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Viscosities of Sodium Dodecyl Sulfate Solutions in Aqueous Ammonium Salts

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Viscosity measurements have been performed on 0.3 M sodium dodecyl sulfate (SDS) micellar solutions containing different ammonium salts, NH_4X (X = OH, Cl, Br, I, NO_3, or SCN) at different temperatures (25 to 40 °C). The viscosity decreased, increased, and again decreased as the salt concentration was increased. This behavior was explained in the light of micellar growth/breakdown, the nature of X, and intermicellar interactions. It was also found that, depending on coion species of the added salt, the viscosities of SDS/NH_4X micellar solutions differ considerably, indicating the effect of hydrophobic interaction on micelle size or viscosity.

Introduction

Ionic micelles are lucrative model systems for ion-binding properties of much more complex systems of natural and synthetic liposomes, vesicles, and biological membranes (Jain, 1988; Israelachvili, 1991). Micelles with charged surfaces bind counterions selectively, and their solution properties, such as size and morphology, phase stability, etc., are sensitive to counterion concentration and type (Missel *et al.*, 1989; Romsted and Yoon, 1993). These changes are likely a result of differing interactions of the counterions with the charged head groups in the Stern layer and/or with the aqueous solvent molecules.

Specific counterion effect on a number of micellar characteristics generally follows the lyotropic series (Mysels, 1959). In addition to the rearrangement on a molecular scale, the micelle−micelle interactions are influenced by the nature of the intermicellar medium, in this case, type and concentration of coions present in the medium (Ikeda *et al.*, 1981). The relationship between affinity for a set of coions and a particular counterion will provide information on the nature of interaction of counterions in the interfacial region. The reasons for the difference in partitioning of the coions are not fully understood. The lyotropic series for some common anions is

$$F^- < IO_3^- < BrO_3^- < Cl^- < ClO_3^- < Br^- < NO_3^- < ClO_4^- < I^- < SCN^-$$

The viewpoint that the valence and concentration of coions have no effect on the critical micelle concentration (cmc) of surfactants (Corrin and Harkins, 1947) cannot be extended to the effect of salts having different coions (and the same counterion) on the viscosity of ionic surfactants (Wang, 1993). The interaction of the coion with water most certainly plays an important role in the counterion−micelle interplay and toward the intermicellar medium. Recent studies of microscopic aggregates by SANS coupled with viscometry demonstrate links between aggregate structure and bulk physical properties (Eastoe *et al.*, 1993; Kumar *et al.*, 1994; Kabir-ud-Din *et al.*, 1996).

In this paper, the effect of ammonium salts (NH_4X; X = OH, Cl, Br, I, NO_3, or SCN) on the viscosity pattern of 0.3 M SDS is described. The choice fell on ammonium salts, as a lower concentration of ammonium chloride (NH_4Cl), relative to sodium chloride (NaCl), is required to induce micellar structural transition (growth) (Nguyen and Bertrand, 1992).

Experimental Section

Reagents. Sodium dodecyl sulfate (CPC, USA, purity >99%) was twice recrystallized from ethanol/water mixture and dried under vacuum. All ammonium salts were special grade "high-purity" chemicals and were used without further purification. Double-distilled water was used in solution preparations for viscosity measurements. The uncertainty in composition of the samples was not more than ±0.02%.

Measurements. The viscosity measurements were performed on 0.3 M SDS in aqueous ammonium salts at different concentrations. The solvent flow time (t) in a precalibrated Ubbelohde viscometer was always longer than 200 s. This viscometer was used for viscosity measurements at low salt concentrations. Density (ρ) corrections were not required because they were negligible. Hence, kinematic viscosity was used to determine the absolute viscosity of the system by using the viscosity of water at 30 °C. Four flow time measurements were made for each sample, and mean deviations from the mean of all measurements were required not to exceed 0.1 s. As the viscosities of all the systems at higher salt concentrations were highly dependent on shear rate (non-Newtonian behavior), a cone/plate Brookfield viscometer (model RV DV-I+, equipped with a constant temperature bath TC-200) was used to measure shear viscosities (η_G) at different shear rates (G), and zero shear viscosities ($\eta_{G=0}$, mentioned hereinafter as η) were obtained by extrapolation of the $\eta_G = f(G)$ plots (representative plots for NH_4Cl are shown in Figure 1). The accuracy and reproducibility of the Brookfield viscometer are within ±1% and 0.2%, respectively.

Results

Representative plots (Figure 2) show the variation of η with added NH_4X at 30 °C. The η-values obtained at different temperatures (25 to 40 °C) are compiled in Tables 1 to 4. The values vary in accordance with the well-known Andrade equation

$$\eta = A\mathrm{e}^{B/RT} \tag{1}$$

in which A and B are constants (R being the gas constant).

