Investigation on the Interaction between Sodium Dodecyl Sulfate and Nonionic Polymer with Electrolytes by Viscosity and Surface Tension

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The interaction between sodium dodecyl sulfate (SDS) and the nonionic water-soluble polymer poly(ethylene glycol) (PEG) with electrolytes has been studied by viscosity and surface tension measurements at different temperatures, (298.15, 308.15, and 318.15) K. The experimental results showed that the critical aggregation concentration (CAC) value of SDS + (1, 3, and 5) $g \cdot kg^{-1}$ PEG with NaOH is lower than the critical micelle concentration (CMC) of SDS and that the PEG concentration has little effect on this value. When the SDS concentration is below the CAC, the viscosity of the SDS + PEG solutions with NaOH decreases with increasing SDS concentration, and the minimum viscosity of SDS + PEG complexes at the binding site confirmed the contraction of the polymer chain and the formation of a more compact structure. When the SDS concentration is above the CAC, the viscosity increases with increasing SDS concentration, indicating that the PEG chains are extended. The surface tension decreases remarkably with increasing SDS concentration, when the SDS concentration is below the CAC, and decreases with increasing temperature. The SDS concentration of the first minimum surface tension corresponds to the CAC of surfactant−polymer−electrolyte solutions. The values of the Gibbs energy change for the transfer of free micelle to polymer-bound micelle were calculated and showed that the addition of NaOH to the SDS−PEG system leads to a decrease of the binding site and an increase in the value of CAC; that is to say, the electroviscosity effect and the interaction strength is decreased.

Introduction

The interactions between surfactants and nonionic water-soluble polymers have been investigated and extensively documented because of their widespread commercial applications and theoretical studies.[1] Surfactants are found to bind cooperatively to nonionic water-soluble polymers to form micelle-polymer complexes, and their interactions are largely confined to anionic surfactants such as sodium dodecyl sulfate (SDS).[2–4] Viscosity,[5] electron spin resonance (ESR),[6,7] and fluorescent probing[8] are the most popular measurements to investigate polymer−surfactant complex formation. Goddard[2] gave an excellent review of the interaction between nonionic polymers and anionic surfactants.

The addition of SDS to many nonionic polymers, such as polyacrylamide,[6] has been reported to lead to an increase in the viscosity of the SDS−polymer aqueous solution. This increase of viscosity has been attributed to surfactant adsorption on the polymer chain and to conformational changes of the chain reduced by electric charge. A minimum in the reduced viscosity of the polymer has been observed during the first stage of addition of the surfactant in some surfactant−polymer systems. This minimum viscosity starts to increase with increasing surfactant concentration and has been attributed to the shrinking of the polymer chains, and a more compact structure has been formed at these binding sites.

The addition of polymers and electrolytes[9,10] to the surfactant solution could effectively reduce the critical micelle concentration (CMC) of surfactants and can also 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. 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 electrolyte on the interaction between the surfactant and the polymer. For the studied anionic surfactant and nonionic polymer systems with electrolytes such as NaCl or NaOH, such systems are widely applied in the oil recovery field. Viscosity and surface tension measurement is seldom employed, and it certainly deserves to be investigated.

The purpose of this work is to attempt to provide more understanding of the viscosity and surface tension of the surfactant−polymer−electrolyte system. An anionic surfactant SDS and nonionic polymer poly(ethylene glycol) (PEG) have been chosen for this work. The effect of polymer concentration and electrolyte on the viscosity and surface tension is assessed, and the thermodynamic properties and interaction strength between surfactant + polymer and electrolyte are discussed.

Experimental Section

Materials. SDS with a purity of 99.5 % from Sigma was used without further purification. PEG with molecular weight of 100 000 $g \cdot mol^{-1}$, NaCl, and NaOH were received from Sigma and used without further purification. Water was deionized water.

Methods. The viscosity measurements of SDS and SDS + (1, 3, and 5) $g \cdot kg^{-1}$ PEG aqueous solutions with 0.1 $mol \cdot kg^{-1}$

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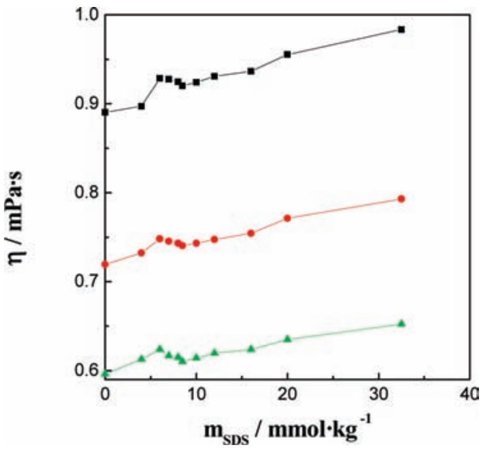

Figure 1. Viscosity of SDS aqueous solutions at different temperatures: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K.

