Articles

Study of Interaction between Sodium Dodecyl Sulfate and Polyacrylamide by Rheological and Conductivity Measurements

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The interaction between sodium dodecyl sulfate (SDS) and nonionic polymer polyacrylamide (PAM) was investigated by viscosity and conductivity measurements at 298 K. The experimental results show that the critical aggregation concentration (CAC) value of SDS + 1 % mass fraction PAM only decreases a little as compared with the value of critical micelle concentration (CMC) of the surfactant SDS. The maximum viscosity of SDS + 1 % mass fraction PAM indicated that PAM chain extended at the binding site. When SDS concentration is above the CAC, the viscosity of SDS + 1 wt % PAM decreases reflecting the contraction of polymer PAM chains. The free energy of polymer-bound micelle is negative, indicating a strong interaction between SDS and PAM.

Introduction

Interactions between ionic and nonionic polymers and surfactants have been studied extensively in recent years from both academic and practical viewpoints.[1−4] These interactions are relevant to biological systems and processes, and they have applications in detergents, paints and coatings, cosmetics, pharmaceuticals, tertiary oil recovery, and other industrial fields. Therefore, an intensive effort has been made to characterize the nature of these interactions as well as their impact on phase separation, rheological, and interfacial properties with special relevance to the various commercial applications.

While the interactions of nonionic polymers with ionic surfactants are well-characterized by highly cooperative surfactant binding arising from hydrophobic interaction between the bound surfactant ions,[5−7] the situation in the oppositely charged systems is more complex and behaves quite differently. There is evidence of a specific binding mechanism involving cooperative and noncooperative steps as well.[8] The formation of salt-like bridging between the opposite charges seems to be responsible for starting the binding, as an "initiation process", while the nearest neighbor hydrophobic interaction between the surfactant molecules bound onto the polymer stabilizes the polymer−surfactant complexation, as micelle-like complex structures (or aggregates) are formed. This cooperative binding has been found to depend on a variety of factors, such as the length of the surfactant ion carbon chain[9−11] and the salt concentration.[12,13]

Another interesting feature of the surfactant−polymer interaction is the changes in the polymer conformation as a consequence of surfactant binding. Fluorescence studies[14,15] revealed a contraction of oppositely charged polymer−surfactant complexes for the aqueous mixtures of poly(acrylic acid) and alkyltrimethylammonium bromides before precipitation. They found that intrapolymer complex formation occurs at low polymer concentration, and in the limit of excess surfactant concentration, strong chain expansion occurs due to the repulsion between the bound micelle. Similar results[16] were observed for sodium hyaluronate/tetradecyltrimethylammonium bromide mixtures by viscosity measurements. A minimum of viscosity as a function of surfactant concentration was found, which was interpreted by an initial contraction followed by an expansion of the polymer coil as a consequence of the intense micellar binding.

Addition of polymers could effectively reduce the critical micelle concentration (CMC) of surfactants and, thus, increase the detergency. Surfactant molecules interact with polymers at a critical aggregation concentration (CAC) forming micelle-like clusters along the polymer chains. Below CAC, there is no interaction between the surfactant and the polymer. CAC is used as a marker to measure the strength of the binding interaction between surfactant and polymer. Meszaros et al.[17] studied the effect of polymer molecular weight on the polymer/surfactant interaction and concluded that the CAC does not depend on the polymer molar mass if the polymer molar mass exceeds 8000.

The structure of soluble polymer−micelle complexes is of interest for several reasons. Polymer−micelle complexes represent a degree of self-organization that is remarkable in purely abiotic systems; surfactant molecules, organized in micelles are bound within the domains of a polymer chain, which then may or may not form a higher-order aggregate.[18] In some cases, it appears that a particular association state is much preferred, and the way in which a combination of hydrophobic and electrostatic forces leads to the stabilization of one particular structure has

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obvious relevance to the understanding of natural polymer assemblies. A final question arises regarding the influence of the relative sizes of the surfactant and the polymer. Polymer−micelle complexes have been described as a "necklace of beads",[18] a model that obviously breaks down when the micelle size approached that of the polymer. It is interested to consider whether there is a structural discontinuity in the region where the ratio of micelle dimensions to polymer dimensions exceeds unity and whether the overall structure depends on the absolute or the relative sizes of the two macroionic species.

