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SHORT COMMUNICATION

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Investigation of the association in water of sodium dodecyl sulfate with a positively charged copolymer based on *N*-isopropylacrylamide

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Abstract The interactions of sodium dodecyl sulfate with a positively charged copolymer based on *N*-isopropylacrylamide (NIPAM) have been investigated in aqueous solution by turbidimetric and viscometric measurements. The copolymer contains mainly NIPAM and only 5 mol % of the charged comonomer [3-(methacryloylamino)propyl]-dimethyloctylammonium bromide. The polymer–surfactant complex is insoluble for mixture compositions near to the charge stoichiometry, while it exhibits lower critical solution temperature behavior for mixtures with an excess of polymer or surfactant. In the case of surfactant excess, the transition from an expanded coil to a globular state upon heating has been observed by viscometry.

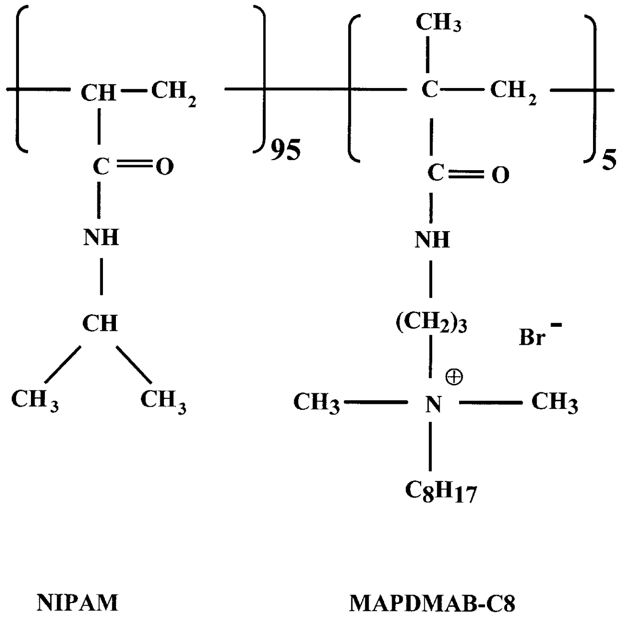
Key words Poly(*N*-isopropylacrylamide) · Sodium dodecyl sulfate · Lower critical solution temperature · Coil-to-globule transition

Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a widely studied [1], rather hydrophobic water-soluble polymer, exhibiting lower critical solution temperature (LCST) behavior in water as it phase-separates from aqueous solution upon heating above about 33 °C [2]. A consequence of the significant hydrophobic character of this polymer is its ability to associate with surfactants [1]. Numerous studies have been devoted to the investigation of the interactions of PNIPAM mainly with the anionic surfactant sodium dodecyl sulfate (SDS). Owing to the charge introduced in the polymer chain, as a result of the association with SDS, a continuous elevation in the phase-separation temperature (cloud point) [3, 4] and a corresponding increase in the reduced viscosity of the polymer [5] are observed with the addition of SDS to the polymer solution. A wide variety of techniques, either simple ones, like turbidimetry [4], conductimetry [6], differential scanning calorimetry [4] and static fluorescence probing [4, 7], or more sophisticated ones, like (dynamic) light scattering [8, 9, 10], low-angle neutron scattering [11] and time-resolved fluorescence quenching [5], have been employed in order to study and to understand the details of the association mechanism. Moreover, the addition of small amounts of SDS facilitates the investigation of the conformational transition of the PNIPAM chains to a globular state [8, 9, 12], which takes place in the LCST region.

The study of the interactions of charged copolymers based on NIPAM with oppositely charged surfactants is very limited [13, 14] owing to the complications arising from the strong electrostatic attractions between the polymer and the surfactant. In fact, the association of highly charged polymers with oppositely charged surfactants leads to a large precipitation zone around charge stoichiometry [15]. The polymer–surfactant complex is soluble at low surfactant concentration owing to the excess charge of the polymer chain, and, depending on the nature of the polymer, it may redissolve at high surfactant concentration.