NaOH were carried out at (298.15, 308.15, and 318.15) K by using an Ostwald viscometer. The viscometer was calibrated by 0.01 mol·kg^{-1} and 0.1 mol·kg^{-1} NaCl solutions and water at different temperatures. The viscosity uncertainty was within ± 0.5 % of full scale range, and the repeatability of the measured viscosity was above 99.8 %.

The surface tension measurements of SDS + 1 g·kg^{-1} PEG + 0.1 mol·kg^{-1} NaOH aqueous solutions were carried out at (298.15, 308.15, and 318.15) K by using a U-shape surface tension apparatus. The temperature was controlled by a HAAKE D3 temperature controller to within ± 0.1 K. The surface tension meter was calibrated by water at different temperatures. The surface tension uncertainty was within ± 0.5 % of full scale range, and the repeatability of the measured surface tension was above 99.5 %. The surface tension was calculated by Young–Laplace equation.

Results and Discussion

Viscosity of SDS Solution at Different Temperatures. Figure 1 shows the viscosity of the SDS aqueous solutions at (298.15, 308.15, and 318.15) K. The viscosity of the SDS aqueous solutions decreases with increasing temperature. At a certain temperature, the viscosity of the SDS solutions first increases unremarkably with increasing SDS concentration, then decreases with increasing SDS concentration to a minimum viscosity, and finally increases with increasing SDS concentration at different temperatures, to the minimum viscosity value which corresponds to the CMC of the SDS solutions. The formation of the SDS micelle leads to the decrease of fluid resistance of the solutions. The value of the CMC for SDS solutions is about 8.5 mmol·kg^{-1}. The CMC value obtained by viscosity agrees well with that from the surface tension and ESR measurements.[5,6,10]

Viscosity/PEG Concentration of SDS–PEG–NaOH Aqueous Solutions at Different Temperatures. Table 1 lists the ratio of viscosity and polymer PEG concentration of SDS + (1, 3, and 5) g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH aqueous solution with various SDS concentrations at different temperatures. C_P represents the polymer PEG concentration. This ratio (η/C_P) of SDS + PEG + NaOH aqueous solution decreases significantly with increasing polymer PEG concentration at all studied temperatures. The viscosity decreases with increasing temperature. The ratio increases significantly with increasing SDS concentration, which leads to the formation of a SDS–PEG complex and an increase in the viscosity of solutions. So, the electroviscosity effect increases, and the complex solutions show the typical behavior of a polyelectrolyte.

Table 1. Viscosity/Polymer Concentration (η/C_P) Ratio of SDS + (1, 3, and 5) g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH Aqueous Solutions at Different Temperatures

m_{SDS}	C_P	(η/C_P)/mPa·s·kg·g^{-1}		
mmol·kg^{-1}	g·kg^{-1}	298.15 K	308.15 K	318.15 K
0	1	0.9995	0.7987	0.6634
0	3	0.4187	0.3234	0.2566
0	5	0.2880	0.2245	0.1801
4.00	1	0.9673	0.7783	0.6440
4.00	3	0.4024	0.3151	0.2538
4.00	5	0.2868	0.2220	0.1764
8.00	1	0.9882	0.7971	0.6588
8.00	3	0.3922	0.3082	0.2480
8.00	5	0.2820	0.2109	0.1730
16.0	1	1.0459	0.8443	0.7020
16.0	3	0.3772	0.3021	0.2484
16.0	5	0.2702	0.2109	0.1689
24.0	1	1.0811	0.8701	0.7177
24.0	3	0.4198	0.3391	0.2791
24.0	5	0.2767	0.2187	0.1774

Table 2. Viscosity (η) of SDS + 1 g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH Aqueous Solutions at Different SDS Concentrations at (298.15, 308.15, and 318.15) K

m_{SDS}	η/mPa·s		
mmol·kg^{-1}	298.15 K	308.15 K	318.15 K
0	0.9995	0.7987	0.6634
2.18	0.9726	0.7842	0.6502
4.00	0.9673	0.7783	0.6440
4.35	0.9621	0.7722	0.6401
5.35	0.9718	0.7832	0.6451
8.00	0.9882	0.7971	0.6588
13.4	1.0372	0.8289	0.6892
16.0	1.0459	0.8443	0.7020
17.5	1.0521	0.8516	0.7091
24.0	1.0811	0.870	0.7177
26.1	1.0901	0.8782	0.7289
34.6	1.1241	0.8923	0.7412
43.2	1.1374	0.9002	0.7496
52.4	1.1683	0.9368	0.7754

