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Investigation on the Interaction between Sodium Dodecyl Sulfate and Cationic Polymer by Dynamic Light Scattering, Rheological, and Conductivity Measurements

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The interaction between sodium dodecyl sulfate (SDS) and the cationic polymer poly(diallyldimethylammonium chloride) (PDAC) was investigated by viscosity, conductivity, and dynamic light scattering measurements at 298 K in order to monitor the changes in the charged nature and size of SDS + PDAC complexes. The experimental results showed that the critical aggregation concentration (CAC) value of SDS + 1 % mass fraction PDAC is almost 2 orders of magnitude lower than the critical micelle concentration of SDS. The viscosity of the SDS + PDAC solution increased with decreasing shear rate, exhibiting non-Newtonian behavior. The minimum viscosity and hydrodynamic diameter of SDS + PDAC complexes at the binding site confirmed the contraction of the polymer chain and the formation of a more compact structure. When the SDS concentration was above the CAC, the viscosity and hydrodynamic diameter increased, indicating that the PDAC chains first extended and finally collapsed and precipitated. The binding degree of SDS + 1 % mass fraction PDAC was from $\beta < 1$ to $\beta \approx 1$. The interaction between SDS and PDAC can be divided into different characteristic SDS concentration ranges. At low SDS concentration, the surfactant-polymer system is a thermodynamically stable solution of the surfactant + polymer complex molecules. Above this critical concentration, the system is an unstable colloid dispersion of SDS + PDAC complex particles. The interaction between SDS and PDAC is favored and strong.

Introduction

An intensive effort has been made to characterize the nature of the interaction between polymers and surfactants due to their wide commercial applications and academic viewpoints. The interaction of oppositely charged polymers with ionic surfactants is more complex and exhibits quite different behavior than the interaction between nonionic polymers and surfactants. There is a growing trend to consider these interactions as basically cooperative in nature and as a kind of surface charge neutralization of a micelle via oppositely charged flexible polymers.[1−6] On the other hand, there is also evidence of noncooperative surfactant binding[7] and also a specific binding mechanism involving cooperative and noncooperative steps as well.[8] The formation of salt-like bridging between 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] the salt concentration,[12,13] and the polyion charge density.[14]

Another interesting feature of the interaction between surfactant and polymer is the changes in the polymer conformation as a consequence of surfactant binding. Fluorescence studies[15,16] have revealed the contraction of oppositely charged polymer−surfactant complexes for aqueous mixtures of poly(acrylic acid) and alkyltrimethylammonium bromides before precipitation. They found that intrapolymer complex formation occurs at low polymer concentration and that, in the limit of excess surfactant concentration, strong chain expansion occurs due to the repulsion between the bound micelle.[15,16] Similar results[17] were observed for sodium hylauronate−tetradecyltrimethylammonium 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 intense micelle binding.

The addition of polymers to the surfactant solution could effectively reduce the critical micelle concentration (CMC) of surfactants and also can increase the detergency. Surfactant molecules interact with polymers at a critical aggregation concentration (CAC) forming micelle-like clusters along the polymer chains. The CAC is used to measure the strength of the binding interaction between surfactant and polymer. 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 preferred, and the way in which a combination of hydrophobic and electrostatic forces leads to the stabilization of one particular structure has 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",[19] a model that obviously breaks down when the micelle size approaches that of the polymer. It is interesting to consider whether there is a structural discontinuity in the region where the ratio of micelle dimensions to polymer dimensions exceeds

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unity, and whether the overall structure depends on the absolute or the relative sizes of the two macro-ionic species.

A central unanswered question is whether the oppositely charged polymer−surfactant complexes, resembling those proposed for complexes of polyethylene 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. Consideration of this type are relevant to the general question of how it is that stable complexes of finite size are formed. Dynamic light scattering (DLS) 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 difficulties arising from the formation of insoluble surfactant−polymer complex salts (the surfactant ion + the polyion) in conjoint presence of a soluble simple salt made from two oppositely charged simple ions that have 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 of shear behavior in such systems.

