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Solution properties and phase behaviour of copolymers of acrylic acid with *N*-isopropylacrylamide: the importance of the intrachain hydrogen bonding

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Abstract

The solution properties and the phase behaviour of random copolymers of *N*-isopropylacrylamide (NIPAM) with acrylic acid (AA) have been investigated. The mole fraction of NIPAM in these copolymers (x) varies from 0 to 0.29. At $\mathrm{pH} = 3.00$, i.e. when the AA groups are in the undissociated form, the intrinsic viscosity decreases substantially as x increases. This chain shrinkage is attributed to the formation of intrachain hydrogen bonds between the two complementary groups, AA and NIPAM. The weakening of the hydrophilic character and the appearance of hydrophobic properties with increasing x is further supported by fluorescence probing studies and potentiometric measurements of the aqueous copolymer solutions. Moreover, the phase behaviour of these copolymers in salt solution changes dramatically with x. The copolymer with $x = 0.10$ presents, like the homopolymer poly(acrylic acid), an Upper Critical Solution Temperature (UCST) behaviour. On the contrary, the copolymer with $x = 0.29$ presents, similar to the homopolymer poly(*N*-isopropylacrylamide), a Lower Critical Solution Temperature (LCST) behaviour. Finally, the copolymer with the intermediate NIPAM content, $x = 0.17$, presents both an UCST and an LCST behaviour. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-isopropylacrylamide); Poly(acrylic acid); Intrachain hydrogen bonding

1. Introduction

Due to the interest in systems exhibiting temperature sensitive properties, numerous studies have been devoted to poly(*N*-isopropylacrylamide) (PNIPAM) [1,2] and to copolymers based on *N*-isopropylacrylamide (NIPAM) [2–26]. The temperature-sensitive character of PNIPAM consists in its inverse temperature solubility behaviour in aqueous solution, i.e. upon heating, the aqueous solutions of PNIPAM separate into two phases at ~33°C, a polymer-rich phase containing almost all the polymer and a water-rich phase [1]. To study this Lower Critical Solution Temperature (LCST) behaviour, it is more convenient to determine the cloud point temperature, as the solution turns turbid upon heating. The displacement of the cloud point to higher or lower temperatures can be achieved by using adequate copolymers of NIPAM with hydrophilic or hydrophobic comonomers, respectively [4,5,14]. The most effective way to increase the cloud point temperature is to use charged comonomers [14,16,18–21,25]. Thus, many studies have been devoted to the copolymers of NIPAM with acrylic acid (AA) [16,18–21], mostly in their salt form. With regard to random copolymers, even a low fraction of AA units, usually of the order of 5 mol%, suffices to shift the cloud point to around 50°C [16,18–20] and, as soon as the ionic fraction reaches 10 mol%, the cloud point increases up to 70°C or even more [18,19,25].

The behaviour of NIPAM/AA copolymers at low pH, i.e. when the carboxylic groups of AA are not ionised, has not been investigated systematically. Nevertheless, in some cases there is evidence for the existence of intramolecular interactions between NIPAM and AA units: the cloud point under acidic conditions is lower than the cloud point of the homopolymer PNIPAM [21] and substantially lower than the cloud point of the corresponding NIPAM copolymers with nonionic hydrophilic monomers like acrylamide (compare, for instance, the data in Refs. [3,19]). This behaviour is possibly due to the formation of hydrogen bonds between the carboxylic groups of the AA units (proton donors) and the amide groups of the NIPAM units (proton acceptors). Indeed, this type of interaction is very important in mixtures

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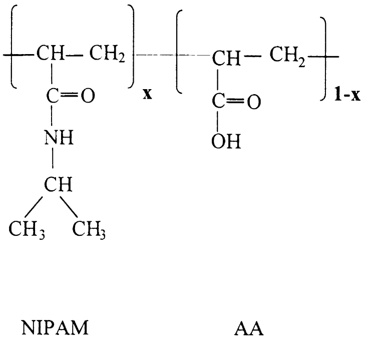

Scheme 1.

of the two homopolymers, PNIPAM and poly(acrylic acid) (PAA), in water under acidic conditions [27]. Interpolymer association via hydrogen bonding [28,29] leads to very compact structures (as revealed by the very low viscosity of these mixtures), often called “interpolymer complexes”. A second consequence of this interpolymer association is the increase of the pH of the mixture as now a large number of carboxylic groups are involved in the intermolecular hydrogen bonding and they are not able to dissociate anymore.