This article deals with the association of SDS with a positively charged NIPAM-based copolymer. This copolymer, denoted PNIPAM5 (Scheme 1), contains 95 mol % NIPAM units and 5 mol % charged units of the comonomer [3-(methacryloylamino)propyl]-di-



Scheme 1

methyloctylammonium bromide (MAPDMAB-C8) randomly distributed in the copolymer chain. The octyl groups of the comonomer moderate the increased hydrophilicity imported to the polymer chain by the charge. The study is focused mainly on the influence of the temperature on the properties of the PNIPAM5–SDS mixtures, as revealed by turbidity and viscometry measurements.

Experimental

Materials

PNIPAM5 was prepared by postmodification in chloroform at 59 °C with octyl bromide of the precursor containing 95 mol % NIPAM units and 5 mol % *N*,*N*-[(dimethylamino)propyl]methacrylamide (MADAP) units. This precursor was synthesized by free-radical copolymerization of NIPAM and MADAP at 27 °C in water by using the $[NH_4]_2S_2O_8/Na_2S_2O_5$ redox couple for the initiation. Its molar mass has been estimated from intrinsic viscosity measurements to be around 1×10^6. Details on the synthesis and the characterization of PNIPAM5 are given elsewhere [18].

SDS was a product of Serva and was used as received. The water used was reagent grade water from a Seralpur Pro90 apparatus.

Sample preparation

Polymer–surfactant mixtures were prepared by mixing appropriate volumes of the corresponding concentrated solutions and diluting them to the desired concentration. The mixtures were left to equilibrate overnight under stirring.

Turbidity measurements

Turbidity measurements were carried out using a UV–vis spectrophotometer (U-2001, Hitachi), equipped with a thermostated cell. The optical density of the sample under stirring at 500 nm was recorded. The solution was left to equilibrate under stirring for at least 15 min at each temperature.

Viscosity measurements

Viscosity measurements were carried out using a Schott-Geräte AVS 300 automated viscosity measuring system equipped with a micro-Ostwald capillary viscometer. The temperature was controlled to ±0.02 °C. The solution was left to equilibrate for at least 15 min at each temperature.

Results and discussion

Phase separation

The variation with temperature of the absorbance of various aqueous mixtures of PNIPAM5 with SDS is presented in Fig. 1. The polymer concentration for all the measurements was fixed at 0.010 g cm^{-3}. The composition of the mixtures is expressed by the ratio r of the SDS molar concentration over the concentration of the charged units of the polymer.

At this polymer concentration, the solution of the pure polymer ($r = 0$) is transparent at low temperature but it gradually turns turbid upon heating. Its cloud point, i.e. the temperature where the onset of the turbidity is observed, is around 36 °C, slightly higher than the cloud point of the PNIPAM homopolymer, that is generally observed at around 33 °C [1]. It is noteworthy that a much more important increase in the cloud point is observed for copolymers of NIPAM with hydrophilic charged groups such as sodium acrylate [16, 17] or 2-acrylamido-2-methyl propane sulfonic acid (AMPSA) [14]: the introduction of 5 mol % of these charged units in the PNIPAM chain leads to the elevation of the cloud point above 50 °C. It seems that the hydrophobic character of the octyl groups attached to the chain of PNIPAM5 significantly moderates the influence of the corresponding introduction of charge. A detailed presentation of the influence of the alkyl groups on the phase behavior of these types of NIPAM copolymers is given elsewhere [18].

Upon addition of SDS (Fig. 1a), the increase in the turbidity with temperature becomes more and more important as r approaches unity, while the cloud point shifts towards lower temperatures. The inverse behavior is observed for r higher than unity (Fig. 1b): as r increases, the turbidity decreases considerably, while the cloud point shifts towards higher temperatures, so that for $r > 3$ the solution is transparent in the whole temperature range studied. Now, the level of turbidity is much lower (note the great difference in the scales of Fig. 1a and b) and the turbidity reaches a plateau at about 10 °C higher than the observed cloud point for each system. In contrast, for $r < 1$ (Fig. 1a), the

