Colloid Polym Sci 275:760–768 (1997)
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ORIGINAL CONTRIBUTION

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Association and phase behavior of hydrophobically modified photoresponsive poly(acrylamide)s in the presence of ionic surfactant

Received: 23 September 1996
Accepted: 11 March 1997

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Abstract The extent of association between the cationic surfactant TTAB and a series of hydrophobically modified polyacrylamides (HPAMs) containing an N-*n*-alkyl and substituted azobenzene hydrophobic sidegroup has been studied utilizing a cationic surfactant-selective membrane electrode. Binding of TTAB to the polymer hydrophobes is found to increase with increasing hydrophobicity of the hydrophobe. In the presence of electrolyte, aqueous solutions of HPAMs and ionic surfactant exhibit an associative phase separation. The temperature or clearing point (CP) at which the system goes from a one phase to two-phase system are reported. The area of the two-phase region is found to increase with increasing electrolyte concentration, hydrophobicity of the hydrophobe for the high molecular weight HPAMs, and decreasing hydrophobicity for low molecular weight HPAMs. Exposure of HPAMs containing an azobenzene hydrophobe to UV light results in a decrease in interaction between the hydrophobe and surfactant and a corresponding decrease in the CP due to conversion of azobenzene from the more hydrophobic *trans* form to the less hydrophobic *cis* isomer.

Key words Hydrophobically modified polymers – azobenzene – photoresponsive polymer – polymer/surfactant complexes – associative phase separation

Introduction

The unusual physio-chemical properties of both dilute and concentrated aqueous mixtures of polymers and surfactants have received considerable attention. Current and future applications in such diverse areas as e.g. coatings, enhanced oil recovery, and pharmaceutical formulations are the basis for the continued interest in these systems. In the case of neutral, water soluble polymers, interactions with ionic surfactants are relatively weak, but can be strongly enhanced by the incorporation of hydrophobic sidegroups on the polymer [1]. In aqueous solutions of such hydrophobically modified polymers (HMPs) aggregation of the hydrophobic sidegroups results in an enhanced viscosity of the solution, and this viscosity increase is strongly affected by the presence of surfactants. These rheological effects have led to an increasing use of HMPs as viscosity enhancers, with applications for instance in tertiary oil recovery and coating formulations [2]. Although the rheological properties of a number of HMP–surfactant systems have been reported, it is difficult to obtain quantitative information on the HMP–surfactant interactions. In this paper, we use a surfactant-selective electrode method to obtain binding isotherms for an ionic surfactant with a number of HMPs of systematically varied hydrophobicity.

In certain polymer systems, association between the polymer and surfactant can result in gel formation and in some instances phase separation. Polymer–surfactant systems exhibit two general types of liquid–liquid phase separation, i.e. associative phase separation or coacervation, and segregative phase separation [3]. Phase separation is termed associative when a one phase (1ϕ) polymer–surfactant system separates to form a two phase (2ϕ) system with one phase concentrated primarily with the polymer–surfactant complex. Phase separation in polymer–surfactant systems is dependent on a number of variables. When an increase in temperature causes a change from a 2-phase to a 1-phase system, the transition temperature is referred to as the clearing point (CP) for systems exhibiting a UCST. At the clearing point a marked change in the turbidity of the solution is observed on cooling [4]. The clearing point of a polymer system is extremely sensitive to the interactions between the polymer and the solvent and a change in the clearing point implies that the interactions in the system have been altered due to a change in the property of the polymer and/or solvent. Thus, CP measurements provide an excellent experimental tool for the study of polymer systems and the role of additives such as inorganic salts and/or a surfactants, and the effects of such additives on the solution behavior of the polymer. For example, polymers that acquire a charge due to hydrolysis or the adsorption of ionic surfactant (polyelectrolyte effect) experience a suppression in phase-separation due to increased solubility [5, 6].

There is considerable interest in the incorporation of functional groups onto a polymer which will lead to a polymer network responsive to external stimuli such as temperature or light. In the case of light-sensitive networks or gels, applications such as photo-rheology, and photoswitching may be envisaged. Polyacrylamides are particularly useful because of their high solubility in water, and the relative ease of incorporation of other monomers on the polymer. The polymers prepared in this study use azobenzene functional groups of various hydrophobicity as the photoswitchable functional group. Upon irradiation the azo functional group undergoes a change in geometry and dipole moment. Azobenzene is well suited to act as a trigger to polymer solution behavior due to the fact that exposure to UV light converts it from the more hydrophobic *trans* isomer to the less hydrophobic *cis* isomer. A number of unusual effects with similar polymers due to light switching have already been reported [7–9]. In this work we show conclusively that switching of the azo group causes significant differences in the surfactant-binding capability of the hydrophobe, leading for instance to large changes in the phase behavior of the polymer–surfactant system.

