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ORIGINAL CONTRIBUTION

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The interaction between sodium dodecylsulfate and the cationic-nonionic random copolymer (3-(2-methylpropionamide)propyl) trimethylammonium chloride–acrylamide of two different charge densities studied using dynamic light scattering and rheometry

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Abstract The effects of complex formation between sodium dodecylsulfate (SDS) and the positively charged (3-(2-methylpropionamide)propyl)trimethyl-ammonium chloride-acrylamide (MAPTAC-AM) copolymer have been studied in dilute and semidilute aqueous solution in the presence of 10 mM NaCl. Two different charge densities of the copolymer have been used in the study: 0.31 and 0.66, corresponding to the proportion of MAPTAC units. Dynamic light scattering (DLS) and rheometry (static low-shear and capillary viscometry) have been performed on the systems at different charge ratios, i.e., SDS/MAPTAC molar ratios, *r*. Regarding the phase behavior, the maximum binding ratio prior to precipitation differs between the copolymers. A 1.0% w/v solution of SDS/31% MAPTAC-AM is soluble at $r = 0.4$, while an SDS/66% MAPTAC-AM solution of 1.0% w/v shows phase separation at this ratio. With excess surfactant, the complex in the former system is resolubilized at $r = 2.0$, whereas the latter system is still phase-separated at $r = 5.0$. DLS results show that, for both copolymers, the hydrodynamic radius, R_h, of the single-chain copolymer-surfactant complex decreases as a function of *r*, but then increases slightly prior to phase separation. The corresponding hydrodynamic virial coefficient, k_D, changes in the same manner as R_h. The light-scattering data also show that the formation of larger structures is promoted as the polymer concentration is increased from 0.2 to 1.0% w/v. This is shown by the increase in the relative aggregate-to-single coil peak areas in the relaxation time distributions. Both systems have this common trend. The results from rheological measurements support the results from DLS. A reduction in intrinsic viscosity, $[\eta]$, is observed on increasing *r* up to phase separation. The major part of the static low-shear measurements showed Newtonian behavior for both systems at different copolymer concentrations (27.6–138 mM), and at different *r*. These systems, partially ionic polymer/oppositely charged surfactant, present very interesting rheological behavior at relatively high polymer concentrations and at low *r* values. Their behavior is similar to those of hydrophobically modified polyelectrolytes.

Key words Cationic copolymers – Sodium dodecylsulfate – Light scattering – Rheometry – Viscometry

Introduction

Polymer-surfactant complex formation has been, and still is, a subject of intense research [1–5]. In recent years increasing interest has been focused on the interactions between surfactants and hydrophobically modified polymers/polyelectrolytes [6–10], which play a significant role in the viscoelastic properties of many industrially important fluids. Interactions between hydrogels and ionic surfactants have been extensively studied [11–13]. Important properties of these gels are critical conformational transitions, collapse or swelling on complexation with surfactants, and selective absorption of organic particles, including surfactants, which is applied in waste water treatment. Cationic polyelectrolyte-anionic surfactant complex systems are among those least frequently investigated. Dubin and coworkers [14–16] have studied the interactions between the polycation PDMDAAC and Sodium dodecylsulfate (SDS)/Triton X-100 negative/neutral mixed micelles, using dynamic and static light scattering. In one of their more recent papers [17], study is made of the effect of polyelectrolyte chain length and micellar size on the structure of the complex. For example, it was found that the degree of binding (mass ratio micelle/polyelectrolyte in the complex) decreases as the polyelectrolyte molecular weight is increased. Moreover, with increasing size of the micelles, the complex structure changes from a structure in which several micelles are bound to a specific chain, to a structure in which huge micelles adsorb to one or more polyelectrolyte chains. Bakeev et al. [18] reported results from studies on the complex formation between poly(*N*-ethyl-4-vinylpyridinium) (PEVP) cations and dodecylsulfate anions in low-polarity solvents. For both equimolar and nonequimolar ($DS^-/EVP^+ < 1$) surfactant-polyion complexes, they found that aggregates, due to interchain association, were present when chlorobenzene was used as the solvent, but were absent in dilute solutions in chloroform.