A central unanswered question is whether the oppositely charged polymer−surfactant complexes, resembling those proposed for complexes of poly(ethylene oxide) and SDS micelles,[19] exist under any conditions. Such complexes might then undergo further association to form higher-order complexes. On the other hand, complexes might always be multipolymer and rather polydisperse. Considerations of this type are relevant to the general question of how it is that stable complexes of finite size are formed. Dynamic light scattering and rheological measurement seems the best method to answer this question.

For the studied surfactant−polymer systems with opposite charges, rheological measurement is seldom employed. This is mainly attributed to the difficulty owing to the formation of the insoluble surfactant−polymer complex salts (the surfactant ion + the polyion) in conjoint presence of the soluble simple salt made of the two oppositely charged simple ions dissociated from surfactants and polymers, respectively. Indeed, the shear behaviors of the SDS solution with the addition of two different cationic polyelectrolytes were reported as "highly irreproducible" by Leung et al.,[20] who instead proposed that the oscillatory-type rheometer was necessary for further studies on the shear behaviors in such systems.

The purpose of this work is an attempt to provide greater understanding of the shear behavior of the ionic surfactant and nonionic polymer system. SDS, an anionic surfactant, and a nonionic polymer, PAM, are chosen for this work. The effect of the shear rate on the rheological behavior and conductivity of the surfactant−polymer solution is assessed. We focused on polymer conformation change; the thermodynamic property and interaction strength between surfactant and polymer was discussed.

Experimental Section

Materials. Sodium dodecyl surfate (SDS) with purity 99.5 % from Sigma was used without further purification. Polyacrylamide (PAM) with average molecular weight of 5 000 000 was received from Aldrich. Water was deionized and Millipore filtered by a Milli-Q system.

Methods. The rheology (viscosity) measurements of SDS + 1 % mass fraction PAM aqueous solutions were carried out at 298 K, using an automatic viscometer (programmable Brookfield DV-II+ viscometer) with spindle S18, shear rate from (0 to 264) s^{-1} (132 rpm), viscosity from (0.5 to 30) Pa·s. The viscosity uncertainty was within 0.5 % of full-scale range, and the repeatability of measured viscosity was above 99.8 %. The sample volume was 8.0 mL.

Conductivity of SDS + 1 % mass fraction PAM aqueous solutions with various SDS concentrations were carried out at 298 K, using the Oyster conductivity/temperature meter (EXTECH Instruments). We used (0.01 and 0.1) $mol·L^{-1}$ NaCl solutions to calibrate the conductance cell. The conductivity uncertainty was within 1.0 % of full-scale range, and the repeatability of measured conductivity was above 99.5 %. The balance used was AY120, which can measure up to 0.1 mg.

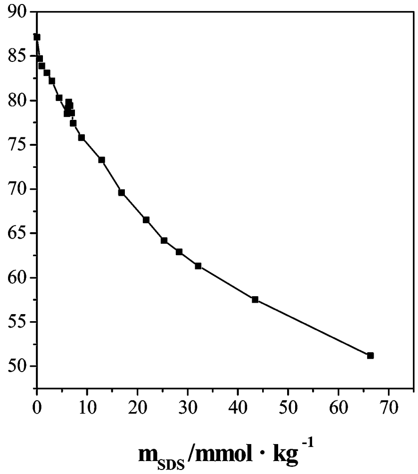

Figure 1. Viscosity η of sodium dodecyl sulfate (SDS) + 1 % mass fraction polyacrylamide (PAM) aqueous solutions at 298 K.

Table 1. Viscosity η and Conductivity κ of Sodium Dodecyl Sulfate (SDS) + 1 % Mass Fraction Polyacrylamide (PAM) Aqueous Solutions at 298 K

m_{SDS}	η	κ	m_{SDS}	η	κ
$mmol·kg^{-1}$	mPa·s	$10^{-2}\,m^2·s·mol^{-1}$	$mmol·kg^{-1}$	mPa·s	$10^{-2}\,m^2·s·mol^{-1}$
0	87.1	1.40	7.2	77.4	1.80
0.5	84.7	1.47	8.9	75.8	1.81
1.0	83.9	1.48	12.9	73.3	1.91
2.0	83.1	1.57	16.9	69.6	1.98
3.0	82.2	1.64	21.8	66.5	2.09
4.4	80.3	1.70	25.3	64.2	2.14
6.0	78.5	1.74	28.3	62.9	2.18
6.2	79.1	1.80	32.1	61.3	2.23
6.3	79.8	1.83	43.5	57.5	2.42
6.6	79.4	1.77	66.4	51.2	2.98
6.9	78.6	1.79			

Results and Discussion

Viscosity of SDS + 1 % Mass Fraction PAM Aqueous Solutions. Table 1 lists the viscosity and conductivity of sodium dodecyl sulfate (SDS) + 1 % mass fraction polyacrylamide (PAM) aqueous solutions with various SDS concentrations at 298 K.