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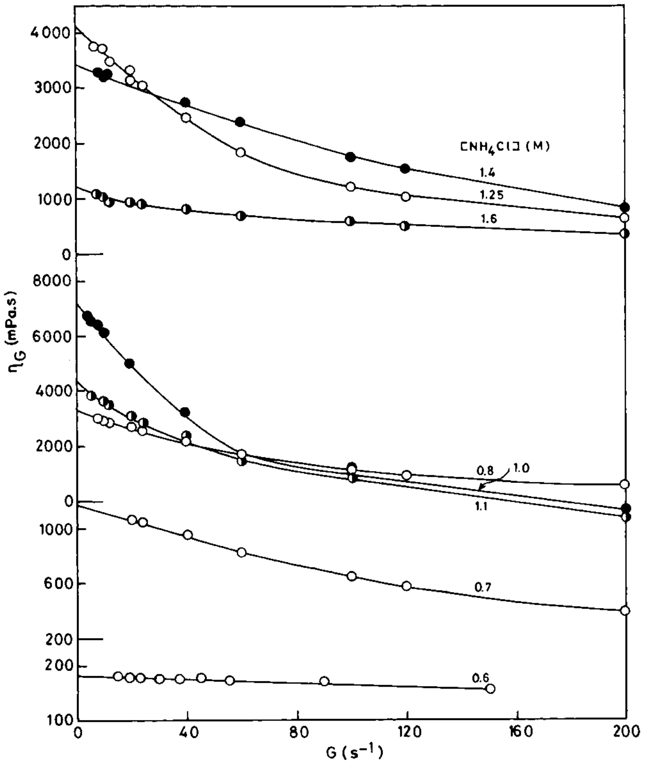

Figure 1. Shear viscosity (η_G) vs shear rate (G) plots for 0.3 M SDS micellar solutions containing various amounts of NH_4Cl at 30 °C. The molar concentration of added NH_4Cl is given above the plots.

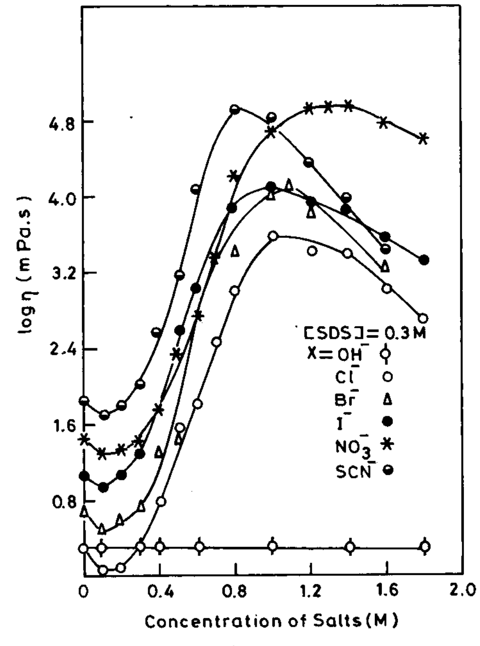

Figure 2. Viscosity variation of 0.3 M SDS micellar solutions with added NH_4X at 30 °C. All the points are shifted vertically by 0.4 units except for OH^- and Cl^-.

Discussion

On the basis of viscosity measurements, we can distinguish three different concentration regimes (see Figure 2). The decrease of the viscous resistance during flow may be due to the orientation process, or it may be explained by structure breakdown. It was reported that viscosity can be interpreted as the product of the average orientation and optical anisotropy of the solution (Rehage and Hoffman, 1988). The optical anisotropy is related to size of the particles, while the orientation is related to interaggregate distances. Here the surfactant concentration is constant, and we are slowly increasing [salt], which will cause the growth of particles with simultaneous increase in interparticle distances. The former factor will tend to increase the $|\eta|$ while the latter will decrease it; this effect possibly dominates in region I and causes a viscosity decrease. The effects of coions have been attributed to the salting-out effect, *i.e.* effects of ionic size and decrease in dielectric constant. The ability of coions to attract a counterion and to repel free surfactant anions decreases with the lyotropic series of anions. Therefore, the difference in η must be caused by a combined effect of all the above factors on the hydrophobic interaction and hydrogen-bonded structure of water. In the case of NH_4OH, due to the low pK value,

Table 1. Viscosities of 0.3 M SDS Micellar Solutions in the Presence of Added NH_4X at 25 °C

C_{NH_4X}/	η/mPa·s					
(mol/L)	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3	NH_4SCN	NH_4OH
0	2	2	2	2	2	2
0.1	1.4	1.3	1.7	1.3	1.5	2.2
0.2	1.7	1.4	2.7	1.5	3.1	
0.3	3.2	3	6.2	2	18.4	
0.4	10	12.8	17.4	5.8	63	2
0.5	61.8	18	107	28	1840	
0.6	190	555	562	74.7	2951	1.8
0.7	1175	1780		398		
0.8	3300	2240	2089	2775	3845	
1.0	7413	7300	3890	6700	7079	1.8
1.1		8900				
1.2	4100	6607	2570	9700	6918	
1.4	3388	4467	1905	9250	5754	1.8
1.6	1210	254	1412	6100	3548	
1.8			676	4325	2089	1.8