The object of this work was to study complex formation between SDS and the polycation (3-(2-methylpropionamide)propyl)trimethylammonium chloride–acrylamide (MAPTAC-AM) at different charge densities, using dynamic light scattering (DLS) and rheology techniques, in order to complement the picture obtained from surface force measurements [19], and also to facilitate comparison with the PCMA-SDS system [20]. It is known that complex formation does not occur between SDS and neutral polyacrylamide and thus interaction between the surfactant and the copolymer is determined by the proportion of MAPTAC units. Data have also been extracted in order to follow the conformational and hydrodynamic changes at a constant polymer concentration when the amount of surfactant is varied. A general trend in the phase behavior of polyelectrolytes and oppositely charged surfactants is that the two-phase region increases with charge density, α. This explains why the copolymer with $\alpha = 0.31$ is resolubilized at a lower r than that with $\alpha = 0.66$. Larger structures, presumably involving several polymer chains as observed in similar systems are also present in the system discussed here.

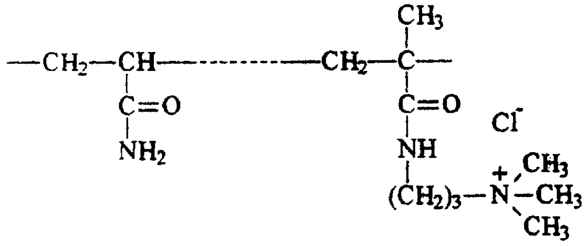
Experimental section

Synthesis of the MAPTAC-AM random copolymers

The pathway of the synthesis of MAPTAC-AM is analogous to that of acryl(*N*, *N*, *N*-trimethyl)aminoethyl chloride–AM (CMA-AM) given in Ref. [21]. The relations between intrinsic viscosity and molecular weight given below have been extracted from the data reported in Ref. [21] concerning the CMA-AM copolymers. We assume that they can also describe the behavior of the MAPTAC-AM copolymers, since the MAPTAC and CMA units should make essentially the same contribution to the coil dimensions.

$$\text{31\% MAPTAC-AM: } [\eta]^{25\,^\circ\text{C, 1 M NaCl}}_{\text{dl/g}} = 1.05 \times 10^{-4}\,\overline{M}_W^{0.73}, \qquad (1)$$

$$\text{66\% MAPTAC-AM: } [\eta]^{25\,^\circ\text{C, 1 M NaCl}}_{\text{dl/g}} = 0.45 \times 10^{-4}\,\overline{M}_W^{0.78}. \qquad (2)$$



AM MAPTAC

Sample preparation and experimental conditions

Stock solutions of SDS and polymers were prepared in 10 mM NaCl (aq). The final samples were obtained after appropriate mixing of the stock solutions. SDS, especially pure grade, was from BDH, and Milli-Q grade water from a Millipore apparatus was used. The stock solutions were constantly stirred for 24 h at room temperature in order to reach equilibrium. For the DLS measurements, the solutions were filtered after dilution through Sartorius Minisart N filters (0.45 μm) into cylindrical glass light-scattering cells (15 mm diameter). The NaCl concentration was 10 mM in all samples, both for rheological and light-scattering measurements. All experiments were carried out at 25 °C, and at surfactant concentrations above the cac. Performing the drop-weight method, the cac was determined to be about 0.2 mM SDS in 10 mM NaCl at 0.1% w/v of the copolymers.

Dynamic light scattering

The technique and apparatus used were those described in an earlier paper [22]. An ALV 5000 wide-band multi-τ, digital autocorrelator from ALV-Langen, Germany, was employed to determine the relaxation time. This instrument has a monitoring capacity of up to nine decades in delay time. The measured time-intensity correlation function is related to the electric field correlation function by the Siegert relation

$$g^{(2)}(t) = B[1 + \beta|g^{(1)}(t)|^2] \ , \tag{3}$$

where B is a baseline and β is a factor accounting for deviations from ideal correlation, for instance fluctuations in the scattering volume. In a continuous distribution corresponding to an infinite range of particle sizes, the inverse Laplace transform (ILT) may be used:

$$g^{(1)}(t) = \int_0^\infty A(\tau)\exp(-t/\tau)\mathrm{d}\tau \ . \tag{4}$$

ILT was performed by using a constrained regularization routine, REPES, developed by Jakeš [23], to obtain the distribution of decay times. This program is similar in many respects to CONTIN by Provencher [24], but directly minimizes the sum of squared differences between the experimental and calculated intensity-intensity correlation functions, $g^{(2)}(t)$, using nonlinear programming and allows selection of the parameter P (probability to reject), which determines the degree of smoothing. The analysis of data, accumulated in 288 exponentially spaced channels using a grid density of 12 per decade can be rapidly performed on an IBM AT desktop computer. Relaxation-time distributions are given in the form $\tau A(\tau)$ versus log τ, providing an equal area representation. Diffusion coefficients are calculated from the ILT moments of the peaks as

$$D = (\Gamma_i/q^2)_{q\to 0} \ , \tag{5}$$

where Γ_i is the decay rate of the ith process and q is the magnitude of the scattering vector.

