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Effect of Polyoxyethylene Chain Length and Electrolyte on the Viscosity of Mixed Micelles

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The viscosity measurements of micelles composed of mixtures of anionic/nonionic surfactants were carried out as a function of the mole fraction of surfactants. The systems studied were sodium dodecyl sulfate (SDS)-polyoxyethylene lauryl ether ($C_{12}POE_n$n = 4, 10 and 23) in water and 0.1 M sodium chloride solution. In the single systems, the relative viscosity of nonionic surfactant is greater than that of SDS, and increases with the increasing level of ethylene oxide. In the mixed surfactant systems, the relative viscosities vary at the mixed molar fraction of SDS, between 0.2 and 0.3, and then the relative viscosities of mixed systems decrease with the increasing mole fraction of SDS. The experimental values show a positive deviation from ideal behavior because of mixed micelle formation and the electroviscous effect. This effect could be suppressed by the addition of an electrolyte (NaCl).

Key Words: Relative viscosity, anionic/nonionic surfactant, mixed micelles.

Introduction

Surface-active compounds used in practical applications virtually always consist of surfactant mixtures. For example, they are used as detergents to increase washing activity and as emulsifiers to stabilize emulsions. On the other hand, some phenomena that are not expected to take place in the single system occur in aqueous solutions containing surfactant mixtures[1−5]. It has been speculated that the tendency to form aggregate in solutions containing surfactant mixtures may be substantially different from that if only pure surfactant is present[6,7]. The performance superiority exhibited by the mixtures of surfactant is attributed to synergism interaction, depending on the properties of the surfactants[8,9]. The most-used pairs of surfactants that show synergism are mixtures of charged and uncharged compound.

Different techniques are used to collect structural information on the mixed micelle formation and to obtain the critical micelle concentration (CMC) as a function of the mixture composition.[10−14]. In a previous study, we considered the surface adsorption and micelle formation of a mixture of sodium dodecylsulfate (SDS) and polyoxyethylene(23) lauryl ether (Brij 35)[15]. The value of the interaction parameter β between SDS and Brij 35 was evaluated by using Rubingh's theory.

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In the present study, the interactions between SDS and $C_{12}POE_n$ (n = 4,10 and 23) binary systems were investigated using the change in the relative viscosity of the mixed surfactant solutions that may result from an increase in the number of micelles involved and intermicellar interactions. The influence of the polyoxyethylene chain length, temperature and electrolyte on the viscous properties of the above systems and the relative viscosities of mixed surfactant systems were determined to visualize the electroviscous effect.

Materials and Methods

Materials

Anionic surfactant: SDS $C_{12}H_{25}OSO_3Na$ was supplied by Merck at 98% purity. It was extracted with ether and recrystallized from ethanol. Nonionic surfactants Brij 30 (polyoxyethylene (4) lauryl ether $C_{12}POE_4$), polyoxyethylene (10) lauryl ether ($C_{12}POE_{10}$) and Brij 35 (polyoxyethylene (23) lauryl ether $C_{12}POE_{23}$) were supplied by Sigma. The purity of the surfactants used was further confirmed by the absence of minima in the surface tension against the logarithm of the concentration curve. Sodium chloride (NaCl) supplied by Merck was used without purification and was dried at 120 °C before use. Water used in the preparation of the surfactant solution was distilled twice from dilute alkaline permanganate solution; its conductivity was about 1. $10^{-6}\Omega^{-1}$ cm^{-1} and the air/water tension was equal to 71-72 m N m^{-1} at 298 K.

Methods

CMC measurements - The surface tension of aqueous solutions of single surfactants at various concentrations was determined using the Du Nouy ring method at constant temperature. The CMC values were determined at sharp break points in surface tension against the logarithm of the concentration curve. In addition, the CMC values were found to be in agreement with measured conductivity and density. These CMC values were found between 8.10^{-3} M (for SDS) and 5.10^{-5}M (for $C_{12}POE_4$).

Preparation of Mixed Surfactant Solutions - Using CMC values found for each surfactant solution, a certain total concentration was selected. At this selected concentration (1.0 10^{-2} M) micellization was present for all surfactant solutions, and so stock solutions were prepared at this concentration. Next, 25 ml quantities of a given concentration of SDS solution were placed into 100 ml beakers. This was followed by the addition of a given concentration of $C_{12}POE_n$ solution. The mixtures were diluted stepwise with water and stirred for 2 h in a thermostat bath at 30 °C and 40 °C in order to establish equilibrium.

Determination of relative viscosities - The kinematic viscosities of aqueous solutions of binary surfactants systems were measured using an Ubbelohde-type viscometer (Schott-Gerate) with an accuracy of ± 0.001 s at 30 °C and 40 °C. Later, the relative viscosities were calculated with respect to the viscosity values of water at 0.7975 cp and 0.6529 cp [16] using the density of solutions at 30 °C and 40 °C.