Co-polymers of acrylamide and 0.5 mol% to 2 mol% N-*n*-decylacrylamide (C10), dodecyl- (C12), tetradecyl- (C14), 4-(phenylazo)phenyl propenoate (PAM Azo(R = H)), 4-[4/-(methylphenyl)azo]phenyl propenoate (PAM Azo(R = Methyl)), 4-[4/-ethylphenyl)azo]phenyl propenoate (PAM Azo(R = Ethyl)), and 4-[4/-(butylphenyl)azo]-phenyl propenoate (PAM Azo(R = Butyl)) (Fig. 1) have been prepared. The polymers are used to study the binding of ionic surfactants and phase behavior in the presence of surfactant as a function of the hydrophobicity of the sidegroup and *trans*/*cis* isomerization of the azobenzene chromophore.

Experimental

Materials

Acrylamide (Aldrich Chemical Company) was recrystallized in chloroform prior to use. N-*n*-decylamine (Aldrich Chemical Company), N-*n*-dodecylamine, N-*n*-tetradecylamine, acryloyl chloride (Aldrich Chemical Company), and phenol (Fisher Scientific Company) were distilled prior to use. The initiator azobis(isobutyronitrile) (AIBN) (Aldrich Chemical Company) was recrystallized from ethanol. Aniline, 4-ethylaniline, and 4-butylaniline (Aldrich Chemical Company) were distilled prior to use. 4-methylaniline (Eastman Kodak) was purified through the use of an acid/base extraction followed by recrystallization two times from an ethanol/water mixture. Sodium dodecyl sulfate, dodecyltrimethylammonium bromide, and tetradecyltrimethylammonium bromide (Aldrich Chemical Company) were used without preliminary purification. Water was purified by a Milli-Q system (Millipore).

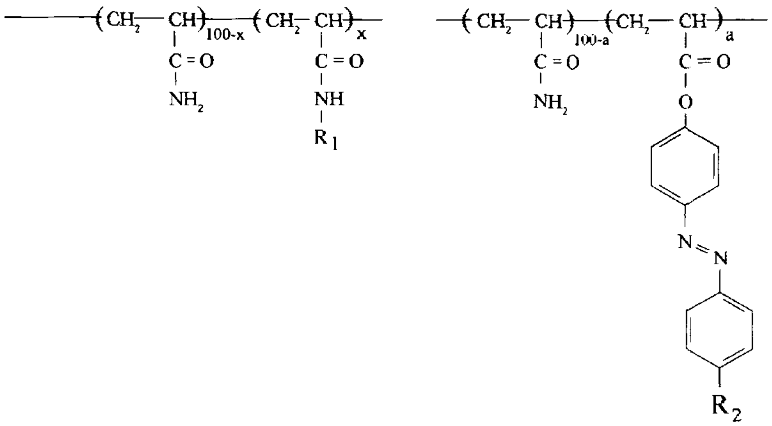
Methods

Synthesis of N-*n*-alkylacrylamide, 4-[4/-(alkylphenyl)azo]-phenyl propenoate, and 4-[4/-(alkylphenyl)azo]phenyl propanoate were prepared from N-*n*-alkylamine and 4-[4/-(alkylphenyl)azo]phenol respectively and is discussed in greater detail elsewhere [9, 10]. Synthesis of 4-[4/-(alkylphenyl)azo]phenol was performed by conversion of the corresponding 4-alkylaniline to a diazonium salt and coupling to phenol and is discussed in greater detail elsewhere [11].

Polymers were prepared by free radical polymerization of acrylamide and N-*n*-alkylacrylamide or 4-[4/-(alkylphenyl)azo]phenyl propenoate using azobis(isobutyronitrile) (AIBN) (0.5 mol%) as the initiator and is discussed in greater detail elsewhere [9, 10]. The polymer structure and nomenclature are illustrated in Fig. 1.

Polymer molecular weights were calculated from intrinsic viscosity values determined by dilute aqueous solution viscometry with an Ostwald viscometer. The Mark–Houwink–Sakurada constants were assumed to be

Fig. 1 HPAM nomenclature used in the text



PAM R_1-x

PAM Azo($R=R_2$)-a

R_1: Alkyl chain: C10-decyl, C12-dodecyl, C14-tetradecyl.

R_2: H, Methyl, Ethyl, Butyl.

Alkyl HPAM Copolymers and terpolymers:

PAM R_1-x

Azobenzene Copolymers:

PAM Azo($R=R_2$)-a

x and a are the % mole of the corresponding monomer.

Table 1 Molecular weight of HPAMs

HPAM	$[\eta]$ $[cm^3/g]$	Molecular weight $[g/mol] \times 10^5$
PAM	77	1.6
PAM C10-1%	76	1.5
PAM C10-2%	77	1.6
PAM C12-1%	71	1.4
PAM C12-2%	68	1.3
PAM C14-1%	78	1.6
PAM Co-Acrylate Azobenzene(R = H)-1%	23	0.23*
PAM Co-Acrylate Azobenzene(R = H)-2%	16	0.13*
PAM Co-Acrylate Azobenzene(R = Ethyl)-2%	18	0.15*
PAM Co-Acrylate Azobenzene(R = Butyl)-2%	18	0.15*
PAM Co-Acrylate Azobenzene(R = H)-0.5%	77	1.6
PAM Co-Acrylate 4-Methylazobenzene(R = Me)-0.5%	65	1.2
PAM Co-Acrylate 4-Ethylazobenzene(R = Eth)-0.5%	51	0.81
PAM Co-Acrylate 4-Butylazobenzene(R = Butyl)-0.5%	59	1.0

1. $[\eta]$ ±2 cm^3/g.
2. MW ±5%.
3. * MW ±10%.

the same as the values determined for polyacrylamide by Hunkeler et al. [12]. The molecular weights calculated in this way therefore should be seen as approximate values only (Table 1). Attempts to determine molecular weight distributions of these associating polymers by GPC are in progress in our laboratory.