Viscometry

Specific viscosity measurements were made using a TI 1 apparatus form Sematech, equiped with a Ubbelohde capillary and an automatic dilution device. Dilute solutions in the concentration range 0.78–1.56 mg ml^{-1} of the polymers were measured. Under these conditions linear fits were obtained and the intrinsic viscosity $[\eta]$ was determined at each r by extrapolation to infinite dilution of the complex. Other viscosity data at higher concentrations (Figs. 6, 7) were obtained with a Low-Shear 30 apparatus from Contraves. The range of the shear gradient 0.3–70 s^{-1} was explored. The viscosity values at low shear rates, corresponding to the Newtonian plateau, are shown in Fig. 6.

Results and discussion

Dynamic light scattering

Figure 1a shows representative relaxation-time distributions for the 31% MAPTAC-AM copolymer at $r = 0.1$. The distributions of relaxation times are very broad, with the single-chain complex represented by the fastest mode in the spectra. This observation, which is generally accepted, is supported by the following facts:

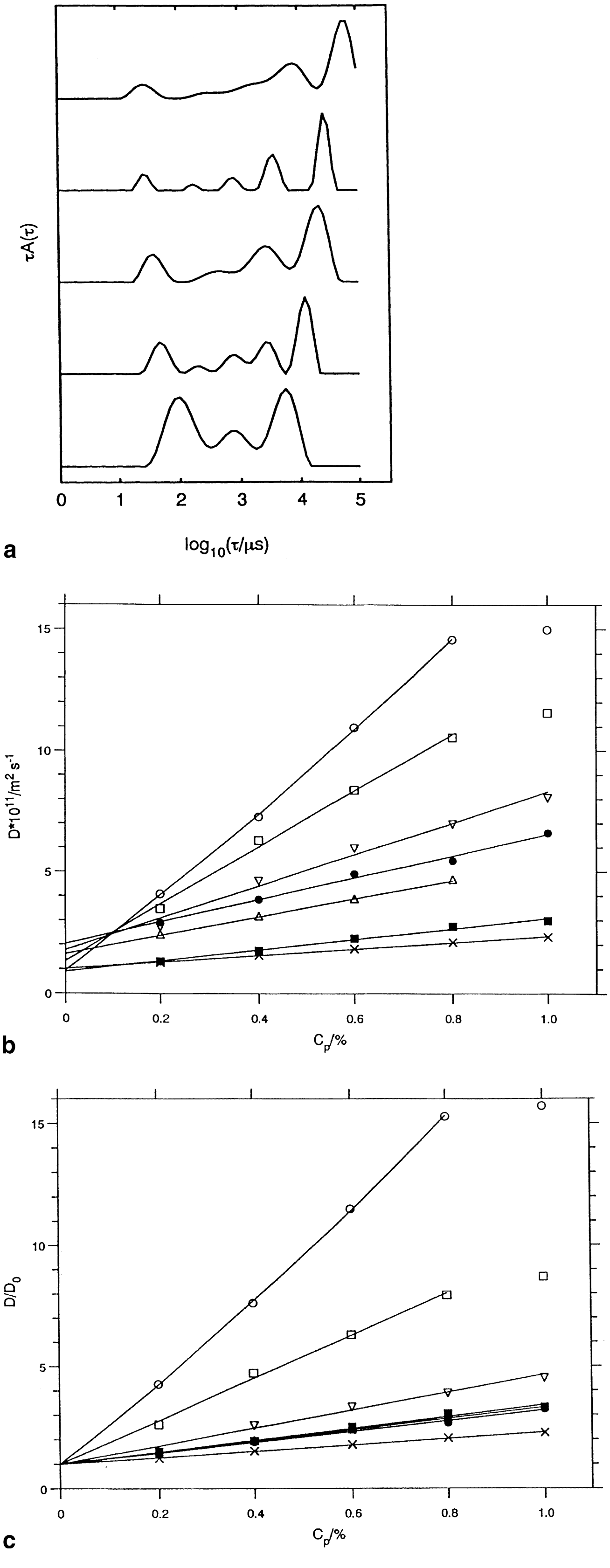
1. The correlation time τ attributed to the fastest mode shows a linear q^2 dependence and the product $qR_\mathrm{h} \ll 1$, i.e., it cannot be an internal relaxation mode.
2. The corresponding R_h value is much larger than that attributable to free SDS micelles (about 2 nm).
3. The fastest mode is the only mode for which τ decreases as a function of concentration of the complex, i.e., there is a positive concentration dependence of D which is the case for a free particle (polymer coil) in a good solvent involving attractive complex-solvent interactions.

