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Upper critical solution temperature—type cononsolvency of poly(*N*,*N*-dimethylacrylamide) in water—organic solvent mixtures

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Abstract

The behaviour of linear poly(*N*,*N*-dimethylacrylamide) (PDMAM) chains was studied by turbidimetry and viscometry in mixtures of water with the polar organic solvents methanol, dioxane and acetone. The swelling–deswelling behaviour of PDMAM gels in the same solvent mixtures was also investigated. Contrary to the behaviour in water–methanol mixtures, in water–dioxane and water–acetone mixtures a significant shrinkage of polymer chains and deswelling of polymer gels, followed by phase separation, was observed for high organic solvent fractions. Cononsolvency phenomena were found to be temperature-dependent, as demixing occurred upon decreasing temperature. This upper critical solution temperature (UCST) phase separation behaviour in mixed solvents was studied by turbidimetry and compared to the well-known lower critical solution temperature (LCST) behaviour of poly(*N*-isopropylacrylamide) (PNIPAM) in similar solvents mixtures.

Keywords: Poly(*N*,*N*-dimethylacrylamide); Cononsolvency; Upper critical solution temperature

1. Introduction

Cononsolvency is a rather rare phenomenon, describing the situation of polymers soluble in two pure solvents but insoluble in their mixtures, for some mixture compositions [1]. The best studied example probably is the case of poly(*N*-isopropylacrylamide) (PNIPAM) in mixtures of water with polar organic solvents, such as methanol, tetrahydrofuran, dioxane and others [2–6]. For this polymer, the phase separation in the solvent mixtures is of the lower critical solution temperature (LCST)-type, as it is also the behaviour of PNIPAM in pure water [7,8]. Moreover, it has been related to the coil to globule transition of single PNIPAM chains [9] and to the reentrance phase transition of PNIPAM gels [10–13] or microgel particles [14]. Also, smart PNIPAM hydrogels based on this phenomenon have been recently proposed [15].

A few more examples can also be found in the literature. Most of them concern water-insoluble polymers, such as poly(ε-caprolactone) and poly(methyl methacrylate) in mixtures of pyridine and formic acid [16] or poly(ether imide) in mixtures of *N*-methyl-2-pyrrolidone and methylene chloride [17]. As it concerns water-soluble polymers, apart PNIPAM, cononsolvency is also found with poly(*N*,*N*-diethylacrylamide) [10] and poly(vinyl alcohol) [18,19] in water–dimethyl sulfoxide mixtures. Nevertheless, in most cases, the type of phase separation, i.e. whether it is a LCST or an upper critical solution temperature (UCST) behaviour, is not discussed.

In the present work, we study the behaviour of another water-soluble polymer, namely poly(*N*,*N*-dimethylacrylamide) (PDMAM) in mixtures of water with polar organic solvents, like dioxane and acetone. Cononsolvency phenomena are investigated as a function of solvent composition and temperature by turbidimetry and reduced viscosity measurements of linear PDMAM chains, while reentrance phase behaviour of PDMAM gels has been observed under similar conditions.

Although less popular than PNIPAM, the scientific and practical interest for PDMAM is continuously increasing. Thus, the role of PDMAM in hydrogen-bonding interpolymer complexes [20–24], interpenetrating networks [25] and hydrogels [26,27] has been investigated, while the properties of *N*,*N*-dimethylacrylamide (DMAM)-based

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derivatives, like thermosensitive [23,26,28] or hydrophobically modified PDMAM copolymers [29–31], have been investigated. Moreover, several applications of PDMAM-based products have been proposed, ranging from two-phase catalysts [32] to hydrogels for drug-delivery purposes [27] or polymer supports for protein synthesis [33]. However, to our knowledge, no cononsolvency phenomena of PDMAM in mixed solvents have been reported.

The chemical structures of PDMAM and PNIPAM differ just by one methylene group (Scheme 1). As a consequence, the two polymers are soluble both in water and in polar organic solvents. Moreover, PDMAM is more hydrophilic than PNIPAM and it does not present any LCST behaviour in water within the full temperature range of liquid water (0–100 °C). In fact, the LCST of PDMAM, if any, is estimated to be higher than 200 °C, by extrapolation data of the behaviour of copolymers of *N*,*N*-dimethylacrylamide, DMAM, with the more hydrophobic monomer *N*,*N*-diethylacrylamide [28]. Due to this difference, the tendencies of the cononsolvency phenomena observed with PDMAM are reversed, as compared with the corresponding behaviour of PNIPAM [2–6]. For instance, for PDMAM cononsolvency is observed in water-poor mixtures, while for PNIPAM, cononsolvency is observed for high water fractions. More important, a UCST-type cononsolvency behaviour is observed with PDMAM, in contrast to the well-studied LCST-type cononsolvency behaviour of PNIPAM.