For NIPAM/AA copolymers containing substantial fractions of both units, we have also to take into account the behaviour of the homopolymer PAA. It is well known that PAA, contrary to PNIPAM, exhibits an Upper Critical Solution Temperature (UCST) behaviour in aqueous solutions [30]. In salt solutions, PAA or partially neutralised PAA samples phase separate at low temperature but they turn homogeneous upon heating [31]. The combination of the UCST behaviour of PAA with the LCST behaviour of PNIPAM is expected to lead to an interesting phase behaviour of their copolymers.

We reported in a previous study [32] the synthesis of such NIPAM/AA copolymers, containing large fractions of AA units. Their chemical structure is given in Scheme 1. They have been synthesised by the random modification with *N*-isopropylamine of a precursor PAA, so that all of them have the same backbone. They are especially rich in AA units: the mole fraction of the introduced NIPAM units, x, covers the range from 0 to $\cong 0.3$. From the study [32] of their interaction with poly(ethylene glycol), we have obtained some indirect evidence on the possibility of the formation of intrachain hydrogen bonds between AA and NIPAM units at low pH. In the present study, we investigate in more detail the behaviour of these copolymers in aqueous solution. The viscometric results, together with potentiometric and fluorescence probing data, support the hypothesis of intramolecular hydrogen bonding, accompanied by the appearance of hydrophobic interactions as x increases. Finally, the phase behaviour of these copolymers, resulting from the delicate balance of the opposite contributions of the two monomers, is investigated in salt solution.

Table 1
Characterisation of the polymers used in this study

Sample	x	M_w ($\times 10^{-3}$)
PAA	0	130[a]
cop10	0.10	137[b]
cop17	0.175	143[b]
cop29	0.29	151[b]
PNIPAM	1	170[c]

[a] Determined viscometrically in 0.5 M NaBr aqueous solution in the fully neutralised form [46].

[b] The copolymers have been obtained by modification of the PAA [32]. Therefore they have the same polymerisation degree as the parent PAA ($DP_w \approx 1400$). M_w has been calculated from x and the polymerisation degree of PAA.

[c] Determined by SEC in THF at 40°C. It corresponds to a polymerisation degree $DP_w \approx 1500$.

2. Experimental

2.1. Materials

The origin of PAA, the synthesis of the NIPAM/AA copolymers and their characterisation have been reported previously [32]. Their characteristics are summarised in Table 1. The notation of the copolymers is based on the fraction in NIPAM units, for instance cop10 is the NIPAM/AA copolymer with $x = 0.10$ (see Scheme 1). The synthesis of the PNIPAM sample, having a degree of polymerisation similar to that of the homopolymer PAA, has been performed by radical polymerisation in water, according to a procedure described elsewhere [33]. Its molar mass has been determined by size exclusion chromatography in THF at 40°C.

Water was purified with a Seralpur Pro 90 C system. All reagents used in this study were of Analytical Grade.

2.2. Methods

Viscosity measurements were performed at 30°C with an automated viscosity measuring system AVS 300 (Schott-Geräte) equipped with an Ubbelohde type viscometer. Kinetic energy corrections were taken into account.

Potentiometric measurements were carried out at 30°C with a WTW 525 pH meter equipped with a pH precision electrode assembly (Metrohm).