The slower modes are attributed to higher-order aggregates involving several polymer chains. The contribution of the polydisperse aggregates to the total scattering intensity increases as a function of the complex concentration as shown by the increase in the relative area under the aggregate peaks in the spectra. As the concentration is increased, the relative intensity deriving from the isolated coil becomes almost negligible in comparison with the intensity scattered by the aggregates. There is also a decrease in the relative peak areas (single chain complex-to-multiple chain aggregates) as the surfactant/polymer ratio is increased.

The concentration dependences of the diffusion coefficients for the single-coil SDS/31% MAPTAC complex are shown in Fig. 1b, where the data were obtained from the relaxation rates of the fastest mode in distributions such as those shown in Fig. 1a. The r values are 0, 0.1, 0.2, 0.3, 0.4, 2.0, and 3.3 from the top. The last two ratios (the filled squares and the crosses) thus correspond to the resolubilized complex at excess surfactant concentration. For $0.4 < r < 2.0$ associative phase separation takes place, where a highly concentrated polymer-surfactant complex separates from a dilute supernatant. Complex formation between surfactant and copolymer involves both hydrophobic and electrostatic interactions, with the latter leading to neutralization of charges. On increasing the ratio up to the phase separation the complex coil becomes more compact as reflected by the increase in the diffusion coefficient at infinite dilution. It is worth noting that the resolubilized complexes have infinite dilution diffusion coefficients which are lower, and thus correspond to larger hydrodynamic radii, than those for the complexes just prior to phase separation.

Figure 1c depicts the corresponding normalized diffusion coefficients of the single-chain complex as a function of polymer concentration reflecting the hydrodynamic complex-solvent interaction at different charge ratios. There is the expected decline in the concentration dependence of D/D_0 as the ratio is increased. However, the slopes are all positive even just prior to phase separation, demonstrating repulsive interactions between the complexes (attractive complex-solvent interactions) probably due to the relatively low concentration of NaCl. For a similar system, SDS interacting with 100% charged PCMA [20], where the effect of ionic strength was studied, it was found that the concentration dependence of the diffusion coefficient was negative prior to phase separation at a high concentration of NaCl, e.g., 100 mM. Another way to visualize the hydro-dynamic changes of the single coil can be made by displaying series of translational diffusion coefficients as a function of surfactant concentration at different constant values of the polymer concentration [19]. Here it is not possible to follow the real radius since each diffusion coefficient has contributions both from particle size and from particle-solvent interactions. As the surfactant concentration is increased charge neutralization will give a progressively dense and more compact complex up to phase separation. At the same time the complex becomes less hydrophilic as reflected in part by the decrease in the effective diffusion coefficient.

ILT results for the resolubilized complexes at high ratios are given in Fig. 2a and b. In Fig. 2a ($r = 2.0$), the multimodal form of the distributions is suppressed at relatively high ionic strength with a large excess of surfactant. We thus conclude that the higher-order aggregates are electrostatically stabilized since they



◀

Fig. 1a Relaxation time distributions for the copolymer of charge density 0.31 at the SDS/MAPTAC molar ratio 0.1. The polymer concentrations are 0.2, 0.4, 0.6, 0.8, and 1.0% w/v from the bottom. **b** The concentration dependence of the translational diffusion coefficient for the single-chain complex for the copolymer of charge density 0.31 at the SDS/MAPTAC molar ratios 0 (O), 0.1 (□), 0.2 (▽), 0.3 (●), 0.4 (△), 2.0 (■), and 3.3 (×). **c** Dependence of the normalized diffusion coefficient on polymer concentration for the single-chain complex for the copolymer of charge density 0.31 at the SDS/MAPTAC molar ratios 0 (O), 0.1 (□), 0.2 (▽), 0.3 (●), 0.4 (△), 2.0 (■), and 3.3 (×)