2. Experimental

2.1. Materials

DMAM, sodium metabisulphite, *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TEMED) and methylene bisacrylamide (BIS) were purchased from Aldrich, while ammonium persulphate was a Serva product. Dioxane, acetone and methanol of HPLC grade were used. Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga laboratory unit.

PDMAM was prepared by free radical polymerisation in water at 35 °C, using the redox couple ammonium persulphate/sodium metabisulphite as initiator. The polymer was purified by dialysis and recovered by freeze-drying. The molar mass of the product was determined viscometrically [34] to be 150,000 Da.

Scheme 1.

For the preparation of PDMAM gel, 5.0 g DMAM and 0.25 g BIS were dissolved in 50 ml water under stirring at room temperature. The solution was deoxygenated and then ammonium persulphate and TEMED were added. The formation of the gel was almost immediate. The reaction was let to proceed for some hours and then the gel was immersed in pure water for 1 week. Water was renewed daily. Finally, the hydrogel was cut in ~0.2 g pieces and freeze-dried.

2.2. Methods

Turbidimetry. The optical density of PDMAM solutions as a function of temperature or solvent composition was determined with a U-2001 Hitatchi UV–vis spectrophotometer equipped with a thermostated circulation system. The solutions were let for 5 min under stirring to equilibrate at each temperature before each measurement. The polymer concentration was for all the turbidity experiments 1×10^{-2} g ml.

Viscometry. The reduced viscosity studies were carried out with an automated viscosity measuring system (Schott-Gerate AVS 300) equipped with a micro-Ostwald- type viscometer. The polymer concentration was fixed at 2.5×10^{-3} g ml.

Swelling of the PDMAM gels. For the swelling measurements, a pre-weighted dry gel sample was immersed in 10 cm^3 of the solvent with the desired mixture composition and let to swell. The mass of the gel was measured daily. The gel was considered to reach equilibrium when its mass did not change (within experimental error) for at least 2 days. For each experimental point, at least two samples were measured. The deviation of the results was less than 5%.

3. Results and discussion

3.1. Cononsolvency of PDMAM in water–dioxane mixtures

In Fig. 1 we present the variation of the optical density of PDMAM solutions in water–dioxane mixtures with temperature, *T*. All the studies were performed with decreasing temperature. The composition of the solvent mixtures is reported as the volume fraction of dioxane, φ :

$$\varphi = V_D/(V_W + V_D) \tag{1}$$

where V_W and V_D are the volumes of water and dioxane, respectively, used for the preparation of the solvent mixture.

As it can be seen, the PDMAM solutions in the pure solvents, water and dioxane, are transparent in the whole temperature range studied. This is also true for the PDMAM solutions in solvent mixtures for $\varphi <\sim 0.8$. For $0.8 < \varphi < 1$, a temperature-sensitive phase separation is observed and

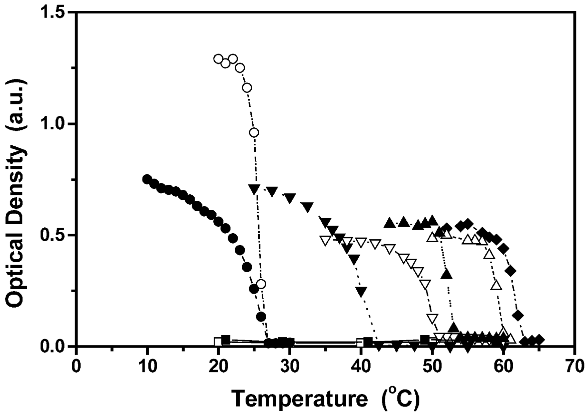

Fig. 1. The temperature-dependence of the optical density of PDMAM solutions in water–dioxane mixtures. (■): $\varphi = 0$, (●): $\varphi = 0.80$, (▼): $\varphi = 0.83$, (▽): $\varphi = 0.85$, (◆): $\varphi = 0.90$, (△): $\varphi = 0.92$, (▲): $\varphi = 0.95$, (○): $\varphi = 0.98$, (□): $\varphi = 1$. The PDMAM concentration is 1×10^{-2} g/ml.

