1} absorptions arise from inter- and intramolecular hydrogen bonding, respectively, in the poly(acrylic acid), 1730 cm^{-1} represents the unbonded species and 1690 cm^{-1} may come from possible interactions with dioxane. A study of PAA17 at several temperatures between 295 and 353 K indicated a general increase in the intensity of the peak at 1720 cm^{-1} (equivalent to 1730 cm^{-1} in PAA50), suggesting that there is a decrease in hydrogen bonding with increase in temperature.

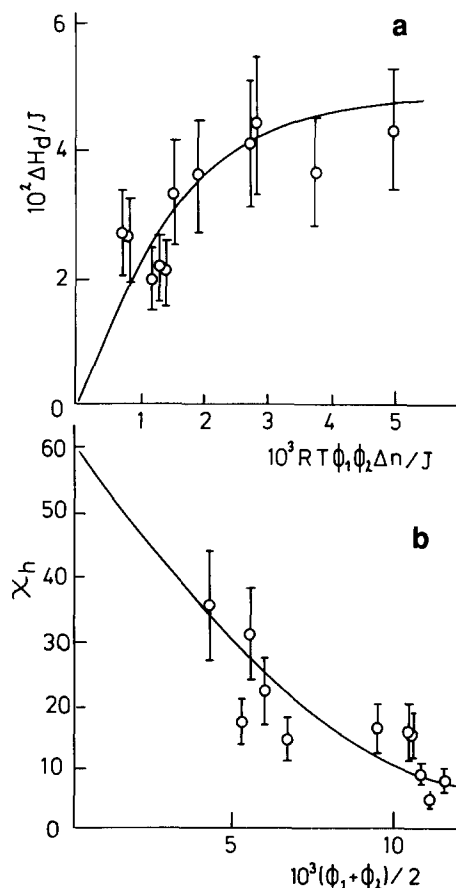


Figure 6 (a) Enthalpy of dilution data for poly(acrylic acid) in dioxane. (b) Corresponding values of χ_H derived from these data for sample PAA150. Error bars are included to give an indication of the expected accuracy

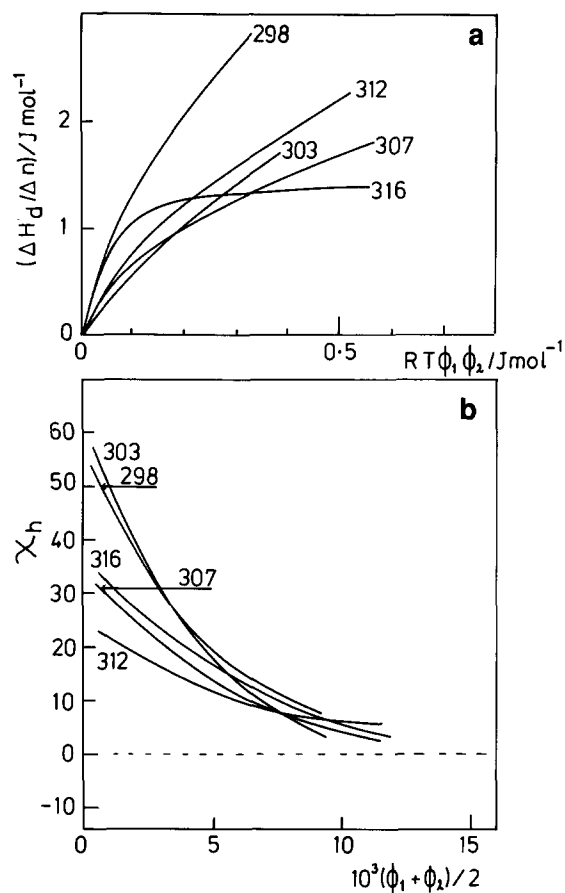


Figure 7 (a) Enthalpy of dilution for PAA50 in dioxane measured at several temperatures. (b) Corresponding trends in χ_H derived from these data. Smoothed curves have been used to avoid confusion of data points

DISCUSSION

Poly(acrylic acid) dissolves in dioxane at room temperature to form stable homogeneous solutions. From the observed behaviour it is thought that the dissolution process at room temperature involves the following series of steps. Addition of dioxane to the polymer first solvates it by disrupting some of the inter- and intra-hydrogen bonding between the carboxylic acid groups in the poly(acrylic acid), and some new solvent-polymer specific bonding sites are formed together with unbound carbonyl groups. The laser Raman data support this hypothesis, and in a recent publication²¹ it was demonstrated that stable complexes are formed between poly(acrylic acid) and poly(vinyl methyl ether). Complex formation was a consequence of the formation of a substantial number of hydrogen bonds between the ether oxygen of poly(vinyl methyl ether) and the carboxyl group of the poly(acrylic acid). Thus the competitive interaction of dioxane with the hydrogen-bonding sites on poly(acrylic acid) is not an unreasonable postulate and will produce a solvated polymer with many of the polar sites negated, thereby producing an essentially non-polar coil. Further dilution by solvent will involve normal dispersion forces and a positive heat of dilution is consistent with this model if the non-polar interactions outweigh the specific polar ones, as seems highly likely in this system.