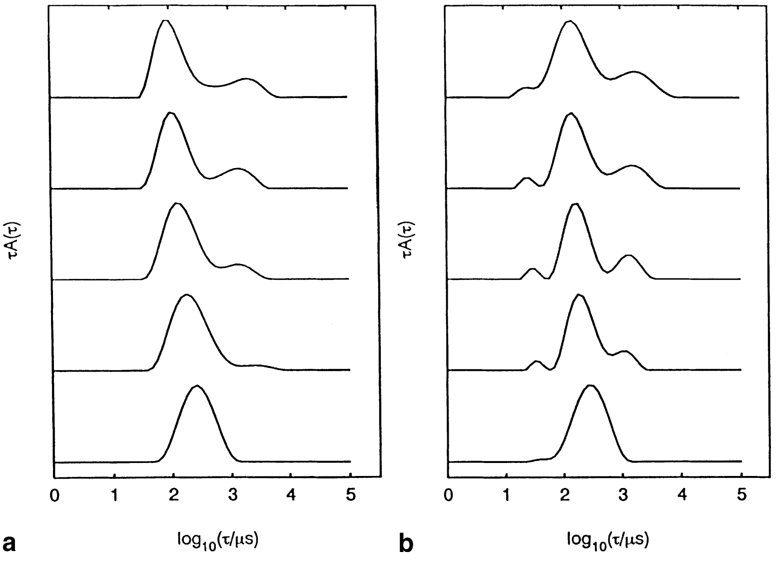


Fig. 2 Relaxation time distributions for the copolymer of charge density 0.31 at the SDS/MAPTAC molar ratios 2.0 **a** and 3.3 **b**. The polymer concentrations are 0.2, 0.4, 0.6, 0.8, and 1.0% w/v from the bottom. At 1.0% w/v, [MAPTAC] = 26.4 mM

vanish at high ionic strength. However, it is remarkable that no relaxation mode attributable to free regular SDS micelles can be observed in the spectra at $r = 2.0$. The reason may be that at this r value for resolubilized complexes the number of free micelles is too low order to give a detectable scattered intensity, I_s, or that I_s for the micelles is suppressed by a larger I_s value for the complexes. In Fig. 2b, where the excess of surfactant is even larger ($r = 3.3$), three relaxation modes are present. The fastest is attributed to free surfactant micelles, the second fastest to the single-coil complex, and the slowest mode again to large structures involving several polymer chains. Apparently, the aggregate mode has a higher number density at $r = 3.3$ in the concentration range 0.4–1.0% w/v than at $r = 2.0$ (as reflected by the larger area under the ILT curve for the aggregate mode at $r = 3.3$ than at $r = 2.0$). The reason may be that since at this point the electrostatic interactions are almost screened, further increase in the ionic strength favors hydrophobic interactions between the complexes.

Similar to the observations at $\alpha = 0.31$ of the copolymer, the scattered intensity from the single-coil complex at $\alpha = 0.66$ decreases while the scattering from the aggregates increases upon increasing the total concentration of the polymer-surfactant mixture. Moreover, with a constant polymer concentration within the range 0.4–1.0% w/v at different r, it appears that the formation of aggregates is promoted by an increase in this ratio, as reflected by the fact that the relative area of the fast mode to the slow multiple modes decreases. This observation is explained by the approach to phase separation. Due to hydrophobic interactions, the larger structures become more numerous as charge neutralization progresses. This is shown by the representative ILT results in Fig. 3 for 66% MAPTAC-AM at a polymer concentration of 1% w/v. Upon variation of the ionic strength, the slow relaxation modes in polymer-surfactant systems sometimes show a response which differs from that of the slow mode in the typically bimodal distributions of surfactant-free aqueous polymer solutions. For both the polyanion NaPSS [25] and the polycation PCMA [20] in aqueous solutions it was concluded that the slow modes result from long-range repulsive electrostatic interactions between polyelectrolyte chains, since they disappear on increasing the salt concentration. The aggregates arising from inter polyion association in PCMA-SDS [20] solutions prior to macroscopic phase separation also appear to be electrostatically stabilized for the same reason. However, the aggregates formed in the NaPSS -CTAB [26] system just

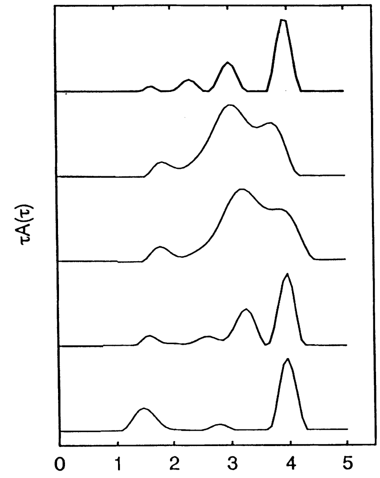


Fig. 3 Relaxation time distributions for the copolymer of charge density 0.66, at the polymer concentration 1.0% w/v. The SDS/MAPTAC molar ratios are 0, 0.1, 0.2, 0.3, and 0.35 from the bottom. At 1.0% w/v, [MAPTAC] = 38.8 mM

before the precipitation point appear to be hydrophobically stabilized since an increase in ionic strength enhances the formation of larger structures. This may be due to the relatively high maximum neutralization degree in the latter system ($r = 0.65$) yielding a large number of hydrophobic domains. In our case, the formation of large aggregates before the phase separation limit and at high polymer concentration has an important impact on the rheological behavior of the system as will be shown in the last section of this discussion.