Density measurements - The density of solutions was measured at temperatures of 30 °C and 40 °C using a Paar DMA 38 Precision densitometer with a resolution of 10^{-4} g.cm^{-3}. Temperature control was within ± 0.005 °C, giving rise to an uncertainty in density calculation of about ± 3 x 10^{-4} g.cm^{-3}.

Results and Discussion

Figures 1 and 2 show the relationship between the relative viscosity and the surfactant concentration in single surfactant systems (SDS and Brij 35) at 30 °C and 40 °C. The relative viscosity of Brij 35 was greater than that of SDS. A property common to each system is that the relative viscosity does not change with increased concentration up to CMC, where a sudden increase is observed due to the micellizations. It can also be seen that the relative viscosity values rise with increasing temperature for SDS and Brij 35.

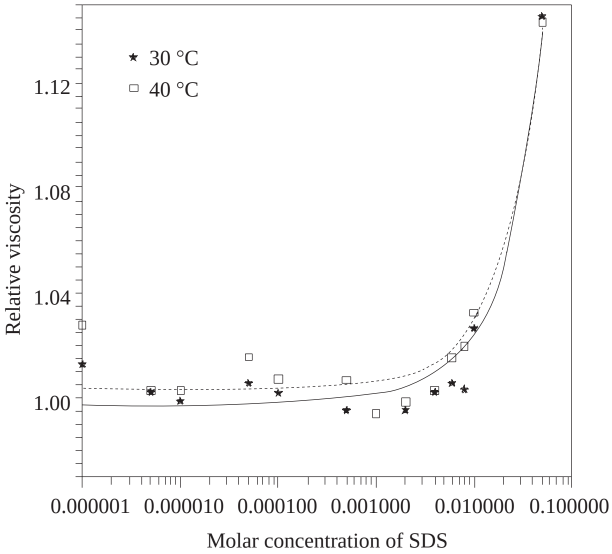

Figure 1. Relation between the relative viscosity and the molar concentration of SDS at 30 °C and 40 °C.

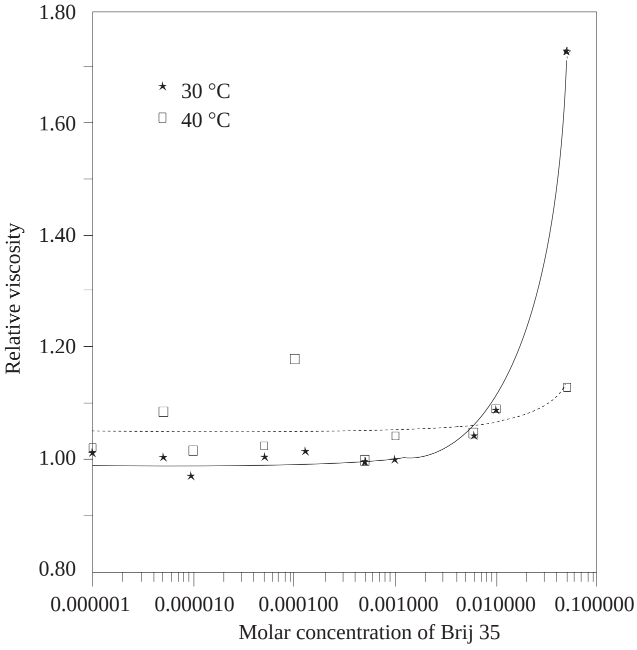

Figure 2. Relation between the relative viscosty and molar concentration of Brij 35 at 30 °C and 40 °C.

The relationship between the relative viscosity and mole fraction of SDS in the SDS–Brij 35 mixed surfactant system is shown in Figure 3. The binding of charged surfactant micelles to a nonionic surfactant has been demonstrated to cause a characteristic change in the hydrodynamic properties of the solution. The phenomenon has been shown to occur because of the expansion of the nonionic surfactant coil due to electrostatic repulsion between the bound micelles. At a low mole fraction of SDS, relative viscosity decreases slightly with increasing temperature. Here, only a few SDS micelles bind to the Brij 35 micelles. Brij 35 becomes less polar with increasing temperature and hence the chain contracts, resulting in a decrease in relative viscosity. At a higher mole fraction of SDS, an increase in solution relative viscosity is observed with increasing temperature. This indicates that a sufficient number of SDS micelles bind to Brij 35 micelles to produce a chain expansion due to electrostatic repulsion between the bound micelles. This result seems consistent with previous studies[17,18] that indicate that a substantial increase in the ionization of bound micelles occurs as temperature increases. At a certain mole fraction of SDS, the viscosity reaches a maximum but then decreases with a further increase in the SDS mole fraction. At the maximum, Brij 35 chains are saturated with surfactant micelles. The decrease in viscosity above the saturation point is interpreted[19,20] as being due to the effect of added counterion (Na^+) in screening repulsive interactions among micelles bound to the Brij 35 chains.