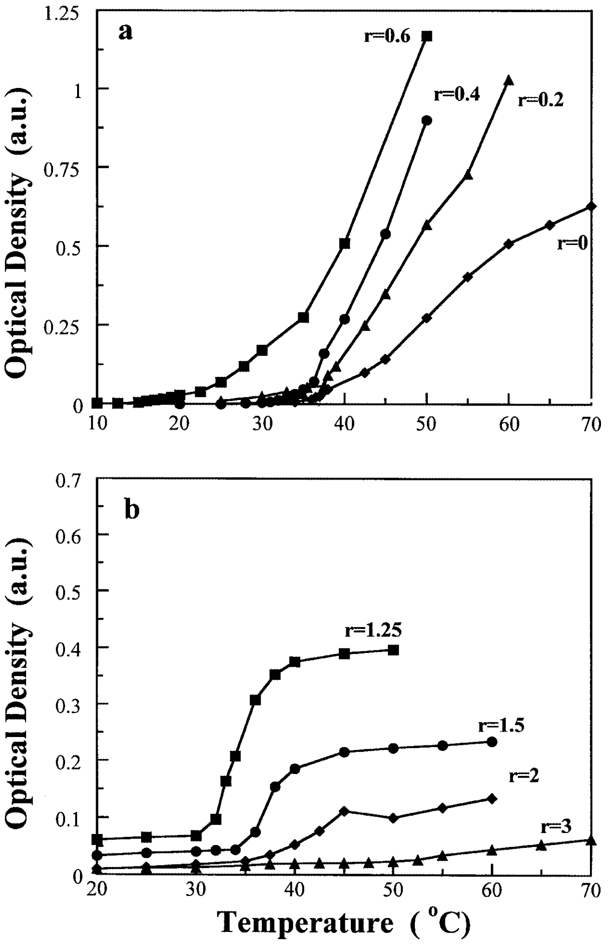


Fig. 1 Turbidity measurements as a function of temperature for aqueous 95 mol % *N*-isopropylacrylamide and 5 mol % [3-(methacryloylamino)propyl]-dimethyloctylammonium bromide copolymer (PNIPAM5)–sodium dodecyl sulfate (SDS) mixtures with various mixtures compositions, *r*. The polymer concentration is 0.010 g cm^{-3}

turbidity does not seem to level off even for temperatures much higher than the observed cloud points.

For all the mixtures, the solutions appear homogeneously turbid with no formation of any precipitates. Moreover, some of the solutions were left for several hours at temperatures higher than their cloud points and no formation of any large particles was observed. This behavior, i.e. the appearance of a stable colloidal suspension rather than the observation of two well-separated phases, also reported for slightly charged PNIPAM copolymers [19], is related to the existence of charges, introduced either by the surfactant molecules or by the comonomer's charge, in the PNIPAM particles. Indeed, for the mixtures near to the charge stoichiometry (*r* very close to unity), the formation of such large particles, in addition to the very high turbidity of the solutions even at very low temperatures, did not allow turbidity measurements to be performed.

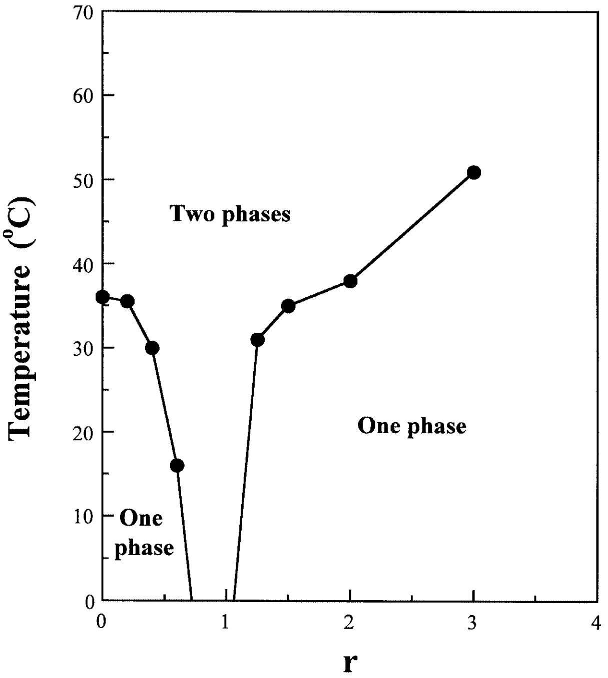


Fig. 2 Variation with *r* of the cloud point of aqueous PNIPAM5–SDS mixtures. The polymer concentration is 0.010 g cm^{-3}