The purpose of this work is to attempt to provide more understanding of the shear behavior of the surfactant−polymer system with opposite charges. An anionic surfactant SDS and cationic polymer PDAC have been chosen for this work. The effect of aggregate size on the rheological behavior is assessed by using DLS. Polymer conformation changes, binding degree, and finite size of polymer and polymer + surfactant complexes have been studied. The thermodynamic properties and interaction strength between surfactant and polymer are discussed.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS) with purity 99.5 % from Sigma was used without further purification. Poly(diallyldimethylammonium chloride) (PDAC) with medium molecular weight of 200 000 to 350 000 was received from Sigma and used without further purification. Water was deionized and Millipore-filtered by a Milli-Q system.

Methods. The rheology (viscosity) measurements of SDS + 1 % mass fraction PDAC aqueous solutions were carried out at 298 K, using an automatic viscometer (programmable Brookfield DV-II+ viscometer) with spindle S18. The shear rate is from (0 to 264) s^{-1}, and the viscosity measurement range is 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 used for measurement is 8.0 mL and kept constant.

The conductivity of SDS + 1 % mass fraction PDAC 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) $\text{mol} \cdot \text{L}^{-1}$ NaCl solutions to calibrate the accuracy of the conductance. The conductivity uncertainty was within ± 1.0 % of full-scale range, and the repeatability of measured conductivity was above 99.5 %.

DLS. The size distribution (particle diameter) was measured using a dynamic light scattering instrument (Malvern, high performance particle sizer (HPPS)). The Malvern HPPS is a unique instrument capable of measuring the size of molecules in solution as well as the size of dispersions and emulsions and up to 20 vol % from sub-nanometer to a few microns (from 0.6 to 6000 nm) using DLS. Measurements are made in conventional cuvettes, eliminating the possibility of sample cross-contamination.

Table 1. Viscosity/Concentration (η_{SP}/c_p) of PDAC at Different Polymer Concentrations at 298 K

$C_p/\text{g} \cdot \text{kg}^{-1}$	$(\eta_{SP}/c_p)/\text{mPa} \cdot \text{s}$
0.1	
0.5	9.06
1.0	6.27
2.0	
3.0	4.27

HPPS has the highest sensitivity of any DLS system available. The uniformity index of the surfactant−polymer aqueous solutions is characterized by a parameter termed the polydispersity index. Despite the polydispersity of the samples, the mean hydrodynamic diameter is used for the presentation of the changes in the hydrodynamic size distribution caused by the addition of the SDS. The size distribution by volume of the sample is from 0.6 nm to 6 μm by HPPS measurement. The size uncertainty was within ± 1.0 % of full-scale range, and the repeatability of measured size was above 99.5 %.

All surfactant + polymer aqueous solutions were filtered through a 0.2 μm Acrodisc filter into a 1.6 mL cuvette. The balance used was AY120, which can measure up to 0.1 mg.

Results and Discussion

Viscosity of SDS−PDAC. Table 1 lists the viscosity of PDAC aqueous solutions at various polymer PDAC concentrations and viscosity/polymer concentrations (η_{SP}/c_p) at 298 K. The (η_{SP}/c_p) decreases with increasing polymer concentration confirming that the cationic polymer PDAC is a polyelectrolyte.

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

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

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

The outcome of 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 collapse of the polymer coils, followed by a rapid expansion after charge reversal has taken place.

Table 2 and Figure 1 detail the viscosity of SDS + 1 % mass fraction PDAC aqueous solution with various SDS concentrations at different shear rates at 298 K. The viscosity of SDS + 1 % mass fraction PDAC aqueous solution decreases with increasing SDS concentration. When the SDS concentration reached 0.11 $\text{mmol} \cdot \text{kg}^{-1}$, then the viscosity increases with SDS concentration up to 16.2 $\text{mmol} \cdot \text{kg}^{-1}$ at all shear rates. The solution viscosity decreases with increasing shear rate and exhibits non-Newtonian behavior. The minimum value of viscosity corresponded to a SDS concentration of 0.11 $\text{mmol} \cdot \text{kg}^{-1}$ and is the CAC of SDS + 1 % mass fraction PDAC aqueous