The viscosity radius R_η based on a theory for spheres can be calculated from the light scattering equation:[21]

$$R_\eta = (3M\eta/10\pi N_A)^{1/3} = A\eta^{1/3} \qquad (1)$$

where η is the viscosity of the surfactant-polymer solution, and A is a constant for the certain surfactant−polymer system. From eq 1, it is clear that the higher the viscosity of surfactant−polymer solution, the larger the R_η value. The viscosity radius is sometimes referred to as the equivalent hydrodynamic radius. Though the viscosity radius cannot be calculated directly from this equation, the relative value at different SDS concentration shows the tendency of polymer chains changes. The viscosity increases confirmed the increase of particle size of surfactant−polymer solution.

The outcome of the surfactant bindings by electrostatic attraction is normally a reduction in the viscosity of the system and a loss of polymer solubility to the point of charge reversal.[22] Macroscopically, the above events may lead to dramatic changes in the viscosity of the system due first to the collapse of the polymer coils, followed by a rapid expansion after charge reversal has taken place.

Our experimental findings convincingly show that SDS addition lowers the viscosity of surfactant−polymer aqueous solution. Figure 1 shows the variation of the viscosity of SDS

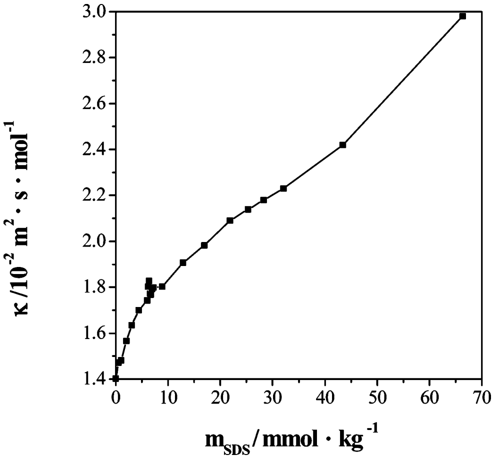

Figure 2. Conductivity κ of sodium dodecyl sulfate (SDS) + 1 % mass fraction polyacrylamide (PAM) aqueous solutions at 298 K.

+ 1 % mass fraction PAM aqueous solutions versus SDS concentrations at 298 K. The viscosity decreases with increasing SDS concentration not so much at first, as SDS concentration reaches 6.0 mmol·kg^{-1}. The reduced viscosity behavior should be related to the formation of polymer−surfactant complexes, resulting in a contraction of the polymer chains, due to the gradual neutralization of their positive charges by the negative surfactant heads.[23,24] Then it increases within a narrow SDS concentration range from (6.1 to 6.3) mmol·kg^{-1}. The relative maximum viscosity corresponding to SDS concentration is CAC of SDS + 1 % mass fraction PAM, which indicated that SDS and PAM complex began to be formed. Electrostatic attraction between the charged micellar headgroup and polymer PAM effectively reduces the headgroup repulsion in the bound micelle and together with the enhancement of the hydrophobic effect contribute to a reduction in the bound micellar free energy, which results in the promotion of polymer-bound micelles at lower surfactant concentration than in pure SDS solutions. The CMC of SDS aqueous solution is about 8.5 mmol·kg^{-1}.[25−27] The CAC value of SDS + 1 % mass fraction PAM is almost at the same magnitude, only little lower than the CMC of SDS. The lower the value of CAC, the stronger is the interaction strength between SDS and PAM. The formation of SDS + PAM complex lead to the expansion of polymer PAM chains and the increase of viscosity at the binding site, which confirmed that the polymer−micelle aggregate forms an extended structure at the binding site. When SDS concentration is above the CAC, the viscosity decreases again with increasing SDS concentration significantly. With surfactant-to-polymer ratio larger than unity, the SDS + PAM complexes will be saturated with surfactant and free micelles coexist with the complexes.[28] This constitutes the so-called “self-salt” effect exhibited by SDS and its counterion and the effect of saturating PAM with SDS. Free counterions and unassociated SDS micelles contribute to the ionic strength of the solution that shields the increasingly SDS + PAM aggregates and counteracts any increase in viscosity. Ultimately, the overall effect is a compact structure induced by electrostatic screening and hydrophobic interaction and leads to the reduction of viscosity and the formation of thermodynamically stable solution. The free micelles of the surfactant exist in the SDS + PAM solutions, and the tails of the surfactant molecules that adsorb onto the polymer reflect a contraction of the polymer coil.