Fluorescence probing measurements were performed at 30°C with a AMINCO 500-SPF apparatus. Pyrene, at a concentration 6×10^{-7} M was used as a probe. The excitation wavelength was 334 nm and the band pass were set at 5 and 0.5 nm for excitation and emission, respectively. The intensities at 373 nm (I_1) and 384 nm (I_3) were monitored in order to determine the characteristic ratio I_1/I_3.

Turbidimetry: Cloud points were determined by visual inspection of the samples under stirring upon heating or cooling, using a thermostated water bath. The temperature was changed manually with a heating (cooling) rate of

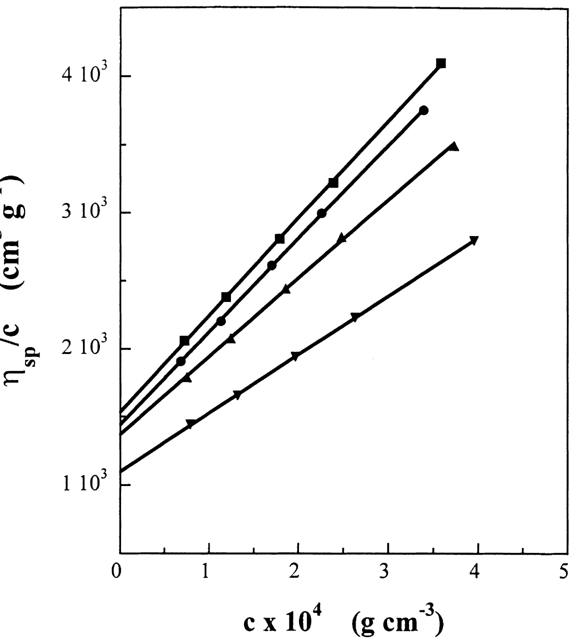

Fig. 1. Isoionic dilution results for PAA and NIPAM/AA copolymers, when all the AA units are neutralised with NaOH. The dilution solvent is a 1×10^{-3} M NaCl solution. $T = 30$°C. (●), PAA; (■), cop10; (▲), cop17; (▼), cop29.

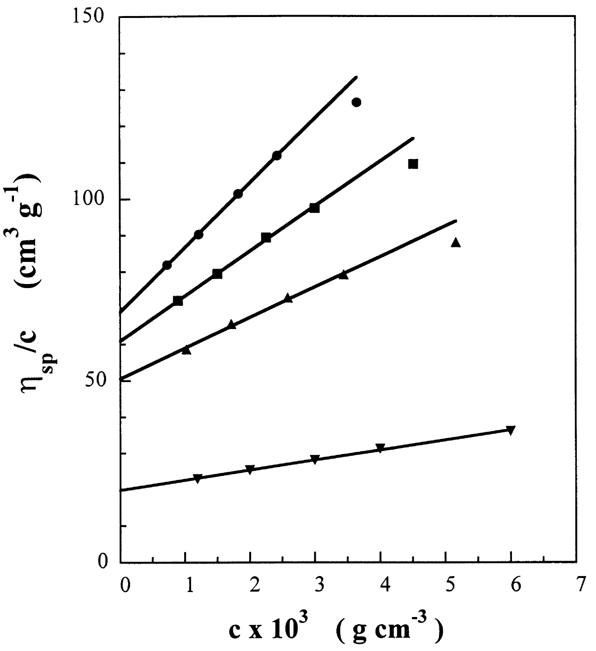

Fig. 2. Isoionic dilution results for PAA and NIPAM/AA copolymers at pH = 3.00. The dilution solvent is a HCl solution with pH = 3.00. $T = 30$°C. (●), PAA; (■), cop10; (▲), cop17; (▼), cop29.

~0.5°C/min. The accuracy of the reported values is better than 0.5°C.