Binding studies were performed using a surfactant-selective electrode. All surfactant and polymer solutions

Table 2 Azobenzene incorporation

Percent incorporation of PAM Co-acrylate-4-alkylazobenzene		
R =	PAM Azo-0.5%	PAM Azo-2%
R = H	0.57 ±0.02	2.2 ±0.2
R = methyl	0.54 ±0.03	–
R = ethyl	0.32 ±0.02	1.9 ±0.1
R = butyl	0.43 ±0.01	1.6 ±0.1

were made up in a 0.01 M NaBr electrolyte. This method is discussed in greater detail elsewhere [13]. All ^{1}H-NMR measurements were performed on a Bruker AC 250 spectrometer operating at 250.133 MHz, using solvent suppression during acquisition. Polymer samples were prepared in 99.8% D_2O (Aldrich). UV spectra of the azobenzene polymers were performed on a Hewlett Packard Diode Array Spectrometer. Polymer samples were prepared in DMSO and their corresponding absorbance maximum compared to that of the standard compound 4-[4/-(alkylphenyl)azo]phenyl propanoate. The percent incorporation of the various azobenzene polymers are summarized in Table 2. Clearing-point studies of systems consisting of polymer, surfactant, and salt were performed by visual observation in glass sample vials. Samples were placed in a water bath and cooled at a rate of 2 °C/min. The phase separation temperature can be observed in runs with ascending or descending temperature, the latter giving more reproducible values. The clearing point was taken as the temperature at which cloudiness was observed. In duplicate runs this temperature is reproducible to ±1 °C.

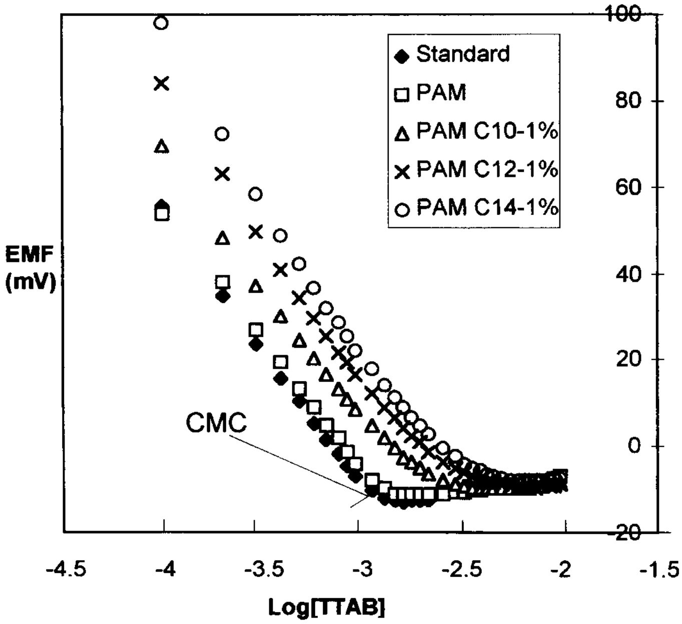
Results and discussion

A series of co-polymers of acrylamide have been prepared with 0.5 mol% to 2 mol% of N-*n*-alkylacrylamide (alkyl = C10, C12, or C14) or with 0.5 mol% and 2 mol% of 4-[4/-(alkylphenyl)azo]phenyl propenoate (alkyl = H, Methyl, Ethyl, Butyl) as the hydrophobe. In Fig. 1 the structure of the polymers and nomenclature are illustrated. For the N-*n*-alkyl co-polymers the polymer composition is assumed to be equivalent to the monomer feed ratio. For the azobenzene co-polymers incorporation can be determined experimentally by UV spectroscopy, using 4-[4/-(alkylphenyl)azo]phenyl propanoate as a standard. Co-polymer compositions are summarized in Table 2. Polymer molecular weights were determined to be approximately 160 000 g/mol except for the 2 mol% of the azobenzene hydrophobe polymer, which had an average molecular weight of only 15 000 g/mol. The low molecular weight of the azobenzene polymers at 2 mol% substitution is attributed to a radical deactivation by the azobenzene sidegroup. The molecular weight range for the other polymers reported here compares well to the molecular weights reported by Haitjema for similar polymers and preparation methods [11].

A typical calibration curve of EMF vs. TTAB concentration is illustrated in Fig. 2. The calibration curves extend beyond the CMC of TTAB in 0.01 M NaBr to show the effect of micellization on electrode response. At 25 °C, a Nernstian response of 58.4 ±0.6 mV for a 10-fold change in surfactant concentration is obtained from the surfactant-selective electrode and the CMC of TTAB in a 0.01 M NaBr solution is determined to be 1.48 mM which is in excellent agreement with the literature value of 1.49 mM [14].