The negative entropy of dilution term estimated from equation (1) is not what one would expect on the basis of the arguments presented and there is some doubt as to the validity of using this method of analysis for a system in which specific solvent-polymer interactions

may be present. However, the parameter is derived from phase separation temperature data and as such may refer only to the boundary conditions. The thermodynamic behaviour below these boundaries may change and so interpretation of this parameter must be regarded with caution in this system.

As the temperature is increased the hydrogen-bonding interactions will tend to weaken and the balance of lyophobic interactions will change. Eventually domination of the solution behaviour by the unfavourable dispersion forces, as the ratio of lyophilic to lyophobic interactions decreases, will lead to phase separation and the appearance of a quasi-LCST.

On heating the system further, the unfavourable enthalpy term will become less and is eventually offset by the favourable entropy of mixing term, thereby encouraging the redissolution of the polymer.

This is shown by the existence of an upper critical phase boundary, and a second region of miscibility where one-phase solutions are stable. Finally, at higher temperatures, a lower critical solution temperature is observed when the free-volume factors dominate and the differences in expansivity between the polymer and the solvent are too great to sustain a one-phase system, so that phase separation again takes place.

Thus the reasons for phase separation occurring at this higher LCST have different origins from those responsible for phase separation in the quasi-LCST region and we should distinguish between the two types. The LCST at temperatures well above the solvent boiling point is caused by differences in free volume between the two components, whereas at the quasi-LCST, observed below the solvent boiling point, phase separation is more likely caused by disruption of specific, polar, solvent-polymer interactions, which are thermally labile. In aqueous systems, the LCST behaviour is also observed at temperatures well below the boiling point of water and has been explained as a manifestation of hydrophobic interactions. The behaviour in aqueous solutions is then dependent on a balance between intercomponent hydrogen bonding and hydrophobic hydration and is associated with changes in the structure of water itself. As such this may lead to differences in the thermodynamic parameters when compared with the present systems and the behaviour observed here in dioxane solutions may not be entirely analogous. A study of poly(acrylic acid) in dioxane-water mixtures will be presented in a forthcoming publication, which will highlight some of these differences.

ACKNOWLEDGEMENTS

The authors wish to thank Dr I. E. Clark (Unilever) for performing the laser Raman spectroscopy experiments.

REFERENCES

- 1 Prigogine, I. (with Bellemans, A. and Mathot, V.) 'Molecular Theory of Solutions', North-Holland, Amsterdam, 1957
- 2 Patterson, D. and Delmas, G. *Disc. Faraday Soc.* 1970, **49**, 98
- 3 Flory, P. J. *Disc. Faraday Soc.* 1970, **49**, 7
- 4 Malcolm, G. N. and Rowlinson, J. S. *Trans. Faraday Soc.* 1957, **53**, 921
- 5 Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M. *Polymer* 1976, **17**, 685
- 6 Rehage, G. *Kunststoffe* 1963, **53**, 605

- 7 For a comprehensive review see Molyneux, P. 'Water Soluble Synthetic Polymers: Properties and Behaviour'. Vols. 1 and 2, CRC Press, Boca Raton, FL, 1983
- 8 Tanford, C. 'The Hydrophobic Effect', Wiley, New York, 1973
- 9 Nemethy, G. and Scheraga, H. A. *J. Chem. Phys.* 1962, **36**, 340
- 10 Morawetz, H. 'Macromolecules in Solution', Interscience, New York, 1965
- 11 Flory, P. J., Krigbaum, W. R. and Schultz, W. B. *J. Chem. Phys.* 1953, **21**, 164
- 12 Flory, P. J. and Osterheld, J. E. *J. Phys. Chem.* 1954, **58**, 683
- 13 Miller, M. L., O'Donnell, K. and Skogman, J. J. *Colloid Sci.* 1962, **17**, 649
- 14 Cuniberti, C. and Bianchi, V. *Polymer* 1974, **15**, 346
- 15 Arichi, S., Matsuura, H., Tanimoto, Y. and Murata, H. *Bull. Chem. Soc. Japan* 1966, **39**, 434
- 16 Koningsveld, R. and Stavermann, A. *J. Polym. Sci. (A2)* 1968, **6**, 325
- 17 Wilhelm, E., Inglese, A., Grolier, J.-P. and Kehiaian, H. V. *J. Chem. Thermodyn.* 1982, **14**, 33, 517
- 18 Jakobsen, R. J., Mikawa, Y., Allkins, J. R. and Carlson, G. L. *J. Mol. Struct.* 1971, **10**, 300
- 19 Colthup, N. B., Daly, L. H. and Wiberley, S. E. 'Introduction to Infrared and Raman Spectroscopy', Academic Press, London, 1964
- 20 Koenig, J. L., Angood, A. C., Semen, J. and Lando, J. B. *J. Am. Chem. Soc.* 1969, **91**, 7250
- 21 Cowie, J. M. G., Garay, M. T., Lath, D. and McEwen, I. J. *Br. Polym. J.* 1989, **21**, 81