3. Results and discussion

3.1. Solution properties

For the viscometric study of the copolymers in dilute aqueous solution we used the method of isoionic dilution [34–37]. This method allows the determination of the intrinsic viscosity of polyelectrolytes at the lowest possible ionic strength. It consists of the dilution of a polyelectrolyte/water solution with a salt solution of the appropriate concentration, so that the effective ionic strength is kept constant during the dilution process. That way, we avoid the known polyelectrolyte behaviour, i.e. the continuous increasing of the reduced viscosity (η_{sp}/c) of the polyelectrolyte upon diluting. When using the isoionic dilution method, the reduced viscosity increases linearly with the polymer concentration (c) following a Huggins behaviour as in the case of nonionic polymers. It has been shown [38,39] that this effective ionic strength is related with the activity of the counterions, determined by the Manning theory [40], so that we could easily calculate the polymer concentration corresponding to a given effective ionic strength.

Fig. 1 presents the dependence of the reduced viscosity on the polymer concentration for PAA and the NIPAM/AA copolymers, fully neutralised with NaOH, under isoionic conditions at 30°C. In all the cases, the initial concentration of the polymer is appropriately chosen so that the counterion activity equals 1×10^{-3} M. The solvent used for the dilutions is a 1×10^{3} M NaCl aqueous solution. From the intercept of the obtained straight lines at zero concentration, we can determine the intrinsic viscosity, $[\eta]$, of our polymers under these conditions.

When the NIPAM/AA copolymers are not neutralised, the polymer chains are only slightly charged due to the dissociation of the AA units (weak acid). In this case, to get isoionic dilution conditions, we only have to keep the pH of the solution constant when diluting. This is achieved by using as dilution solvent an HCl solution of the same pH as the pH of the initial polymer solution. This way we keep simultaneously the effective ionic strength of the solution and the degree of dissociation of the AA units constant [39]. In Fig. 2 are presented the viscosity results for our polymers at pH = 3.00 (30°C). As the polymer chains are only slightly charged, the intrinsic viscosity values are much lower than those obtained for the fully neutralised samples (Fig. 1), indicating that their hydrodynamic dimensions are now much smaller. Further, the intrinsic viscosity of the copolymers at pH = 3.00 decreases substantially (compared to PAA) as the NIPAM content (x) increases, contrary to the behaviour of the fully neutralised samples where the obtained $[\eta]$ values do not depend strongly on x.

This is better evidenced in Fig. 3, where the intrinsic viscosity of the copolymers at either the fully ionised form or at pH = 3.00 is plotted against the copolymer composition, x. When the copolymers are fully neutralised, the variation of $[\eta]$ with x is very smooth at this composition range and the intrinsic viscosities of the copolymers are

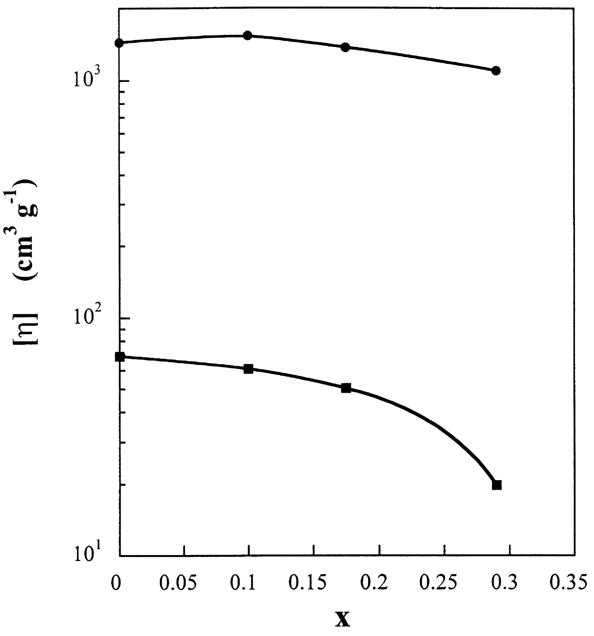

Fig. 3. The variation of $[\eta]$ with the copolymer composition, x. $T = 30$°C. (●), neutralised form the polymers; (■), pH = 3.00.