From the calibration curve shown in Fig. 2, it is apparent that the electrode detects a lower surfactant concentration in the presence of hydrophobically modified polyacrylamide (HPAM). The difference between the free surfactant concentration in the presence and absence of polymer increases with both increasing percent incorporation and hydrophobicity of the hydrophobe. The presence of unmodified polyacrylamide has only a very small effect on the EMF, indicating weak or no binding. The change in the measured EMF is due to the presence of polymer hydrophobic domains which solubilize (bind) surfactant ions, thereby lowering the concentration of free surfactant ions. This observation is similar to the lowering of the free

Fig. 2 Calibration curves of EMF vs. the log of the concentration of free TTAB in the absence and presence of nonmodified and hydrophobically modified polyacrylamide (concentration: 1% wt/wt)



surfactant concentration due to the presence of nonionic micelles [15], ethyl(hydroxyethyl) cellulose [16], and hydrophobically modified ethyl hydroxyethyl cellulose (HMEHEC) [17]. After the completion of titration curves both in the presence and absence of polymer, binding isotherms are constructed by calculating and plotting $\log[S]_{\text{free}}$ vs. the ratio of the number of TTAB molecules bound per hydrophobe. Binding isotherms for polymers containing a *n*-alkyl hydrophobe and an alkyl substituted azobenzene hydrophobe are illustrated in Fig. 3.

The noncooperative binding isotherms observed in Fig. 3 are typical for the binding of cationic surfactants to a neutral polymer [15–18]. Different from cooperative binding isotherms, there is no well-defined start of the binding region, and binding increases monotonically with increasing surfactant concentration. Also, the greater the hydrophobicity of the hydrophobe, the greater the interaction between the polymer and TTAB. The binding isotherms of the substituted azobenzene polymers exhibit the same general trends observed with the N-*n*-alkyl substituted HPAMs. As the size of the terminal substituent on the azobenzene chromophore is increased from R = H to R = Butyl, the amount of bound TTAB increases in magnitude. The degree of binding with the azobenzene substituted HPAMs is much lower than that with the N-*n*-alkyl substituted HPAMs (on the basis of surfactant ions bound per polymer hydrophobe), which is believed to be due to the low percent substitution of the hydrophobe (0.5%) leading to less well-defined hydrophobic domains, and/or the fact that hydrophobic interactions are stronger for *n*-alkyl sidegroups than for aromatic azo sidegroups [19].

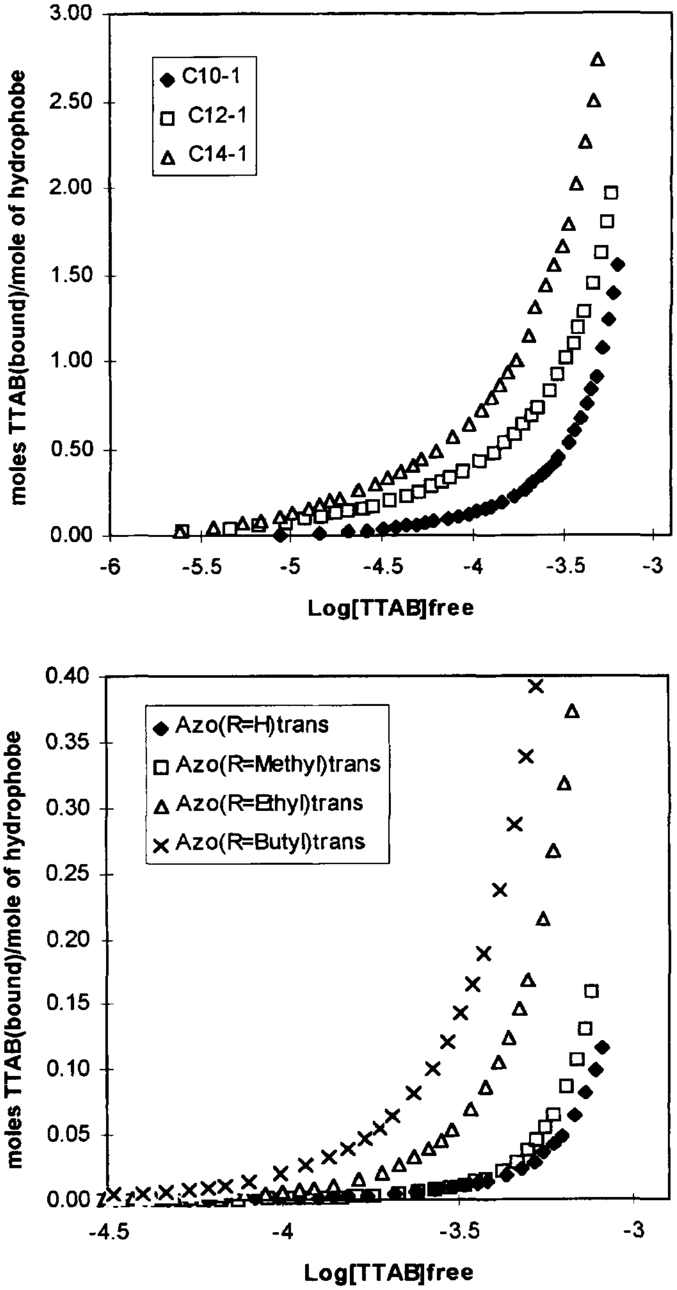


Fig. 3 Binding isotherms for PAM C10, C12, and C14-1% (concentration: 1% wt/wt) and PAM Azo(R = H, Methyl, Ethyl, Butyl)-0.5%: *trans* (concentration: 2% wt/wt)