The variation of the cloud point (defined as the onset of the turbidity curves) of the PNIPAM5- SDS mixtures with the ratio *r* is presented in Fig. 2. The observed behavior combines both the LCST properties of PNIPAM and the well-known phase behavior of the mixtures of a charged polymer with an oppositely charged surfactant in aqueous solution: starting from the value of 36 °C for the pure polymer, the cloud point of the mixtures initially decreases upon addition of SDS, so that for *r* around unity it is shifted well below 0 °C. After a two-phase zone, the polymer–surfactant complex redissolves and the cloud point increases continuously upon addition of SDS. A similar trend has also been reported for aqueous mixtures of the positively charged surfactant dodecylpyridinium chloride with the negatively charged NIPAM–AMPSA copolymers [14]. The results presented in Figs. 1 and 2 are in line with the variation of the net charge of the polymer–surfactant complex with the SDS concentration. For $r < 1$, the net charge of the complex, due to the excess of the polymer charge content, decreases upon addition of SDS, the complex becomes more and more hydrophobic and the cloud point decreases, while the turbidity of the solution increases. For $r > 1$, the net charge of the complex arising from the surfactant aggregates bound to the polymer chain increases upon addition of SDS. This enables the redissolution of the complex and an elevation of the cloud point, accompanied by a decrease in the turbidity, is observed with increasing *r*. This second part (for $r > 1$) of the curve in Fig. 2 is, in fact, comparable to the well-studied behavior of mixtures of SDS with the PNIPAM homopolymer [4].

Viscosity

Viscosity measurements were performed at a relatively low polymer concentration, 2.5×10^{-3} g cm^{-3}, in order to avoid turbidity problems. At this concentration, the pure PNIPAM5 and most of the PNIPAM5–SDS mixtures (with the exception of those with r very close to unity) are transparent over the whole temperature range studied.

The variation with temperature of the reduced viscosity (on a logarithmic scale) of PNIPAM5–SDS mixtures for various mixture compositions, r, are presented in Fig. 3. The reduced viscosity of the pure polymer remains high over the whole temperature range. Upon addition of surfactant, the reduced viscosity at low temperature decreases with r for $r < 1$ (Fig. 3a), while for $r > 1$ it increases (Fig. 3b), in accordance with the variation of the net charge of the polymer–surfactant complex with r. However, the most important observation in Fig. 3 is the variation of the reduced viscosity of the mixtures upon heating: initially the reduced viscosity is constant with temperature, but it breaks down sharply when the temperature reaches a value characteristic for each mixture, indicating a collapse of the chain conformation above a critical temperature. For $r < 1$, the full collapse of the polymer chains is not attained (except for $r = 0.6$, where phase separation is observed) even at high temperatures. In contrast, for $r > 1$ a plateau is observed for all the mixtures at a temperature of about 10 °C higher than the temperature where the breakdown of the viscosity is observed. This transition from an expanded state to a globular state, observed also for the PNIPAM homopolymer mixed with small amounts of SDS [12], is displaced to higher temperatures as r increases. Moreover, the lower plateau value tends to decrease slightly with r. For $r > 1$, as r increases, the net charge of the polymer chain should also increase owing to the adsorption of SDS. As a result, the collapse of the chain occurs at higher temperature. Nevertheless, the density of the particles formed seems to increase with r. This is probably related to the worsening of the hydration of the chain as the temperature increases. Indeed, the reduced viscosity value of 6 ± 1 cm^3 g^{-1} measured around 40 °C for $r = 1.5$ and $r = 2$ corresponds to a density of 0.42 ± 0.07 g cm^{-3} according to the Stokes–Einstein relation for compact spheres. This value is in reasonable agreement with the reported values measured for PNIPAM chains by viscometry [12] and dynamic light scattering [9] measurements at this temperature or calculated through a space-filling model [8]. Moreover, for $r = 5$, the lower viscosity plateau is observed at about 70 °C and the density of the particles is calculated to be about 1.1 g cm^{-3}, indicating the formation of very compact particles.