Conductivity of SDS + 1 % Mass Fraction PAM. The formation and dissociation of micelles was monitored by conductivity measurement if the system was ionic. Figure 2 shows the conductivity of SDS + 1 % mass fraction PAM solutions with various SDS concentrations at 298 K. The conductivity increases first with SDS concentration,then decreases a little within a narrow SDS concentration range, and finally increases significantly again with increasing SDS concentration. On the first stage, below the CAC, there is no interaction between the surfactant SDS and the polymer PAM. Na$^+$ ion concentration increases with increasing SDS concentration, leading to the increase of the conductivity. The relative maximum conductivity SDS value corresponds to the CAC value of SDS + 1 % mass fraction PAM solution, which is 6.3 mmol·kg^{-1}, and agrees well with that obtained from viscosity measurement. As the surfactant concentration exceeds the CAC, the surfactant SDS starts to bind the polymer PAM. As the total surfactant concentration increases, the bound amount rapidly increases, which is accompanied by a slow increase of the monomer surfactant activity until it reaches the critical micelle concentration (CMC) of the surfactant SDS. Above this CAC concentration within a narrow SDS concentration range, the complexes of SDS and PAM are formed, the polymer may be saturated with the surfactant, and the polymer chain extends resulted in the decrease of absorbed negative charges on the polymer chain leads to the decrease of Na$^+$ ion concentration. After this range, SDS concentration increases, free SDS micelles are formed in the solution, and the monomer surfactant activity increases leads to the increase of the conductivity of the solution. The hydrophobic interaction between SDS and PAM is the main contribution to the interaction where polymer PAM chains curl and Na$^+$ ion concentration increases abruptly, so the conductivity increases significantly.

Table 2. Values of Critical Micelle Concentration (CMC), Critical Aggregation Concentration (CAC), and Free Energy Change (ΔG_{ps}) of Sodium Dodecyl Sulfate (SDS), SDS + 1 % Mass Fraction Polyacrylamide (PAM) Aqueous Solutions at 298 K

	SDS	SDS + 1 % mass fraction PAM
CMC/(mmol·kg^{-1})	8.5	
CAC/(mmol·kg^{-1})		6.3
ΔG_{ps}/(kJ·mol^{-1})		−1.2

Interaction Strength between Surfactant and Polymer. The free energy of micellization ΔG_{mic} in absence of polymer and the free energy of aggregation ΔG_{agg} in the presence of polymer can be calculated using the following equations:[29]

$$\Delta G_{mic} = (1 + K)RT \ln C(\mathrm{CMC}) \tag{2}$$

$$\Delta G_{agg} = (1 + K)RT \ln C(\mathrm{CAC}) \tag{3}$$

where K is the effective micellar charge fraction. For SDS, K was found to be 0.85.[29] We can derive the free energy per mole of surfactant for the reaction: free micelle = polymer-bound micelle, as

$$\Delta G_{ps} = \Delta G_{agg} - \Delta G_{mic} = (1 + K)RT \ln C(\mathrm{CAC/CMC}) \tag{4}$$

This quantity is a convenient measure of the interaction strength between the surfactant and the polymer. The lower the value of CAC, the stronger is the binding strength between surfactant and polymer. The values of CAC obtained by viscosity and conductivity in SDS + 1 % mass fraction PAM aqueous solutions at 298 K and the calculated ΔG_{ps} according to eq 4 are listed in Table 2. ΔG_{ps} of SDS + 1 % mass fraction PAM is a large negative value, indicating that the interaction between surfactant SDS and nonionic polymer PAM is strong.

Conclusion

The interaction between surfactant SDS and polymer PAM was investigated by viscosity and conductivity measurements.

The CAC value of SDS + 1 % mass fraction PAM is at the same magnitude of CMC of surfactant SDS and only decreases a little. The PAM chain extended at the binding site due to the increase of viscosity. Above the CAC, the viscosity of SDS + 1 % mass fraction PAM aqueous solutions decreasing with increasing SDS concentration confirmed the shrinking of PAM chains and formed a more compact structure. The interaction between surfactant SDS and nonionic polymer PAM is strong.

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