Light induced *trans*-to-*cis* isomerization has a striking effect on the surfactant binding isotherm, as shown in Fig. 4. The influence of irradiation of the azobenzene sidegroup with UV light and the corresponding isomerization to *cis*-azobenzene results in a decrease in the amount of TTAB bound and an increase in the concentration of free surfactant. Similar shifts in the binding isotherms with exposure to UV light are observed with the other substituted azobenzene polymers. The decrease in the interaction between azobenzene and TTAB when azobenzene changes from *trans*- to *cis*-form is due to the fact that during *trans-cis* isomerization the dipole moment increases from about zero to three Debye [7, 8, 20–22]. This results in a decrease in hydrophobicity of the polymer and an increase in the solubility of the hydrophobic azobenzene group in aqueous medium, thus inducing large changes in the properties of the polymer system to which it is bound. This direct experimental evidence of the change in sidegroup hydrophobicity leading to a large change in surfactant binding opens the possibility of designing polymer–surfactant systems with light sensitive properties. In earlier studies, Konak et al. [7] reported on N-(2-hydroxypropyl)methacrylamide polymers in which azobenzene side chains were incorporated. These authors attempted to influence the polymer self-association by exploiting the difference in solubility of azobenzene when exposed to UV-visible light. Their results indicate that

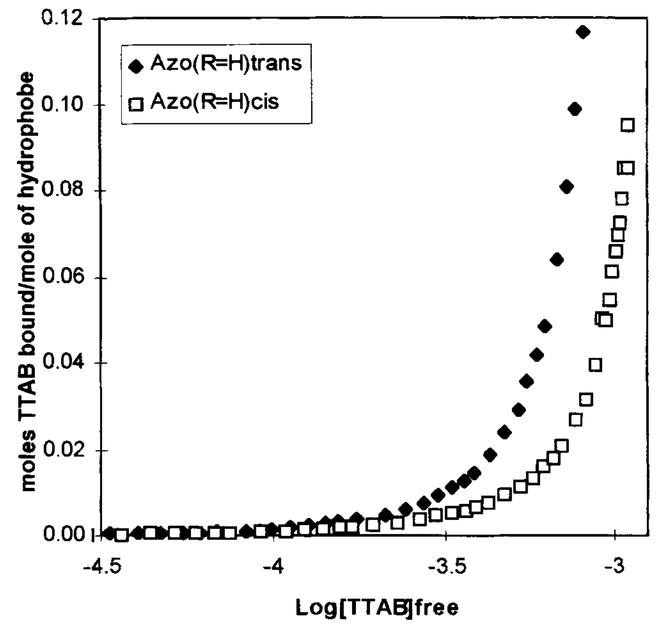


Fig. 4 Binding isotherm of PAM Azo(R = H)-0.5%/TTAB system (concentration: 2% wt/wt)

polymers prepared with 39.3 mol% azobenzene side-groups are only soluble in water in a pseudo-micellar form. Through the use of light scattering methods to determine the number of azobenzene chromophores comprising these aggregates, they found that irradiation resulted in a pronounced decrease in the aggregation number of these aggregates due to dissolution of the azobenzene side-groups in the aqueous solvent.

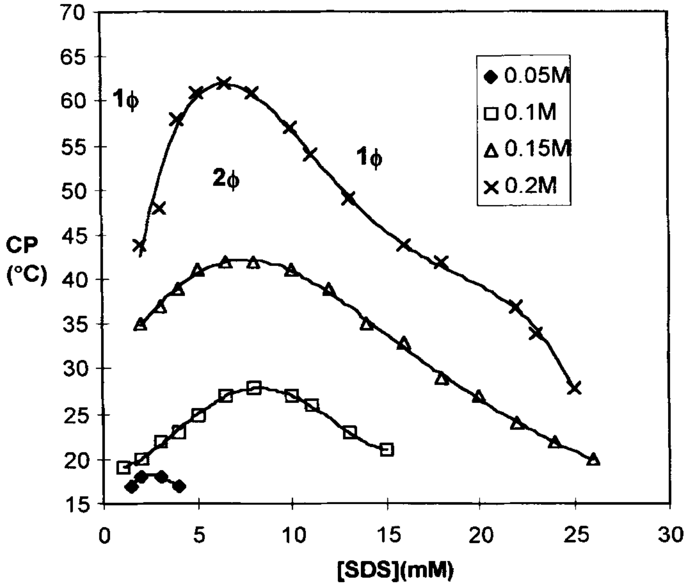
Previous work in our laboratory discovered evidence of an associative phase separation induced by the presence of inorganic salts in mixtures of SDS and nonclouding polymers of polyacrylamide, where the polymers contained 2 mol% of either N-*n*-decylacrylamide [9] or 4-acrylamidoazobenzene [10] as the hydrophobe. These systems exhibit a characteristic upper critical solution temperature (UCST), depending on the solution composition, with the two-phase region at lower temperatures relative to the one-phase region. Phase separation in these HPAM–surfactant systems has been explained as an entropy driven process [3, 23]. In the absence of salt, mixtures of HPAMs and surfactant do not exhibit phase separation due to the fact that phase separation would result in the enrichment of surfactant counterions in one phase and would cause an unfavorable loss in the entropy of mixing. By the addition of inorganic salt to these systems, however, the loss in the entropy of mixing is suppressed and phase separation can occur.