the PDMAM solutions, although homogeneous and transparent at high temperature, turn cloudy as T decreases. This UCST behaviour, i.e. phase separation upon cooling, is very sensitive to the composition of the solvent mixture. Thus, by a small increase of φ from 0.8 to 0.9, the phase separation temperature of the solution increases from 27 °C up to 62 °C. Although no detailed study has been performed to investigate whether the turbid solutions would result in two well-separated phases or not, under the conditions of these experiments no macroscopic phase separation was evidenced and the turbidity curves were quite reproducible. On the contrary, for high polymer concentrations macroscopic phase separation takes place, as PDMAM precipitates out from the solution.

Defining the cloud point temperature of the solution as the temperature where the onset of turbidity is observed, we can construct the 'phase diagram' of PDMAM in water–dioxane solutions. The results are presented in Fig. 2 as a function of φ and they are compared to the behaviour of PNIPAM in water–dioxane and water–methanol solutions. As known, the phase behaviour of PNIPAM is of the LCST type. In contrast, PDMAM exhibits a UCST-type phase behaviour: phase separation takes place with decreasing temperature. Moreover, for PDMAM the whole phenomenon is observed at dioxane-rich solutions, whereas for PNIPAM this occurs at water-rich solutions. Also, note that dioxane is a solvent of PDMAM within the whole temperature range, whereas PNIPAM exhibits LCST behaviour in pure water. Nevertheless, in the case of PDMAM just a very small quantity of water (less than 2%, v:v) suffices to turn the solvent (dioxane) to a nonsolvent at a certain temperature. In contrast, the addition of dioxane to a PNIPAM aqueous solution hardly influences its cloud point. This conclusion also holds even if we compare to solvents that decrease more effectively the LCST of PNIPAM. The addition of methanol, for instance, to an aqueous PNIPAM solution leads to a rather gradual decrease of its cloud point and not to an abrupt change, as it can be seen in Fig. 2.

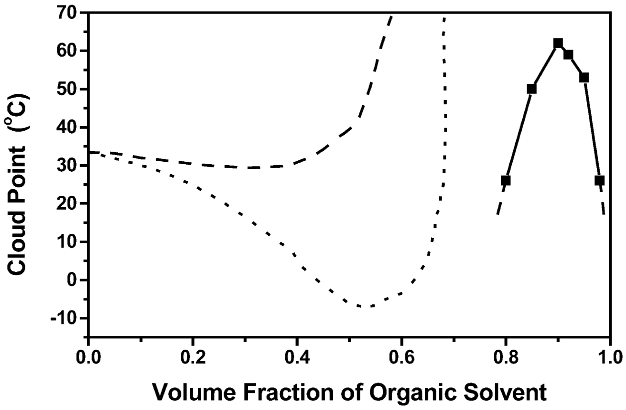

Fig. 2. The variation of cloud point of PDMAM with the volume fraction of dioxane in water–dioxane mixtures (■). The results are compared with the phase behaviour of PNIPAM in water–dioxane (dashed line) or water–methanol (dotted line) mixtures (redrawn from reference [3]). The PDMAM concentration is 1×10^{-2} g/ml.

Additional information on the change of the solvent quality can be obtained from Fig. 3, where the variation of the reduced viscosity, η_{sp}/c, of PDMAM solutions as a function of φ at a constant temperature is presented. η_{sp}/c is calculated from the equation

$$\eta_{sp}/c = (\eta - \eta_0)/(\eta_0 c) \quad (2)$$

where η and η_0 are the viscosities of the polymer solution and the solvent, respectively, while c is the polymer concentration.

In the same figure, we have also plotted the variation of the swelling ratio, S, of PDMAM gels under the same conditions. S is defined as

$$S = (w_s - w_d)/w_d \quad (3)$$

where w_d and w_s is the weight of the gel before (dry) and after (swollen) equilibration with the solvent mixture, respectively.