Viscosity of SDS–PEG–NaOH Aqueous Solutions. Table 2 lists the viscosity of SDS + (1, 3, and 5) g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH aqueous solutions versus SDS concentration at (298.15, 308.15, and 318.15) K. Figure 2 shows the viscosity of SDS + 1 g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH aqueous solutions versus SDS concentration at (298.15, 308.15, and 318.15) K. The viscosity first decreases unremarkably with increasing SDS concentration and finally increases significantly

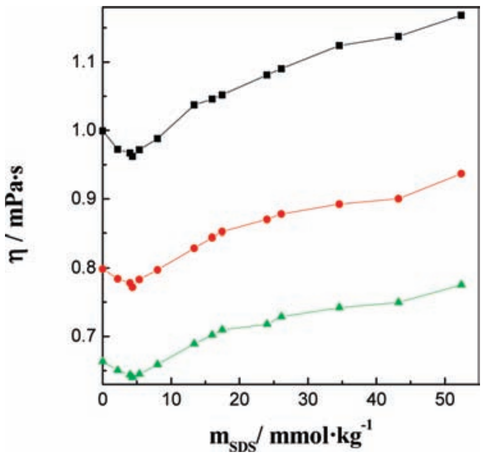

Figure 2. Viscosity of SDS + 1 g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH aqueous solutions at different temperatures: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K.

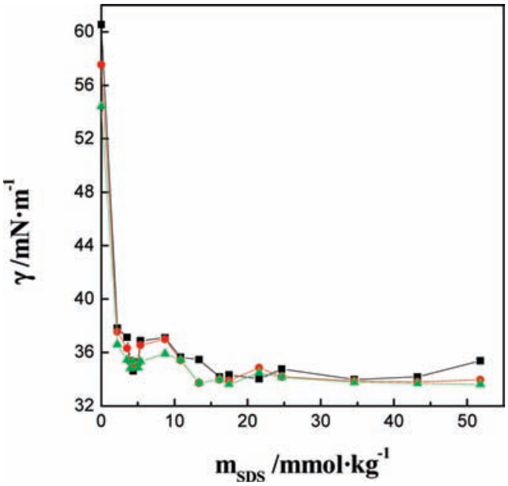

Figure 3. Surface tension of SDS + 1 g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH aqueous solutions at different temperatures: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K.

with SDS concentration. In the first stage, the viscosity decreases with increasing SDS concentration, and there are no free SDS micelle and SDS + PEG complexes that exist in solution. In the last stage, the viscosity increases with increasing SDS concentration because a lot of free SDS micelles and SDS + PEG complexes exist in the solution; thus, the Na$^+$ ion concentration increases, leading to an increase of the solution viscosity. In the first stage, viscosity decreases with increasing SDS concentration, and the polymer−micelle aggregate formed a more compact structure at this binding site and yielded a decrease in the viscosity, the relative minimum viscosity SDS concentration which corresponded to the CAC value of SDS−PEG−NaOH, 4.4 mmol·kg^{-1}. In the last 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 PEG and reflects the increase of fluid resistance of the solutions. The CAC value obtained by viscosity agrees well with that from the surface tension measurements.

Surface Tension of SDS−PEG−NaOH Aqueous Solutions. Figure 3 shows the surface tension of SDS + 1 g·kg^{-1} PEG + 0.1 mmol·kg^{-1} NaOH aqueous solution versus SDS concentration at (298.15, 308.15, and 318.15) K. The surface tension decreases with increasing temperature. The surface tension first decreases significantly with increasing SDS concentration and then increases unremarkably with SDS concentration too. In the first stage, the surface tension decreases remarkably with increasing SDS concentration because of the decreasing surface tension ability of the surfactant. At this stage there is no free SDS micelle, and SDS + PEG complexes exist in solution, the relative minimum surface tension value of SDS concentration which corresponds to the CAC value of SDS−PEG−NaOH, 4.35 mmol·kg^{-1}. At this binding site, the SDS and PEG formed a more compact structure and yielded a relative minimum surface tension value. 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 PEG and reflects the changes of surface tension. The CAC value obtained by surface tension agrees well with that from the viscosity measurements.