Phase separation has been observed for polyacrylamide-co-acrylate based azobenzene polymers at 2 mol% hydrophobe incorporation. A minimum hydrophobe content is required to produce sufficiently strong interactions between the polymer and surfactant to induce phase separation and therefore one condition required for phase separation is that the hydrophobicity of the polymer must be relatively large.

A series of plots of the clearing-point CP) vs. surfactant concentration at different concentrations of an inorganic electrolyte was obtained for the azobenzene polymers. Typical data for PAM Azo(R = H)-2% in the presence of SDS and Na_2SO_4 is presented in Fig. 5. Similar phase behavior was observed for all these polymers in the presence of TTAB and $MgSO_4$. It may be seen from Fig. 5 that two trends are observed clearly: the UCST increases and the SDS concentration range at which phase separation occurs broadens with increasing salt concentration.

The observed phase separation in the hydrophobically modified polyacrylamide–surfactant systems is due to an attractive interaction between the polymer and surfactant. Indeed, in the two-phase system the concentrated phase is high in both polymer and surfactant concentration [9]. In the presence of salt and surfactant at a concentration below the CMC, mixed micelle formation occurs between the polymer hydrophobes and surfactant. Mixed micelle formation involving more than one polymer chain results in a more hydrophobic aggregate. As the surfactant concentration is increased, the degree of crosslinking and hydrophobicity of the polymer–surfactant complex increases and eventually phase separation occurs and the CP

Fig. 5 Clearing-point curves for PAM Azo(R = H)-2% (concentration: 1% wt/vol) vs. SDS and sodium sulfate (0.05 M, 0.1 M, 0.15 M, 0.2 M)



increases in magnitude. Beyond the CMC, the polymer hydrophobes become saturated with surfactant ions, and in addition free surfactant micelles form. As a result the hydrophobicity of the polymer–surfactant complex decreases in magnitude. In addition, the increasing concentration of adsorbed ionic surfactant on the polymer causes electrostatic repulsion between polymer–surfactant complexes and results in a decrease in the CP with increasing surfactant concentration and eventually no phase separation.

The salt dependence of the observed phase behavior of these systems is believed to be due to two main factors. The first is the fact that the increase in the electrolyte concentration results in a better screening of repulsive charges between polymer–surfactant complexes, leading to increased aggregation. The second factor deals with the effect of the added electrolyte on the solvent, i.e. water. The addition of electrolyte results in a salting out effect which increases the difference in polarity between the solvent and the polymer–surfactant complex and thus, phase separation increases with increasing electrolyte concentration. In addition, an increase in the CP with increasing electrolyte concentration will occur due to greater suppression of the loss of entropy of mixing of the surfactant counterions.

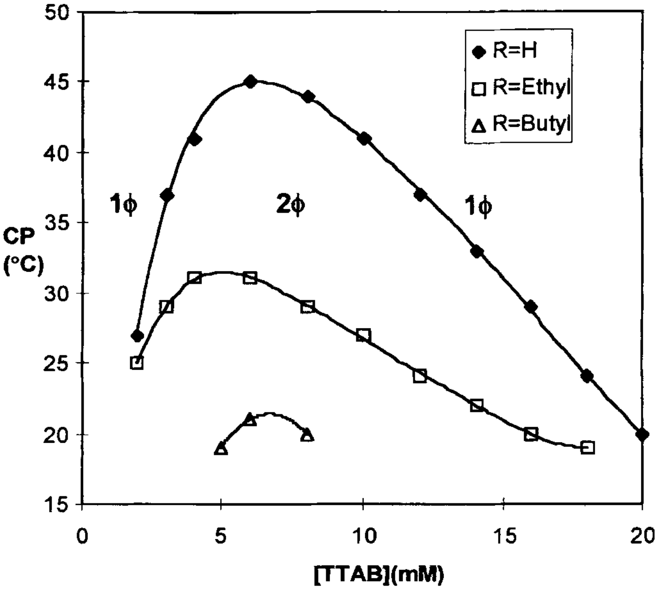


Fig. 6 Clearing-point curves for PAM Azo(R = H, Ethyl, Butyl)-2% (concentration 1%wt/vol) vs. TTAB and 0.2 M magnesium sulfate