similar to that of the precursor PAA. On the contrary, when the AA units are not charged (pH = 3.00), $[\eta]$ decreases substantially as x increases, so that for cop29 the intrinsic viscosity is almost one fourth of that of PAA. It is worthy to note that the intrinsic viscosity of the PNIPAM sample at 30°C is 55 cm^3 g^{-1}, i.e. almost three times higher than that of cop29. The above comparisons reveal an especially compact structure for cop29. Such a structure could be the result of strong attractive intramolecular interactions, like the formation of hydrogen bonds between the two types of monomer units, NIPAM and AA. As in the case of the interpolymer complexes between PAA and PNIPAM, the formation of such hydrogen bonds should also lead: (i) to the strengthening of the hydrophobicity of the copolymer, as compared to the hydrophobic/hydrophilic character of the two homopolymers [41]; and (ii) to the decrease of the dissociation of the AA units [27].

The changes in the hydrophobicity of the NIPAM/AA copolymers can be monitored by the changes in the fluorescence emission spectrum of pyrene, used as a microenvironment polarity-sensitive probe. As it is known, the ratio of the intensities of the first over the third vibronic peak, I_1/I_3, of the fluorescence emission spectrum of pyrene, gives information on the existence of hydrophobic domains in the investigated solution. For instance, in pure water I_1/I_3 takes values close to 1.9, but it is only 0.6 in cyclohexane. In a surfactant solution, the I_1/I_3 value shows a sharp transition at the critical micelle concentration (from ~1.9 to ~1.2–1.4), revealing the preferential solubilisation of pyrene in the micelle, a lower polarity microenvironment [42,43].

Table 2
The ratio I_1/I_3 of the fluorescence emission spectrum of pyrene in water solutions of the studied polymers at 30°C. Polymer concentration: 0.01 g cm^{-3}

Polymer	I_1/I_3
No polymer	1.91
PAA	1.79
cop10	1.75
cop17	1.68
cop29	1.50
PNIPAM	1.44

Table 3
The dissociation degree a and the corrected dissociation degree a_{corr} of PAA and NIPAM/AA copolymers at pH = 3.00

Sample	a	a_{corr}
PAA	0.020	0.020
cop10	0.019	0.021
cop17	0.018	0.023
cop29	0.013	0.022

In Table 2, we report the values of I_1/I_3 at 30°C for the solutions of our polymers at a concentration of 0.01 g cm^{-3}. The I_1/I_3 value for the PAA solution, 1.79, shows that there are not hydrophobic domains in this case. Compared to pure water, it indicates a slightly lower polarity, apparently due to the vinylic backbone of the polymer. In the PNIPAM solution, on the other hand, I_1/I_3 takes the value ~1.44 due to the intrinsic hydrophobic character of this polymer [44].[1] The I_1/I_3 values for the NIPAM/AA copolymers are within these two limiting values. Although the hydrophilicity of cop10 is comparable to that of PAA, already the cop17 exhibits an hydrophobic character, as it is revealed by the lower I_1/I_3 value, 1.68. Finally, for the cop29, I_1/I_3 is 1.50, a value very close to that of the PNIPAM solution. Thus, the hydrophobic character of this copolymer is comparable to PNIPAM, although it mainly contains hydrophilic AA units and only ~30 mol% NIPAM units.

In addition to the fluorescence data, pH measurements give complementary information on the behaviour of these NIPAM/AA copolymers in water solution. In Table 3, we present the apparent dissociation degree (a) of the carboxylic units,

$$a = [\mathrm{H}^+]/[\mathrm{AA}] \qquad (1)$$

where $[\mathrm{H}^+]$ is the molar concentration of H^+ and [AA] is the total molar concentration of the AA repeating units. The solutions have been prepared by using appropriate polymer concentrations so that their pH is ~3.0 and, thus, the H^+

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[1] The value 1.44 is substantially lower than that reported by Schild. This discrepancy is probably due to the difference in polymer concentration, as, contrary to our experiments, the results reported by Schild concern very dilute PNIPAM solutions. In the near future, we will discuss in more detail the influence of the PNIPAM concentration on the fluorescence spectrum of pyrene.