Figure 4a shows the hydrodynamic radii, R_h, calculated from the diffusion coefficients of the single-coil complexes at infinite dilution for the 31% and 66% MAPTAC-AM copolymers at different r. When a quantitative comparison between the R_h values of the two copolymers is made there are several factors which have to be considered. For technical reasons related to the synthesis of the copolymers, their molecular weights, M_w, are different. $M_w = 7.8$ and 3.4×10^5 for the 31 and 66% MAPTAC-AM, respectively. The degrees of polymerization are approximately 6600 and 2000, respectively. Thus, the 31% MAPTAC-AM chain is relatively long with many small AM units, while the 66% MAPTAC-AM chain is shorter with many bulky MAPTAC units. Of course, the more charged polyelectrolyte contributes more to the total ionic strength than the less charged one. Considering the copolymer with $\alpha = 0.31$, $R_h = 25.8$ nm in the absence of surfactant. As r is increased, complex formation takes place between the polymer and the surfactant micelles by electrostatic interactions resulting in charge neutralization, and also through hydrophobic interactions as the dodecyl chains of the surfactant are shielded by the propylmethacrylamide of the MAPTAC units and by association of each other from contact with water molecules. The complex then becomes more compact than the polymer in the absence of SDS. Prior to phase separation, $R_h = 15.2$ nm. An increase in R_h, in this case from $r = 0.3$ to 0.4, prior to phase separation was also observed in the PCMA-SDS system [20]. In the latter system, however, the maximum degree of charge neutralization was only 0.2 due to the high charge density of the polymer, 1.0, and consequently the system possesses a larger two-phase region. The dotted line in Fig. 4a indicates the two-phase region for the present system. At $r = 2.0$ the complex is resolubilized, and $R_h = 27.2$ nm which is larger than that prior to the precipitation point at $r = 0.4$. This is mainly attributed to steric effects, since the resolubilized complexes contain much more surfactant. The net charge of the resolubilized complexes is negative. The R_h values of the SDS/31% MAPTAC-AM complex are overall larger than those for the other system at corresponding degrees of neutralization (SDS/MAPTAC) owing to the higher molecular weight. At $r = 3.3$, at which free regular micelles are present, R_h has decreased to 24.0 nm due to screening of the electrostatic interaction by surrounding unbound micelles. De Oliveira et al. [27] studied the interaction between cationic surfactants and acrylic acid-ethyl methacrylate copolymers. In that system, the neutral units of the copolymer participate in the interaction due to their pronounced hydrophobicity. They found a reduction in both the cac and the surfactant aggregation number as the number of neutral units increased. It was concluded that complexation started where intramolecular hydrophobic moieties on the polymer were already formed. Satake et al. [28] made studies on the cooperative binding isotherm of dodecyltrimethylammonium ions to partially hydrolyzed poly(potassium vinyl sulfate), where the charge density α of the latter was varied between 0.07 and 1.0. They found a rapid decrease in the cooperative binding constant, u, with decreasing α from 1.0 to 0.6, followed by a gradual decrease to unity at $\alpha = 0.07$. These results