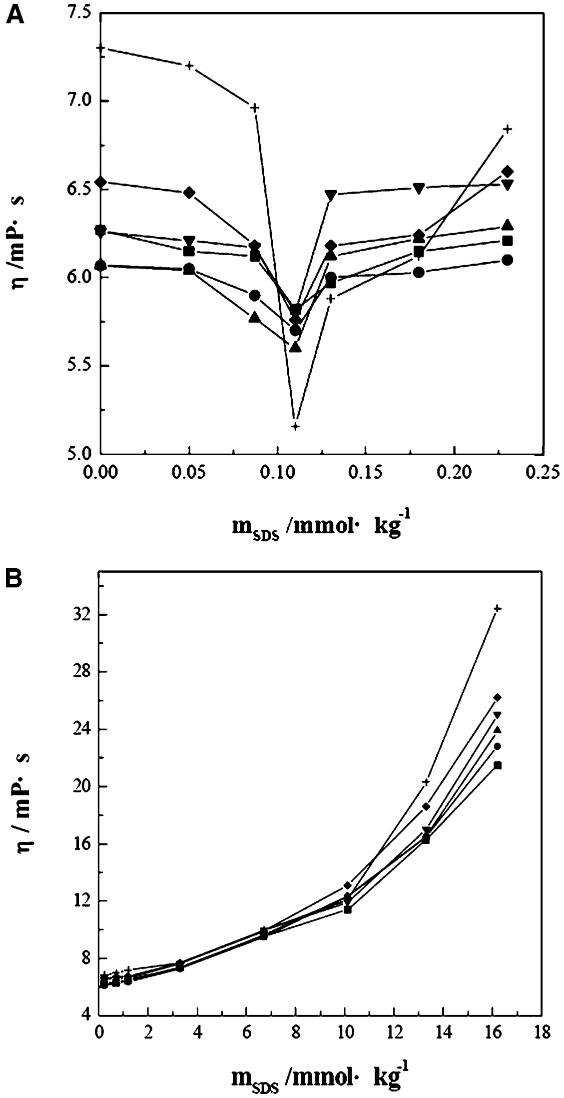

Figure 1. (a) Viscosity of SDS + 1 % mass fraction PDAC aqueous solutions with various SDS (0 to 0.2 mmol·kg^{-1}) concentration at different shear rate at 298 K. Shear rate: ■, 100; ●, 90; ▲, 80; ▼, 70; ◆, 50; +, 25 rpm. (b) Viscosity of SDS + 1 % mass fraction PDAC aqueous solutions with various SDS (0.2 to 16.2 mmol·kg^{-1}) concentration at different shear rate at 298 K. Shear rate: ■, 100; ●, 90; ▲, 80; ▼, 70; ◆, 50; +, 25 rpm.

Table 2. Viscosity (η/mPa·s) of SDS + 1 % Mass Fraction PDAC Aqueous Solutions at Different Shear Rates at 298 K

m_{SDS}/mmol·kg^{-1}	100 rpm	90 rpm	80 rpm	70 rpm	50 rpm	25 rpm
0	6.27	6.07	6.07	6.26	6.54	7.30
0.05	6.15	6.05	6.04	6.21	6.48	7.20
0.09	6.12	5.90	5.77	6.17	6.18	6.96
0.11	5.82	5.70	5.60	5.80	5.76	5.16
0.13	5.97	6.00	6.12	6.47	6.18	5.88
0.18	6.15	6.03	6.22	6.51	6.24	6.12
0.23	6.21	6.10	6.29	6.53	6.60	6.84
0.70	6.30	6.27	6.35	6.56	6.72	6.96
1.20	6.48	6.37	6.49	6.64	6.76	7.20
3.30	7.35	7.27	7.31	7.63	7.68	7.68
6.70	9.57	9.53	9.64	9.94	9.90	9.96
10.10	11.40	12.30	12.30	11.90	13.10	12.10
13.30	16.30	16.50	16.50	17.00	18.60	20.30
16.20	21.50	22.80	23.90	25.00	26.20	32.40

Table 3. Conductivity (κ) of SDS + 1 % Mass Fraction PDAC Aqueous Solutions at Different SDS Concentrations at 298 K

m_{SDS}/mmol·kg^{-1}	κ/10^{-2} m^2·s·mol^{-1}
0	2.73
0.03	2.61
0.05	2.57
0.09	2.63
0.11	2.67
0.13	2.63
0.18	2.60
0.27	2.60
0.70	2.60
1.20	2.60
3.30	2.72
6.74	2.97
10.10	3.06
13.30	3.20
30.90	4.03