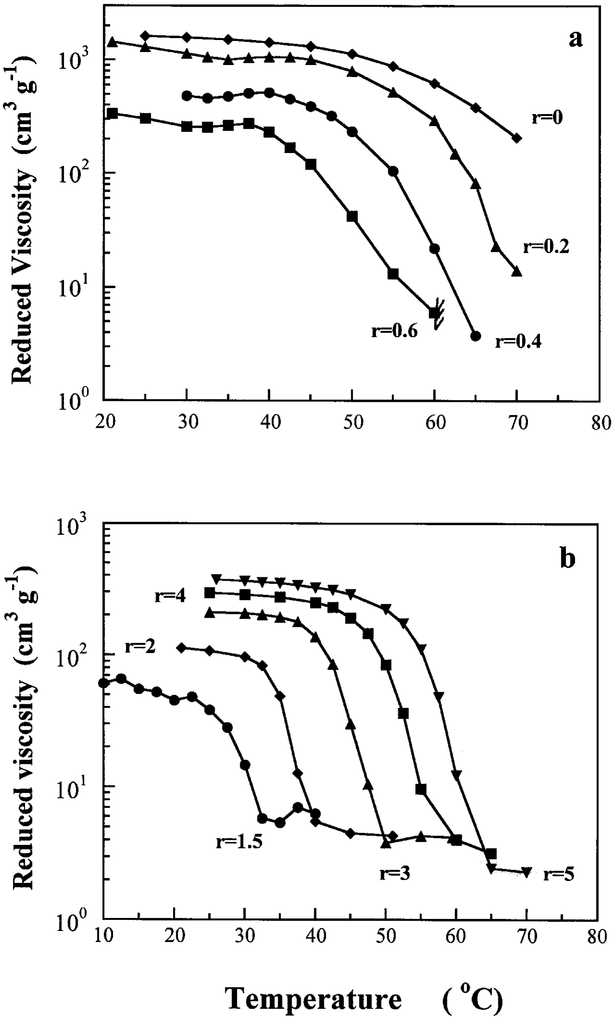


Fig. 3 The reduced viscosity of aqueous PNIPAM5–SDS mixtures as a function of temperature for various mixtures compositions, r. The polymer concentration is 0.00250 g cm^{-3}

Conclusion

The association of SDS with the positively charged copolymer based on NIPAM, PNIPAM5, leads to the formation of polymer–surfactant complexes combining both the thermosensitive properties of the NIPAM backbone and the phase behavior of the complexes formed between polyelectrolytes and oppositely charged surfactants. It is found that for mixtures with compositions near to the charge stoichiometry (i.e. when the ratio r of the SDS concentration over the concentration of the charged units of the polymer is close to unity) insoluble precipitates are formed, while, in excess polymer or surfactant, LCST behavior is observed. The cloud point of the mixtures increases as we go far from the charge stoichiometry, either to lower or to higher surfactant concentrations.

For mixtures with $r > 1$, a coil-to-globule transition with temperature is observed by viscometry. This transition is displaced to higher temperatures as r increases. For mixtures with $r < 1$, the globular state could not be reached by viscometry, although a sharp breakdown of the intrinsic viscosity is also observed upon heating. This behavior should be related to the turbidimetry measurements, where for $r < 1$ the turbidity increases continuously above the cloud point with increasing temperature, while for $r > 1$ the turbidity very soon reaches a plateau upon heating, indicating the formation of stable colloidal particles.

The study presented here is based on the macroscopic features of the association between PNIPAM5 and SDS. Of course, to better understand the different conformation and aggregation states of the system on a molecular level additional methods related to structural features are needed.

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