Table 2. Viscosities of 0.3 M SDS Micellar Solutions in the Presence of Added NH_4X at 30 °C

C_{NH_4X}/	η/mPa·s					
(mol/L)	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3	NH_4SCN	NH_4OH
0	2	2	2	2	2	2
0.1	1.1	1.2	1.3	1.2	1.3	2.2
0.2	1.2	1.2	2.9	1.2	1.6	
0.3	1.9	2.2	3.2	1.5	2.8	
0.4	6	7.9	8.6	3.5	9.8	2.1
0.5	36	11.6	67	14	37	
0.6	64.9	297	177	35	46	1.9
0.7	1097	794		126		
0.8	1100	1025	1276	1090	251	
1.0	3715	4285	1986	3100	722	1.9
1.1		5110			886	
1.2	2450	2550	1250	5100		
1.4	2290	945	1152	5350	1803	1.9
1.6	1025	660	609	3600	1085	
1.8	528		346	2600	950	

Table 3. Viscosities of 0.3 M SDS Micellar Solutions in the Presence of Added NH_4X at 35 °C

C_{NH_4X}/	η/mPa·s					
(mol/L)	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3	NH_4SCN	NH_4OH
0	1.2	1.2	1.2	1.2	1.2	1.2
0.1	0.9	0.9	1.2	0.5	1.2	1.9
0.2	0.9	1	1.5	0.9	1.7	
0.3	1.1	1.2	1.9	1	5.7	
0.4	2.9	3.6	2.8	1.8	15	2.2
0.5	11.4	4.1	27	2.7	478	
0.6	47	155	41	14.4	631	2.32
0.7	375	631		63		
0.8	432	1412	475	510	1175	
1.0	1882	2270	1106	1425	813	1.8
1.1		4005				
1.2	1318	2535	711	2950	269	
1.4	933	812	399	2500	91	1.9
1.6	688	575	368	2175	32	
1.8			250	1500	7.9	1.90

Table 4. Viscosities of 0.3 M SDS Micellar Solutions in the Presence of Added NH_4X at 40 °C

C_{NH_4X}/	η/mPa·s					
(mol/L)	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3	NH_4SCN	NH_4OH
0	1.1	1.1	1.1	1.1	1.1	1.1
0.1	1	0.4	1.1	0.6	1	2.1
0.2	1	1	1.1	1	1.4	
0.3	1.1	1.2	1.4	1.5	3.5	
0.4	2.1	2.6	1.7	3.8	7.3	2.2
0.5	7.9	2.7	4.4	5	263	
0.6	19	83	9	7.2	402	2.3
0.7	197	232		66		
0.8	390	316	182	300	559	
1.0	933	1355	436	722	562	2
1.1		1720				
1.2	794	850	417	1700	198	
1.4	524	501	251	1300	63	1.88
1.6	331	241	199	930	72	
1.8			110	380	14.4	

the availability of NH_4^+ is markedly decreased and hence no overall significant effect on the viscosity of the 0.3 M SDS is seen (Figure 2).

In the region II of Figure 2, where the η values increase steeply with salt concentration, contribution of the growth of the micelle toward viscosity rise is significant. Due to this growth, micelle interference with each other would increase and thus cause the sharp increase in η. The lengthening (growth) may be responsible for ordered structures. Since a SDS micelle in higher salt concentrations is sufficiently shielded from its electrostatic effect, it may be treated like nonionic polymer structures (Cates and Candau, 1990), which may interact more closely. These two interdependable terms will cause high viscous resistance in the solution.

It has recently been proposed (Mileva, 1996), on the basis of theoretical treatments, that systems with lower electrolyte concentrations are more sensitive to intermicellar interactions than systems at higher salt concentrations. The shape of the micelles will also be different in the two concentration regimes. Therefore, intermicellar interaction will contribute differently for the two structures with a concomitant effect on η.

With further salt addition, once again a decrease in η was observed (region III). It is interesting to note that rate of decrease of η with salt (*i.e.*, dη/d[salt]) is higher with SCN^- than with Cl^-. An excess amount of the salt may diminish certain physical interactions among the grown micelles such as hydrogen bonding by a salting-out effect (Hu *et al.*, 1994). The excess salt decreases the micelle lifetime. In other words, the micelle breakup rate increases when an excess of NH_4X is present. In addition, at high [NH_4X] the flexibility of micelles may increase (Hayashi and Ikeda, 1980). The large rod-shaped micelles formed in these systems coalesce to form hydrodynamic particles (Corti and Degiorgio, 1979), which could be close to undergoing a phase separation. The viscosity decrease in region III (before phase separation) is, therefore, rationalized in the light of above three factors.

It is, therefore, concluded that coions do play an important role in micellar growth and the effective order of the coions is dependent on the micelle shape; it also changes with the concentration of the salt in the system. The nature, shape, and concentration of coion all will affect affinity orders of counterions in various biologically important assemblies (Strauss and Leung, 1965; Anderson and Record, 1990; Cevc, 1990).

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