solution at which the complex of SDS and PDAC began to be formed. The CMC of the SDS aqueous solution is about 8.5 mmol·kg^{-1}.[23,24] The CAC value of the SDS + 1 % mass fraction PDAC aqueous solution is almost 2 orders of magnitude lower than the CMC of SDS. 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.[25,26] After reaching the minimum value, the viscosity increases but only slightly, and the solutions are clear when the SDS concentration is below 1.2 mmol·kg^{-1}. The resulting repulsive electrostatic interactions prevent polymer chain collapse and precipitation. The complexes are soluble. The neutralization of their positive charges by the negative surfactant heads is not complete, and the binding degree is less than 1. The viscosity increases with increasing SDS concentration when the SDS concentration is above 1.2 mmol·kg^{-1}, which leads to the expansion of the PDAC coil. Above this concentration, the solution is not clear and the viscosity and viscosity radius of the surfactant + polymer system increases significantly. The observed significant increase in viscosity is, after a point, explained by the formation of insoluble polymer + surfactant complexes, and the binding degree β is close to 1. This lack in solubility should be related to the complete neutralization of the polyelectrolyte charges by negative SDS heads and to the attractive hydrophobic interactions between the SDS molecules bound onto the polymer PDAC and to the increased content of the complex in the hydrophobic surfactant tails. This increasing viscosity behavior confirmed a substantial expansion of the polymer coil (collapse and precipitation), indicating that the hydrophobic interaction between the bound surfactant molecules is much stronger than the electrostatic interaction between PDAC and SDS molecules. Such an explanation of the polymer coil and viscosity changes is further supported by the DLS results discussed below. The interaction between SDS and PDAC can be clearly divided into different characteristic SDS concentration ranges. At low SDS concentration, below 150 times the CAC, the surfactant + polymer system is a thermodynamically stable solution of the surfactant + polymer complex molecules. Above this critical concentration, the system is an unstable colloid dispersion of SDS + PDAC complex particles.

Conductivity of SDS + PDAC. The formation and dissociation of micelles can be monitored using conductivity measurements if the system is ionic. Table 3 and Figure 2 show the conductivity of SDS + 1 % mass fraction PDAC solutions versus SDS concentration at 298 K. The conductivity first decreases a little with increasing SDS concentration, then increases slightly within a narrow SDS concentration, after that decreases a little again, and finally increases significantly with SDS concentration. In the first stage, the conductivity decreases with SDS concentration is due to the fractional neutralization of the positive charges of PDAC by the negative surfactant heads

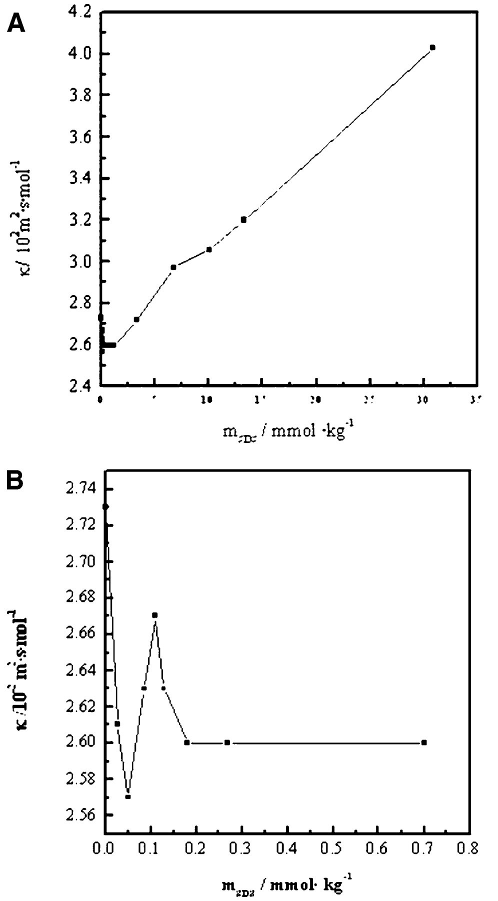

Figure 2. (a) Conductivity of SDS + 1 % mass fraction PDAC with various SDS concentration at 298 K. (b) Conductivity of SDS + 1 % mass fraction PDAC with various SDS (0 to 0.7 mmol $\cdot$kg^{-1}) concentration at 298 K.