Although slightly lower, the reduced viscosity of PDMAM in dioxane is comparable to that in water, indicating that both pure water and pure dioxane are rather good solvents for this polymer. Similarly, the swelling ratio of PDMAM gel in dioxane is comparable to that in water, though slightly lower. Moreover, both the reduced viscosity and the swelling ratio change in a similar manner upon addition of dioxane to the aqueous PDMAM solution or gel, respectively. Thus, for $0 < \varphi <\sim 0.6$, both quantities remain rather constant, taking values similar to those for $\varphi = 0$. Both observations indicate, therefore, that these mixed solvents are qualitatively comparable to pure water. Nevertheless, by further increasing φ, η_{sp}/c and S decrease abruptly, because now the linear PDMAM chains or gel sense an increasingly worsening solvent. Finally, as φ increases further, the shrunked PDMAM chains and the collapsed PDMAM gel start to reswell, reaching the behaviour of PDMAM in pure dioxane. The shadow area

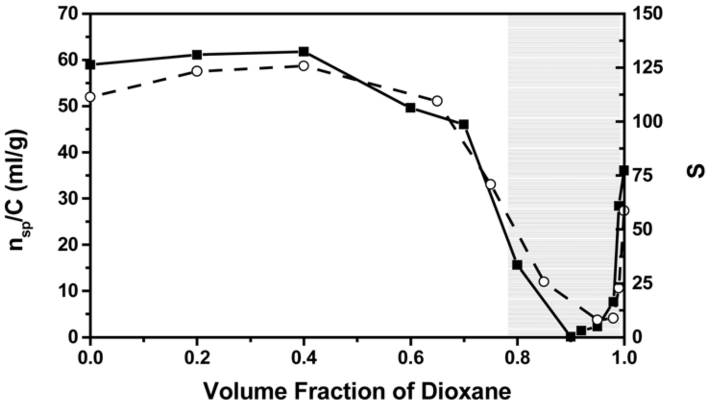

Fig. 3. The variation of the reduced viscosity of linear PDMAM chains (■, solid line) and the swelling ratio of PDMAM gels (○, dashed line) in water–dioxane mixtures. $T = 22$ °C. The concentration of PDMAM solutions is 2.5×10^{-3} g/ml.

in Fig. 3 represent the area of turbidity at 22 °C as determined from Fig. 1. It is evident that the evolution of η_{sp}/c follows the turbidity results. Moreover, the minimum η_{sp}/c and S are found at $\varphi \sim 0.9$–0.95. Note that the maximum found in Fig. 2 is placed at the same volume fraction of dioxane.

3.2. Other water—organic cononsolvent mixtures for PDMAM

To investigate whether this cononsolvency phenomenon is observed just for water–dioxane mixtures or it is more general, we checked the behaviour of PDMAM in mixtures of water with other polar organic solvents of varying polarity, namely methanol and acetone.

The optical density at 22 °C of PDMAM solutions in mixtures of water with methanol, dioxane or acetone is presented in Fig. 4 as a function of the volume fraction of the organic solvent. When the second solvent is the highly polar methanol, the mixtures with water form a good solvent for PDMAM and the solutions are transparent within the whole composition range. On the other hand, both acetone and dioxane form solvent mixtures with water that are bad solvents for PDMAM at $T = 22$ °C, when $0.75 < \varphi <\sim 1$. As a consequence, the solutions in both solvent mixtures are turbid in this composition region. Turbidity is higher in water–acetone mixtures, indicating the formation of larger PDMAM particles, while the maximum in turbidity seems to be shifted slightly to a higher water content when acetone is used as a cononsolvent.

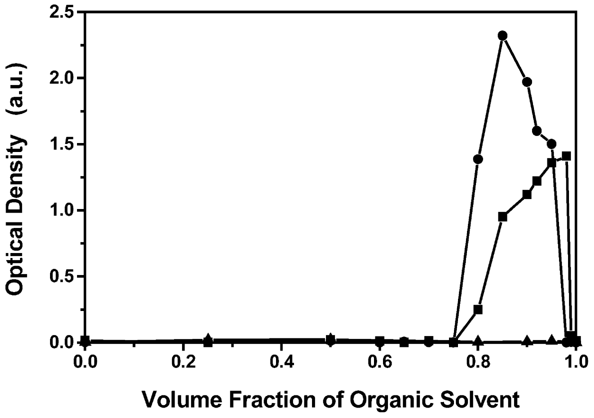

Fig. 4. The variation of the optical density of PDMAM solutions as a function of the volume fraction of the organic solvent, in mixtures of water with methanol (▲), dioxane (■) and acetone (●). The concentration of PDMAM solutions is 1×10^{-2} g/ml. $T = 22$ °C.