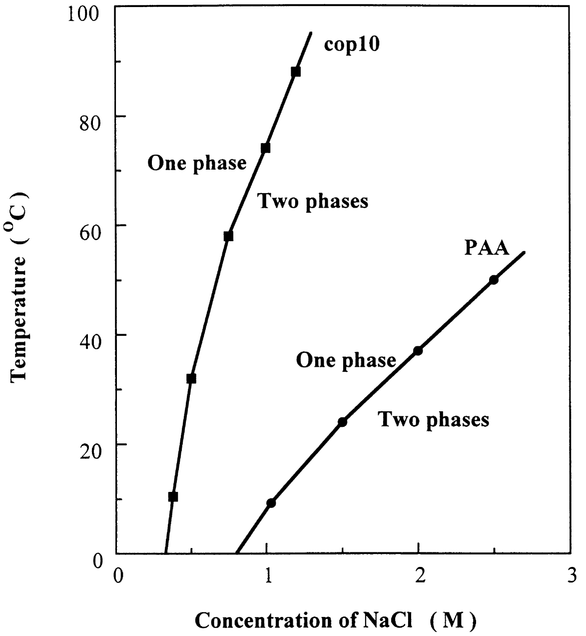

Fig. 4. The influence of the concentration of NaCl on the cloud point of PAA and cop10. The polymer concentrations is 0.01 g cm^{-3}. The polymers are in the acid form. (●), PAA; (■), cop10.

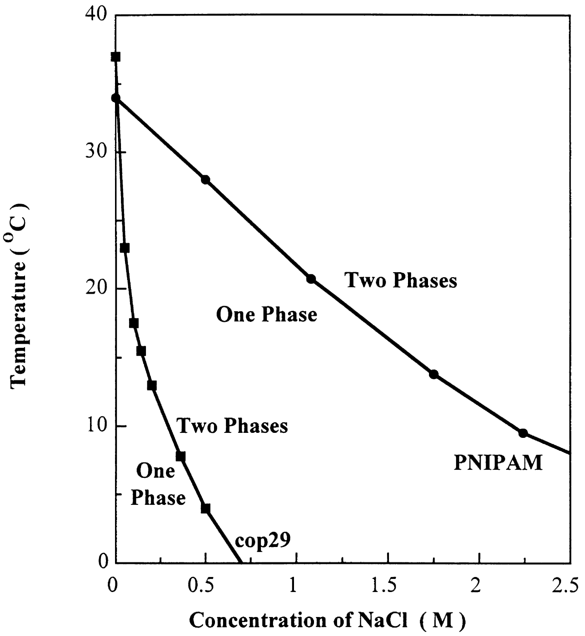

Fig. 5. The influence of the concentration of NaCl on the cloud point of PNIPAM and cop29. The polymer concentration is 0.01 g cm^{-3}. The cop29 is in the acid form. (●), PNIPAM; (■), cop29.

ions come essentially from the dissociation of the AA units. In Table 3, we see that a decreases as the NIPAM content (x) in the copolymers increases, so that for cop29 the dissociation degree of the AA units is about two thirds of the corresponding one of the AA units in the homopolymer, PAA. This behaviour reminds the pH variation observed in the case of PAA/PNIPAM interpolymer complexes where hydrogen bonding is effective [27].

The degree of dissociation a, as obtained from Eq. (1), is an apparent one, since it has been calculated by assuming that all AA units are able to freely dissociate. A corrected dissociation degree, a_{corr} (the actual one), could be extracted from a by taking into account that the AA units involved in hydrogen bonding can hardly dissociate [45] and only the free AA units participate in the dissociation equilibrium. Thus,

$$a_{\mathrm{corr}} = [\mathrm{H}^+]/[\mathrm{AA}]_{\mathrm{free}} \tag{2}$$

A reasonable assumption is to suppose a 1:1 stoichiometry for the AA/NIPAM association. Therefore,

$$[\mathrm{AA}]_{\mathrm{free}} = [\mathrm{AA}] - [\mathrm{NIPAM}] \tag{3}$$

where [NIPAM] is the total molar concentration of the NIPAM repeating units. The a_{corr} values are also given in Table 3. Interestingly, we observe that a_{corr} is roughly constant (contrary to a), bringing an additional evidence for the validity of our assumption on the existence of intra-chain hydrogen bonding between the two complementary units.