For the azo co-polymers the ratio of the number of SDS molecules per hydrophobe at the UCST can be calculated from ^{1}H-NMR spectra of the gel phase of phase-separated systems at compositions corresponding to the UCST. The number of SDS molecules per hydrophobe is determined from the ratio of the integrated area of the chemical shift of the α methylene group of the surfactant ($\delta = 3.93$) to the integrated area of the chemical shift of the azobenzene hydrophobe ($\delta = 7$–8 ppm). Calculated surfactant to hydrophobe ratios at the UCST are summarized in Table 3, showing that the aggregates are approximately a 3:1 mixture of surfactant to polymer hydrophobe. Our results indicate that for the 2% substituted azo polymers higher salt concentrations are required to induce phase separation as the hydrophobicity of the chromophore increases, i.e. as the length of the terminal alkyl (R2) increases. In other words, for a fixed electrolyte concentration, the UCST and the area of the two-phase region decreases with increasing hydrophobicity of the chromophore. This was observed for PAM Azo-2% in the presence SDS/0.2 M Na_2SO_4 and TTAB/0.2 M $MgSO_4$. This unexpected behavior for PAM Azo-2% is depicted in Fig. 6 for the case of TTAB/0.2 M $MgSO_4$ is and is indeed opposite to the data obtained for the *n*-alkyl HPAMs shown in Fig. 7, where phase separation is much stronger for the C12 sidegroup polymer.

The explanation for this decrease in the two-phase region for the PAM Azo-2% polymers with increasing R2 hydrophobicity may be due to the significantly lower molecular weight of these polymers (Table 2). While the PAM Azo-2% polymers have an average molecular weight of only 15000 g/mol, the PAM C10/C12-2% polymers have an average molecular weight of 160000 g/mol. Due to the difference in molecular weight between the N-*n*-alkyl and azobenzene polymers, the azobenzene HPAMs have on average four hydrophobes per polymer chain while the *n*-alkyl HPAMs have fifty per polymer chain. As the hydrophobicity of the hydrophobe is increased, the amount of surfactant bound to it increases as shown by the binding studies. The increase in the UCST and two-phase region with increasing hydrophobicity of the hydrophobe of the *n*-alkyl polymers is due to the fact that with increasing hydrophobicity for the *n*-alkyl polymers, greater

Table 3 Ratio of the number of SDS molecules/hydrophobe at the UCST

PAM Azo-2%	Integrated area ($\delta = 3.93$)	Integrated area ($\delta = 7$–8)	SDS/hydrophobe (^{1}H-NMR)	SDS/hydrophobe (plot)
R = H	4.9×10^4	9.5×10^4	2	2–3
R = Ethyl	5.0×10^5	6.8×10^5	3	3
R = Butyl	4.7×10^5	6.8×10^5	3	3–4

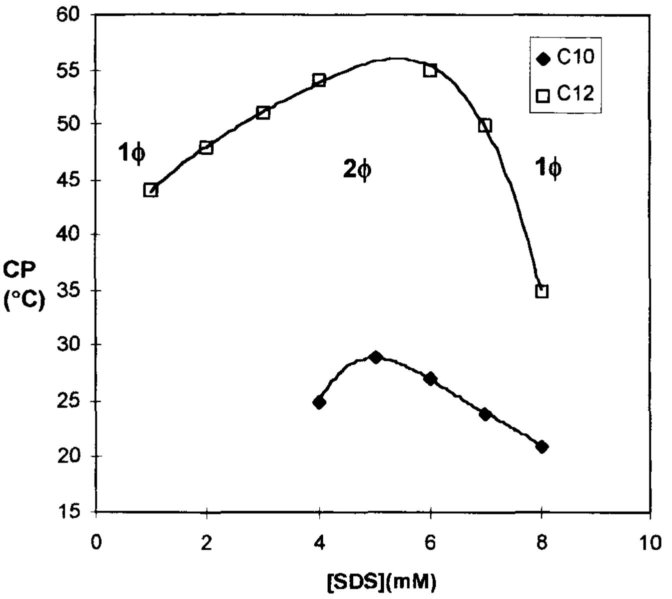


Fig. 7 Clearing-point curves for PAM C10/C12-2% (concentration 0.5% wt/vol) vs. SDS and 0.02 M sodium sulfate