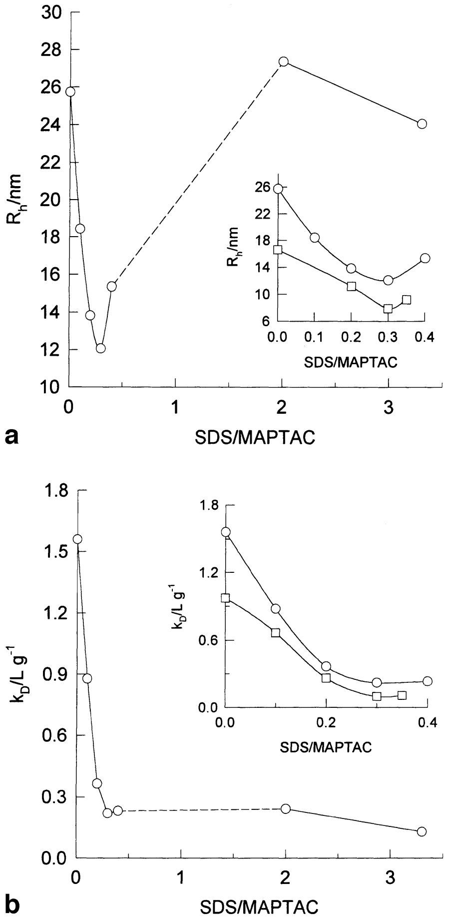


Fig. 4a Hydrodynamic radii of the single-chain complex at different SDS/MAPTAC molar ratios for the copolymers of charge density 0.31 (O) and 0.66 (□). **b** Hydrodynamic virial coefficients attributed to the fast relaxation mode at different SDS/MAPTAC molar ratios for the copolymers of charge density 0.31 (O) and 0.66 (□)

showed that a strong hydrophobic interaction between neighboring bound surfactant ions appears at α values higher than 0.6.

Figure 4b shows the hydrodynamic virial coefficients, k_D, of the single-coil complexes formed between SDS and 31 and 66% MAPTAC-AM, respectively, at different r. As expected, the complex-solvent attraction (i.e., the complex-complex repulsion) decreases as the charge density of the complex decreases upon binding of surfactant. At a fixed r value, the copolymer of charge density 0.31 should have a higher k_D value since it possesses a larger percentage of hydrophilic units: a major fraction of neutral AM units which does not interact with SDS, and a minor fraction of charged MAPTAC units not occupied by SDS. For example, at $r = 0.2$, 20% of the MAPTAC units are neutralized. This means that 6.2 and 13.2% of the segments in the 31 and 66% MAPTAC-AM copolymer chains, respectively, are associated with surfactant. Thus at a fixed value of r, the number of hydrophobic moieties in the complex, deriving from the neutralization of MAPTAC units by SDS, increases with the charge density of the copolymer, i.e., there will be a reduction in k_D.

Viscometry

Figure 5 depicts the intrinsic viscosities of the two surfactant-copolymer systems at different values of r. For both systems there is a decrease in $[\eta]$ with increasing neutralization degree up to phase separation, reflecting the complex coil transition from extended to more compact structures with increasing hydrophobic moieties. At $r = 2.0$ and 3.3 (for the copolymer with $\alpha = 0.31$), $[\eta]$ is still much lower than in the absence of surfactant and also lower than prior to phase separation, while R_h has a magnitude comparable to that in the absence of SDS. Since viscosity is a bulk property of the system, the observations would not be expected to be identical to those using DLS. However, both R_h and $[\eta]$ are related to the hydrodynamic volume of the complexes, where the former is determined from the fastest relaxation mode, attributed to the single-coil complex, from the ILT data. The $[\eta]$ values from capillary viscometry are determined from measurements in which the aggregates will have an impact on the concentration dependence of the reduced viscosity, since they are present even at low concentrations. $[\eta]$ will reflect the entire spectrum of the relaxation modes from ILT, including small and large aggregates. The main relaxation mode in Fig. 1a (corresponding to larger particles) is much slower than the main relaxation mode in Fig. 2b. This is in line with the $[\eta]$ data, as $[\eta]$ at $r = 0.1$ is higher than at $r = 3.3$.

Figure 6 shows the apparent viscosity, η, as a function of polymer concentration for 66% and 31% MAPTAC-AM at different values of r and for relatively high polymer concentrations up to about 2.5%. The values are determined by the Newtonian plateau values measured during transient shear experiments. At a fixed polymer concentration C_p in the lower concentration range, there is a reduction in η as a function of added SDS up to the precipitation point. This effect arises from the neutralization of polyelectrolyte charges on binding the oppositely charged surfactant micelles. On the other hand, considering a fixed C_p above 1.2%, there is a very strong increase in η with increasing SDS concentration as clearly indicated by the logarithmic scale of the y-axis, in particular at $C_p = 2.4\%$. There is a similarity between this picture and that found by Wang et al. [7, 29] for hydrophobically modified polyacrylic acid in aqueous solution, where the viscosity

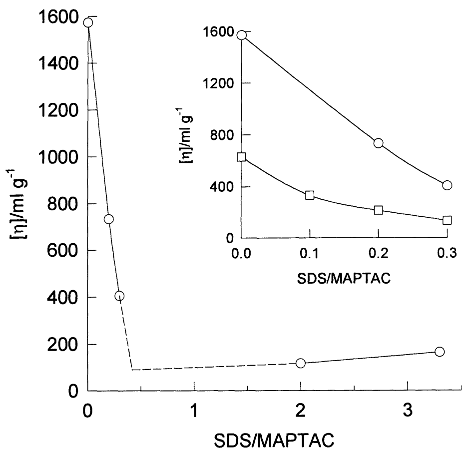


Fig. 5 Intrinsic viscosities at different SDS/MAPTAC molar ratios for the copolymers of charge density 0.31 (O) and 0.66 (□)