3.2. Phase behaviour

The influence of the addition of NaCl on the cloud point temperature of the homopolymer PAA and the copolymer cop10 is presented in Fig. 4. Both polymers show an UCST behaviour, i.e. they are well soluble at high temperatures but they phase separate upon cooling. This well-known behaviour of PAA is affected by several factors, like for instance, the concentration, molar mass and ionisation degree of the polyacid [30,31]. Taking into account these effects, the behaviour of our PAA sample is well comparable to the literature data.

The copolymer cop10, containing a large fraction of AA units, still shows the same general UCST behaviour but it is much more sensitive to the salt concentration as compared to PAA. In fact, it suffices a salt concentration of only slightly higher than 1.2 M to extend the two-phase region over the whole temperature range, up to ~100°C. This is probably due to the introduction of NIPAM units in the polymer chain, which (i) are hydrophobic and (ii) form hydrogen bonds with the AA units, resulting in the worse hydration of the polymer chain, as compared to PAA.

Contrary to cop10, the phase behaviour of cop29 is more similar to that of PNIPAM, i.e. an LCST phase behaviour is observed for both polymers as a function of salt (Fig. 5). In pure water, PNIPAM phase separates when the temperature increases above ≅ 33°C, but it is soluble at lower temperatures. The addition of salt leads to the lowering of its cloud point, so that at ~2.5 M NaCl the cloud point of PNIPAM is depressed below 10°C. Similarly, the copolymer cop29 presents in pure water a cloud point at 38°C,

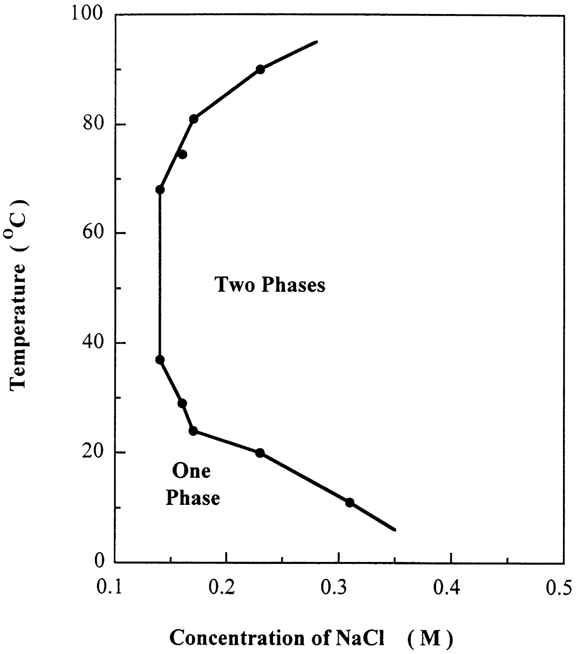

Fig. 6. The influence of the concentration of NaCl on the cloud point of cop17. The polymer is in the acid form acid its concentration is 0.01 g cm^{-3}.