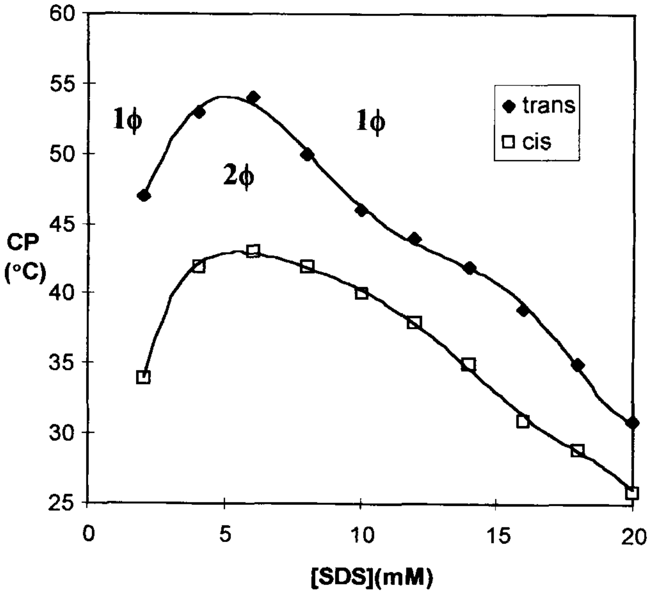
crosslinking between adjacent polymer chains upon the addition of surfactant will occur. Greater crosslinking results in the formation of a more hydrophobic polymer–surfactant complex and thus a larger two-phase region is the result. For the PAM Azo-2% polymers, an increase in the hydrophobicity of the chromophore also results in greater interaction between the hydrophobe and surfactant as evidenced by ^{1}H-NMR data. While this does result in an increase in the amount of crosslinking between polymer molecules, it also results in the absorption of more ionic charge onto the polymer molecules which would have more of the surfactant headgroups exposed at the outside of the small aggregate, thereby decreasing the hydrophobicity of the polymer–surfactant complex and thus decrease the CP. This ionic effect is less noticeable or absent for the *n*-alkyl polymers due to the fact that they are much more effective at crosslinking than the low molecular weight azobenzene polymers, forming much larger aggregates.

Another reason for the difference in the phase behavior between the *n*-alkyl HPAMs and the polyacrylamideco-acrylateazobenzene polymers is related to the difference in the entropy changes on phase separation. As stated earlier, phase separation in these systems is an entropy driven process and is suppressed in the salt-free systems due to the fact that the enrichment of surfactant counterions in one phase would result in a decrease in the entropy of mixing. However, the strong tendency for HPAMs to associate with micelles must also be taken into account [24]. When the hydrophobes are involved in mixed micelle formation, a restriction in the motion of the polymer backbone is likely to occur and this leads to a decrease in the number of degrees of freedom and a decrease in configurational or translational entropy. This effect is much less an additional contribution to the loss of entropy, which increases with the hydrophobicity of the chromophore, for PAM C10/C12 than PAM Azo due to their greater molecular weights.

UV irradiation is found to have a large effect on the phase behavior of the PAM Azo(R = H)-2% polymer. For this polymer conversion from the *trans*- to *cis* isomer results in a decrease in the CP as illustrated in Fig. 8. However, only a negligible decrease in the CP is observed for the ethyl and butyl substituted derivatives. The observed decrease in the CP for PAM Azo(R = H)-2% polymer is due to the fact that when azobenzene converts from the *trans*- to the *cis* isomer, its dipole moment increases in magnitude resulting in a decrease in the hydrophobicity of the azobenzene group. The binding isotherms shown in Fig. 4 indeed demonstrate the significant decrease in TTAB binding upon irradiation. A similar decrease in binding may take place with SDS, resulting in a lower tendency towards phase separation.

However, for the ethyl and butyl substituted azobenzene polymers a negligible decrease in the CP with UV irradiation is observed. This is believed to be due to the fact that the difference in binding of surfactant with isomerization is less for these polymers due to the presence of the terminal *n*-alkyl substituent and the fact that the thermal *cis*- to *trans* (i.e. reverse) isomerization of azobenzene is increased with the incorporation of substituents in the ortho and para positions [11].

Fig. 8 Effect of *cis-trans* isomerization of PAM Azo(R = H)-2% in SDS/0.17 M Na_2SO_4



Conclusion

The incorporation of hydrophobic groups on a water-soluble polymer results in the formation of polymeric micelles which aids in the binding of surfactants due to the formation of mixed micelles at low surfactant concentrations. The binding of the cationic surfactant TTAB to hydrophobically modified polyacrylamide (HPAM) is found to increase with increasing hydrophobicity of the hydrophobe. For substituted azobenzene containing polymers, the binding of TTAB is found to be dependent on the hydrophobicity of the hydrophobic sidegroup.

Aqueous systems consisting of polyacrylamides with 2 mol% of a *n*-alkyl or azobenzene hydrophobe undergo an associative phase separation in the presence of ionic surfactant and electrolyte. When the clearing point (CP) is determined as a function of surfactant concentration, a characteristic two-phase region is observed with a maximum in the CP and UCST at approximately the CMC of the ionic surfactant SDS. In these systems the UCST and the concentration range of surfactant at which phase separation is observed increases with increasing electrolyte concentration. For the *n*-alkyl polymers the two-phase region is observed to increase with increasing hydrophobicity of the polymer sidegroup. The opposite trend is observed with the azobenzene polymers. This is attributed to the difference in molecular weight between these two classes of HPAMs. Of particular interest is the effect of UV irradiation on the azobenzene polymer-surfactant systems. *Trans*- to *cis* isomerization of the azobenzene sidegroup results in a lower degree of TTAB binding, and a decrease in the CP for the SDS system, both observations consistent with the known decrease in the hydrophobicity of the chromophore with photoisomerization. As a result, surfactant concentration ranges and temperature regions can be defined where irradiation produces significantly different rheology and phase behavior. The extent and position of these regions of irradiation induced property differences can be controlled by varying polymer composition, sidegroup and surfactant hydrophobicity. In this paper, emphasis is on the quantitative binding studies and phase behavior. Rheological behavior will be discussed in a forthcoming paper.

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