Table 3. Values of CMC, CAC, and ΔG_{ps} at 298 K in SDS and SDS + 1 g·kg^{-1} PEG with or without 0.1 mmol·kg^{-1} NaOH Aqueous Solutions

	SDS	SDS + PEG	SDS + PEG + NaOH
CMC/mmol·kg^{-1}	8.5		
CAC/mmol·kg^{-1}		4.00[5]	4.35
ΔG_{ps}/kJ·mol^{-1}		−3.46	−3.07

Interaction Strength between the Surfactant and the Polymer. The Gibbs energy change for the transfer of free micelle to the surfactant + polymer complex can be calculated using the following equation[5,11]

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

where K is the effective micellar charge fraction, which for SDS was found to be 0.85.[11]

The Gibbs energy change and interaction strength between the surfactant and the polymer can be conveniently measured by using eq 1. The lower the value of the CAC, the stronger is the interaction strength. The CAC value by viscosity for SDS + 1 g·kg^{-1} PEG[5] with or without NaOH aqueous solutions at 298.15 K and the calculated ΔG_{ps} according to eq 1 are listed in Table 3. ΔG_{ps} of SDS + PEG is a large negative value, indicating a strong interaction between the SDS and the nonionic polymer PEG with or without electrolytes, and the addition of electrolyte NaOH decreases the interaction strength between SDS and PEG unremarkably.

Conclusion

The interaction between the ionic surfactant SDS and the nonionic polymer PEG with electrolyte NaOH has been investigated by viscosity and surface tension measurements at different temperatures. The viscosity of SDS + PEG + NaOH aqueous solutions first decrease with increasing SDS concentration and finally increase with increasing SDS concentration at different temperatures. All measured viscosities of SDS−PEG with electrolyte solutions decrease with increasing temperature. The CAC value of SDS + PEG with NaOH solutions is only a little lower than the CMC of SDS. The minimum viscosity at the binding site of SDS and PEG indicated a contraction of the polymer PEG chain and the formation of a more compact structure. Above the CAC value, the viscosity of SDS + 1 g·kg^{-1} PEG aqueous solutions increases with increasing SDS concentration indicating an expansion of the polymer PEG chains. The surface tension decreases with increasing temperature and decreases significantly with increasing SDS concentration when SDS concentration is below the CAC. The interaction strength between SDS and PEG decreased unremarkably with the addition of electrolyte NaOH.

Literature Cited

(1) Goddard, E. D. In *Interactions of Surfactants with Polymers and Proteins*; CRC Press: Boca Raton, FL, 1993.

(2) Goddard, E. D. Polymer−surfactant interaction part II. Polymer and surfactant of opposite charge. *Colloids Surf.* **1986**, *19*, 301–329.

(3) Cabin, B. Structure of some polymer-detergent aggregates in water. *J. Phys. Chem.* **1977**, *81*, 1639–1645.

(4) Fishman, M. L.; Elrich, F. R. Interactions of aqueous poly(N-vinylpyrrolidone) with sodium dodecyl sulfate. II. Correlation of electric conductance and viscosity measurements with equilibrium dialysis measurements. *J. Phys. Chem.* **1975**, *89*, 2740–2744.

(5) Cao, M.; Hai, M. T. Investigation on the interaction between Sodium Dodecyl Sulfate and Polyethylene Glycol by Electron Spin Resonance, Ultraviolet Spectrum, and Viscosity. *J. Chem. Eng. Data* **2006**, *51*, 1576–1581.

(6) Hai, M. T.; Han, B. X.; Yan, H. K. Investigation on Interaction between Sodium Dodecyl Sulfate and Polyacrylamide by Electron Spin Resonance and Ultraviolet Spectrum. *J. Phys. Chem. B* **2001**, *105* (21), 4824–4826.

(7) Witte, F. M.; Engberts, J. B. F. N. ESR spin probe study of micelle-polymer complexes. Poly(ethylene oxide)- and poly(propylene oxide)-complexed sodium dodecyl sulfate and cetyltrimethylammonium bromide micelles. *J. Org. Chem.* **1988**, *53*, 3085–3088.

(8) Zana, R.; Lianos, P.; Lang, J. Fluorescence probe studies of the interactions between poly(oxyethylene) and surfactant micelles and microemulsion droplets in aqueous solutions. *J. Phys. Chem.* **1985**, *89*, 41–44.

(9) Hai, M. T.; Han, B. X.; Yan, H. K.; Han, Q. Y. Vapor pressure of Aqueous Solutions of Polyacrulamide + Sodium Dodecyl Sulfate with and without NaOH. *J. Chem. Eng. Data* **1998**, *43* (6), 1056–1058.

(10) Hai, M. T.; Han, B. X.; Yan, H. K. The solubilization of n-pentane gas in Sodium Dodecyl Sulfate-polyethylene glycol solutions with and without electrolyte. *J. Colloid Interface Sci.* **2003**, *267*, 173–177.

(11) Lu, J. R.; Marrocco, A.; Su, T. J.; et al. Adsorption of Dodecyl Sulfate Surfactants with Monovalent Metal Counterions at the Air-Water Interface Studied by Neutron Reflection and Surface Tension. *J. Colloid Interface Sci.* **1993**, *158*, 303–316.

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