slightly higher than that of PNIPAM. However, the cloud point of cop29 drastically decreases with the NaCl concentration: 0.7 M NaCl suffices to extend the two-phase region down to ~0°C, revealing that the hydrophobic character of cop29 is stronger than that of the homopolymer. This is further supported by the fluorescence data combined with the very compact structure of the chains of cop29 at 30°C (viscometry). Considering the composition of this copolymer, which is still rich in AA units, this enhanced hydrophobicity should be attributed to the formation of intrachain hydrogen bonds: most of the AA units are involved in such hydrogen bonding and only ~42% of them are expected to be free. In pure water, cop29 remains soluble at temperatures higher than the cloud point of PNIPAM, due to the dissociation of the AA groups, which favours the solubility of the copolymer. Nevertheless, these few charges can be easily screened by a relatively small salt concentration. Thus, by adding salt, the strong hydrophobic character of cop29 is revealed. It is of interest here to compare cop29 to NIPAM/AM copolymers (AM = acrylamide). Such a NIPAM/AM copolymer, with $x = 0.29$, is expected to be soluble in water in the whole temperature range (0–100°C) [3–5]. This is another indication that the behaviour of NIPAM/AA copolymers is greatly influenced by the intrachain hydrogen bonding.

More interesting is the phase behaviour of cop17 as a function of the salt concentration, presented in Fig. 6. This copolymer has an intermediate NIPAM content between cop10 and cop29. Although in the absence of salt it is soluble in the whole temperature range, a relatively low salt concentration (lower than 0.15 M) is sufficient to induce phase separation. However, cop17 presents both LCST and UCST behaviours, i.e. the system phase separates at intermediate temperatures and the one phase domain is observed at low and high temperatures. Increasing the NaCl concentration leads to the extension of the two-phase region, so that at a NaCl concentration ~0.4 M, this region covers the whole temperature range. More detailed studies are needed in order to understand the details of this behaviour. Nevertheless from the present study it is obvious that the solution behaviour of these copolymers is the result of a delicate balance between several contributions: intrachain hydrogen bonding, hydrophobic character, polymer hydration and electrostatic effects.

4. Conclusions

By using NIPAM/AA copolymers (rich in AA units) at low pH (~3.00), it is possible to investigate how the opposing behaviours of the two components, i.e. the UCST behaviour of PAA and the LCST behaviour of PNIPAM, can combine within the same chain. At this low pH, the behaviour of the copolymers is not simply the sum of the behaviours of the two components because the AA units can form hydrogen bonds with NIPAM units. This intrachain hydrogen bonding influences, in some cases dramatically, their solution and phase behaviour.

At pH = 3.00, the structure of the copolymers in aqueous solution gets more and more compact as the NIPAM content (x) increases. At the same time, the degree of dissociation of the AA units decreases. Both properties are usually observed for mixtures of complementary homopolymers associated via hydrogen bonding. Further, the fluorescence data reveal an enhanced overall hydrophobicity of the copolymers. For instance, the ratio I_1/I_3 for the copolymer with $x = 0.29$ is very close to that of PNIPAM, revealing a similar hydrophobic character. Only the contribution of the NIPAM units does not suffice to explain this increased hydrophobicity, as the copolymer is still rich in hydrophilic AA units. Thus, we have to assume that the hydrogen bonded structures are in the origin of this enhancement of the hydrophobic character of the copolymers, probably in combination with the release of water molecules (i.e. the water molecules forming hydrogen bonds with the polar parts of AA and NIPAM in the case of the solutions of the corresponding homopolymers).

All these special properties observed in solution are also evidenced in the phase behaviour of these copolymers. Thus, the more compact structure of the copolymers and their enhanced hydrophobicity, combined also with their lower charge content, lead to an easier phase separation upon addition of NaCl. Further, the kind of the phase behaviour (UCST or LCST behaviour), depends strongly on x. The copolymer with $x = 0.10$ (i.e. very rich in AA units) follows the UCST behaviour of the homopolymer PAA. On the contrary, the copolymer with $x = 0.29$

(i.e. having a substantial amount of NIPAM units) follows the LCST behaviour of the homopolymer PNIPAM. The fact that this copolymer, even in the absence of salt, shows a cloud point close to that of PNIPAM supports further the concept that the hydrophobicity of these copolymers is strongly enhanced by intrachain hydrogen bonding. Finally, the copolymer with an intermediate NIPAM content ($x = 0.175$ shows an original phase behaviour combining both UCST and LCST.

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