lead to a decrease in the Na$^+$ ion concentration. At this stage there is no free SDS micelle, and SDS + PDAC complexes exist in solution. In the last stage, the SDS concentration is over 200 times that of the CAC, the solution is not clear and a lot of free SDS micelles and SDS + PDAC complexes exist in the solution, and neutralization of polyelectrolyte charges by negative SDS heads is complete, which confirms that the hydrophobic interaction is much stronger than the electrostatic interaction between SDS and PDAC. Thus Na$^+$ ion concentration increases lead to an increase of the solution conductivity. In the second stage, conductivity increases with SDS concentration, the relative maximum conductivity SDS concentration corresponds to the CAC of surfactant and polymer (0.11 mmol$\cdot$kg^{-1}). Polyelectrolyte charges are fractionally neutralized, and the formation of SDS + PDAC complexes begins. An excess of absorbed surfactant molecules onto the polymer PDAC leads to an excess of negative charges in the polymer + surfactant complex, so conductivity increases. There is also no free SDS micelle at this stage. In the third stage, when the SDS concentration is above the CAC value, surfactant + polymer complexes are formed more and more and lead to an increased hydrophobic interaction that weakens the electrostatic interaction between SDS and PDAC. Relative negative charges in the complexes decrease reflecting a decrease in the conductivity, and the solution is also clear. The CAC value obtained by conductivity agrees well with that from the viscosity measurements.

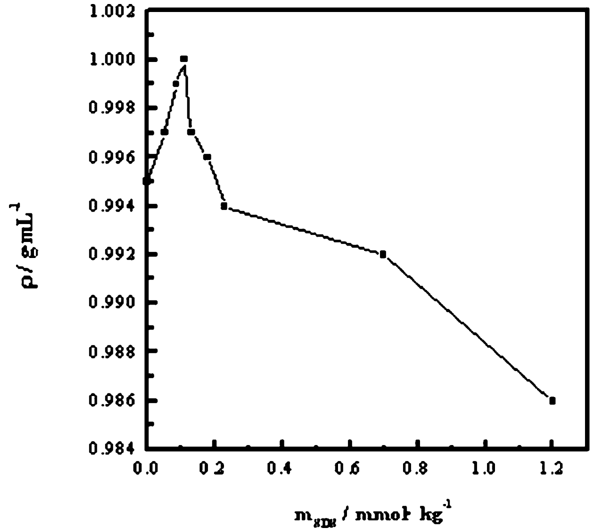

Figure 3. Density of SDS + 1 % mass fraction PDAC with various SDS (0 to 1.2 mmol$\cdot$kg^{-1}) concentration at 298 K.

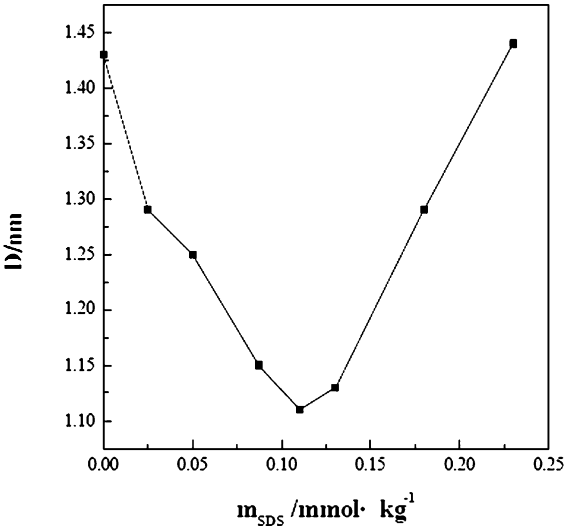

Figure 4. Relationship between the hydrodynamic diameter of SDS + 1 % mass fraction PDAC aqueous solutions and SDS concentration at 298.15 K.

Density of SDS + PDAC. The formation and dissociation of micelles can be monitored by density measurements. Figure 3 shows the density of SDS + 1 % mass fraction PDAC solutions versus SDS concentration at 298 K. The conductivity first increased a little with increasing SDS concentration and then finally decreased significantly with increasing SDS concentration. The minimum value of density corresponded to a SDS concentration of 0.11 mmol$\cdot$kg^{-1}, the CAC of SDS + 1 % mass fraction PDAC aqueous solution. The CMC of SDS aqueous solution is about 8.5mmol$\cdot$kg^{-1}.[23−24] The increased density behavior should be related to the formation of polymer + surfactant complexes and decreasing viscosity of the solution, resulting in a contraction of the polymer chains due to the gradual neutralization of their positive charges by the negative surfactant heads. The decreased density behavior should be related to the expansion of polymer chain and the viscosity increase of solution. The CAC value obtained by density agrees well with that from viscosity and conductivity measurements.