The aforementioned observations are further supported by the evolution of the reduced viscosity and the swelling ratio of PDMAM in these mixed solvents as a function of φ. These results are presented in Fig. 5(a) and (b), respectively. In water–methanol mixtures, both the reduced viscosity of linear PDMAM chains and the swelling ratio of PDMAM gels are high and change rather regularly with φ. On the contrary, when the second solvent is the less polar dioxane or acetone, the water–acetone or watere–dioxane mixtures turn rapidly to a cononsolvent when φ increases above ~ 0.6. From the results of Fig. 5 (especially Fig. 5(b)) in combination with the results presented in Fig. 4, we could conclude that cononsolvency phenomena are slightly more important in the case of water–acetone mixtures. The difference, however, is rather marginal, probably due to the similar polarity of acetone and dioxane.

4. Conclusions

Cononsolvency phenomena are observed when PDMAM is dissolved in mixtures of water with polar organic solvents, like dioxane or acetone. As compared to the well-studied LCST-type cononsolvency behaviour of PNIPAM, the respective behaviour of PDMAM is qualitatively reversed, probably due to the higher hydrophilicity of this polymer. Thus, in this case, (a) less polar organic solvents are needed (compare, for instance, the behaviour of both polymers in water–methanol mixtures), (b) cononsolvency is observed at high organic solvent fractions, and (c) a UCST temperature-dependence is observed. As a result, PDMAM offer a nice alternative to PNIPAM for the

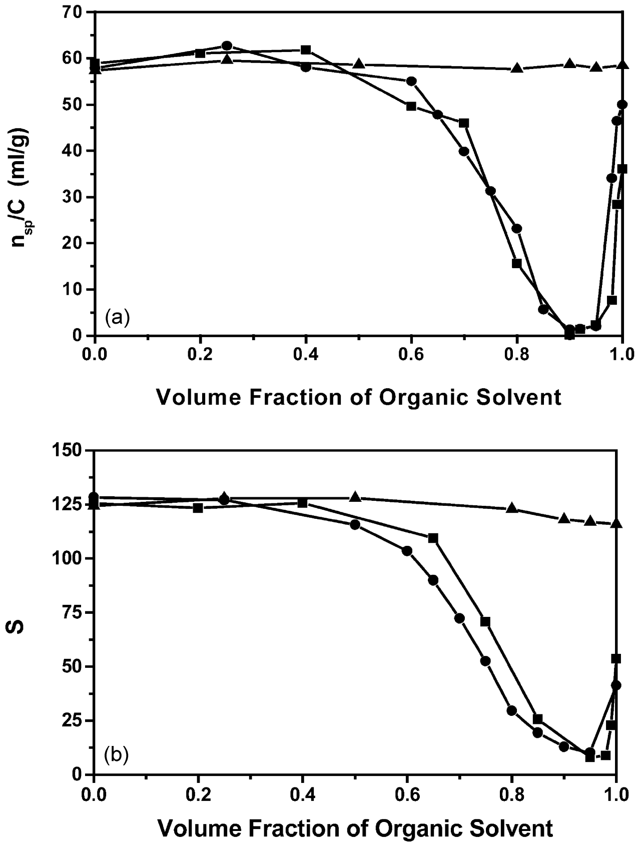

Fig. 5. (a) The variation of the reduced viscosity of PDMAM solutions as a function of the volume fraction of the organic solvent, in mixtures of water with methanol (▲), dioxane (■) and acetone (●) at $T = 22$ °C. The concentration of PDMAM solutions is 2.5×10^{-3} g/ml. (b) The variation of the swelling ratio of PDMAM gels as a function of the volume fraction of the organic solvent, in mixtures of water with methanol (▲), dioxane (■) and acetone (●) at $T = 22$ °C.

designing of novel applications. For instance, smart hydrogels with a UCST-type response to solvent composition could be envisaged. Furthermore, the synthesis of copolymers of various structures, containing both DMAM and NIPAM, is expected to lead to materials combining in an intelligent way both a UCST- and an LCST-type response to solvent composition.

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