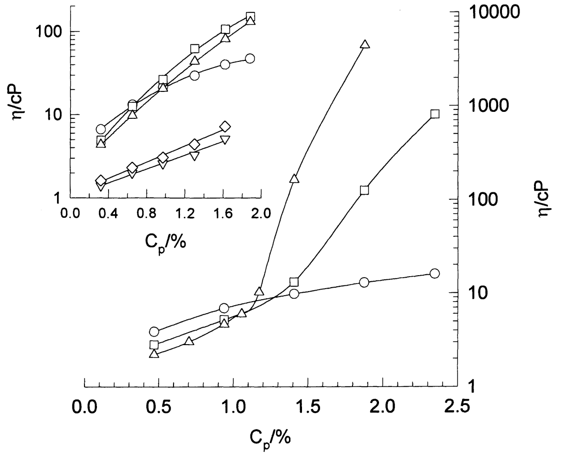


Fig. 6 Concentration dependence of the static viscosity at zero shear rate for the copolymers of charge densities 0.66 and 0.31 (insert) at the SDS/MAPTAC molar ratios 0 (O), 0.1 (□), 0.2 (△), 2.0 (▽), and 3.3 (◇)

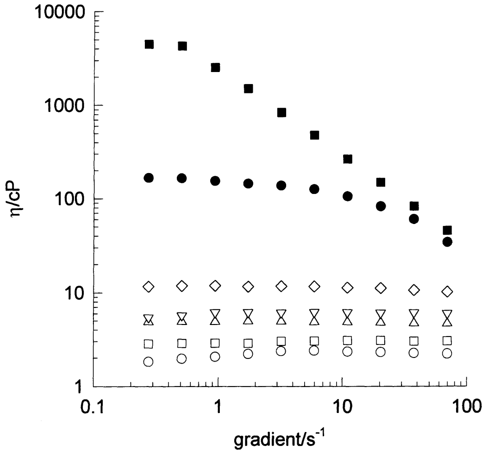


Fig. 7 The static viscosity as a function of the shear gradient for the copolymer of charge density 0.66 at the SDS/MAPTAC molar ratio 0.2. The polymer concentrations are 0.24 (O), 0.47 (□), 0.71 (△), 0.94 (▽), 1.41 (◇), 1.88 (●), and 2.35% w/v (■). At 2.35% w/v (138 mM), [MAPTAC] = 91.1 mM

initially increases as the number of hydrocarbon side chains is increased. Similar behavior has also been observed for other hydrophobically modified water-soluble polymers (HMWSP) [30]. Thus, by increasing the surfactant/polyelectrolyte charge ratio, implying an increase in the hydrophobic content of the complex on neutralization, one may obtain the same rheological behavior of the system as when the extent of hydrophobic modification of the polyelectrolyte in the absence of surfactant is increased. However, in the case of HMWSP a maximum in the viscosity is observed at an optimal degree of modification, due to the transition from intra- to intermolecular hydrophobic interactions [31]. In our case, the system passes sharply from the high-viscosity regime to phase separation at high polymer concentrations. This pronounced increase in viscosity with increasing r was not observed for a 95% charged cationic homopolymer (only 5% of AM units). In the latter system association with SDS at $C_{\mathrm{p}} = 2.4\%$ leads directly to phase separation. Obviously, a minimum number of AM units in the cationic copolymer is necessary in order to balance the strong electrostatic interactions with SDS. Finally, there is a strong increase in η as a function of C_{p}, especially at an r value prior to precipitation. Apparently an increase in polymer concentration promotes the formation of an incipient network. This effect is observed at both charge densities of the copolymer, but is more emphasized at $\alpha = 0.66$.

In Figure 7, η values are depicted as a function of the shear gradient at different polymer concentrations at $r = 0.2$ and $\alpha = 0.66$. At 1.9 w/v, the system resembles a reversible gel with an apparent viscosity of 4500 cP. Moreover, it exhibits shear-thinning behavior at high concentrations and at high shear rates. The main reason for the non-Newtonian behavior is the orientation of molecular segments by the flow field, and this orientation is increased by entanglements or crosslinks in the system. At high shear rates the crosslinks will be broken, resulting in a decrease in η. These results reinforce the conclusion of network formation in the present surfactant-copolymer system.

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