Size of SDS + PDAC Solution by DLS. The hydrodynamic radius distribution caused by the addition of SDS reflects directly the polymer coil changes due to the interaction between surfactant and polymer. Figure 4 shows the hydrodynamic diameter by volume of SDS + 1 % mass fraction PDAC aqueous solutions with various SDS concentrations at 298.15 K. The hydrodynamic diameter (size by volume) of 1 % mass

Table 4. Values of CMC, CAC, and ΔG_{ps} at 298 K in SDS and SDS + 1.0 % Mass Fraction PDAC Aqueous Solutions

	SDS	SDS + 1.0 % mass fraction PDAC
CMC/mmol·kg^{-1}	8.5	
CAC/mmol·kg^{-1}		0.11
ΔG_{ps}/kJ·mol^{-1}		−19.9

fraction PDAC aqueous solution at 298.15 K is (1.43 ± 0.01) nm (99 % by volume). The hydrodynamic diameter of SDS + 1 % mass fraction PDAC aqueous solutions decreases from (1.43 to 1.11) nm with increasing SDS concentration until the SDS concentration reached 0.11 mmol·kg^{-1}. The minimum value of size diameter corresponds to the CAC value of SDS + 1 % mass fraction PDAC aqueous solution, which confirmed the shrinking of the polymer coil and the forming of a more compact structure at the binding site. When the SDS concentration is higher than the CAC value of SDS + 1 % mass fraction PDAC aqueous solution, the hydrodynamic diameter of SDS + PDAC complexes increases with increasing SDS concentration, and expansion of polymer coil occurred. When the SDS concentration reached 0.7 mmol·kg^{-1}, the size of the complex is over 11 nm and is polydisperse. Above 1.2 mmol·kg^{-1}, the solution is opaque, and the collapse of the polymer chain leads to increasing dispersion forces acting between the complex molecules. The size of solution cannot be measured correctly.

Interaction Strength between the Surfactant and the Polymer. The following equation can be used to calculate the free energy of surfactant + polymer complex interaction:[27,28]

$$\Delta G_{ps} = (1 + K)RT \ln(\mathrm{CAC}/\mathrm{CMC}) \qquad (2)$$

where K is the effective micellar charge fraction, which for SDS was found to be 0.85.[28]

The interaction strength between the surfactant and the polymer can be conveniently measured by using eq 2. The lower the value of CAC, the stronger the binding strength is. The value of the CAC obtained by viscosity and conductivity for SDS + 1 % mass fraction PDAC aqueous solutions at 298 K and the calculated ΔG_{ps} according to eq 2 are listed in Table 4. ΔG_{ps} of SDS + PDAC is a large negative value, indicating a strong interaction between SDS and the cationic polymer PDAC.

Conclusions

The interaction between the ionic surfactant SDS and cationic polymer PDAC has been shown by viscosity, conductivity, and DLS measurements to be strong. The viscosity of SDS + PDAC increases with decreasing shear rate and exhibits non-Newtonian behavior. The CAC value of SDS + 1 % mass fraction PDAC is almost 2 orders of magnitude lower than the CMC of SDS. The minimum viscosity and hydrodynamic diameter at the binding site of SDS and PDAC indicated a contraction of the polymer PDAC chain and the formation of a more compact structure. Above the CAC value, the viscosity and hydrodynamic diameter of SDS + 1 % mass fraction PDAC aqueous solutions increases with SDS concentration, indicating an expansion of the polymer PDAC chains. When the SDS concentration is above 1.2 mmol·kg^{-1}, the binding degree is close to unity and the solution is opaque due to the formation of insoluble surfactant + polymer complexes; the viscosity and hydrodynamic diameter increase significantly with SDS concentration; and the polymer chains extends and finally collapses. The interaction between SDS and PDAC can be clearly divided into different characteristics according to the SDS concentration ranges. At low SDS concentration, below 150 times the CAC, the surfactant + polymer system is a thermodynamically stable solution of the surfactant + polymer complex molecules. Above this critical concentration, the system is an unstable colloid dispersion of SDS + PDAC complex particles.

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