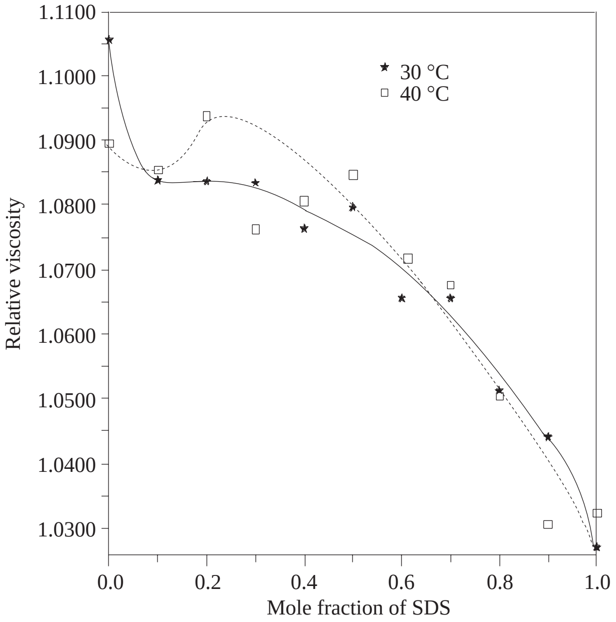

Figure 3. Effect of temperature on the relative viscosity of the SDS + $C_{12}POE_{23}$ mixed system as function of the mole fraction of SDS. Total concentration of surfactant is 1.0 x 10 $^{-2}$ M.

The relative viscosity plotted against the mole fraction of SDS in SDS-Brij series mixed systems is shown in Figure 4. It can be seen that the relative viscosities of nonionic surfactants are greater in comparison to the anionic surfactant and for nonionic surfactants alone. In addition, the nonionic surfactant which has the lowest number of oxyethylene units has the lowest relative value in Figure 4, so that relative viscosity increases with the increase in the number of oxyethylene units. It was previously reported that most of the water molecules were mechanically trapped in the polyoxyethylene chain of nonionic surfactants, with 5.2 to 10.5 water molecules per ethylene unit[21]. Therefore, this increase in relative viscosities with an increase in the number of oxyethylene units may be attributed to the increased hydration by water molecules around the hydrophilic portion of the surfactants.

In Figure 4, it can also be observed that the relative viscosities initially increased and then reached a maximum at a mixed molar ratio of about 0.3. They then decreased steadily for the SDS - $C_{12}POE_4$ and SDS - $C_{12}POE_{10}$systems. In the case of SDS - $C_{12}POE_{23}$, after an initial decrease it remained constant and then showed a linear decrease. Assuming that no interaction takes places between the two surfactants, the ideal line can be drawn between the relative viscosities of two single surfactants as shown by the dashed line in Figure 4. The deviation of the relative viscosities in the mixed surfactant system from the ideal behavior is greater for a nonionic surfactant with a shorter polyoxyethylene chain length than for one with a longer chain length. Ogino et al.[22] have reported that the mixed micelle is formed more easily by a nonionic surfactant including a short polyoxyethylene chain than by one having a long polyoxyethylene chain. In other words, systems in which the mixed micelle forms most easily have a greater deviation from the ideal behavior. We can conclude that the mixed micelle formation increases the viscosity. The maximum in relative viscosity, therefore, does not seem to exist in the SDS - $C_{12}POE_{23}$ mixed systems.

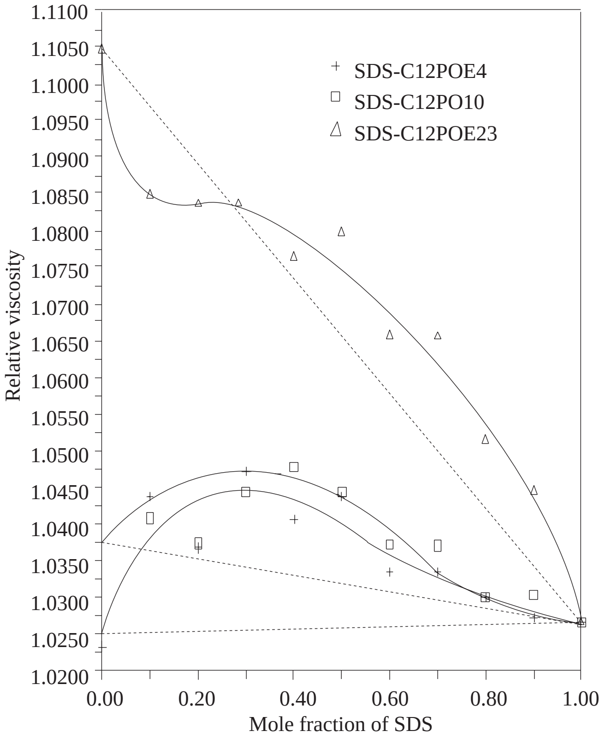

Figure 4. Relationship between the relative viscosity and mole fraction of SDS for SDS + $C_{12}POE_n$(n = 4, 10 and 23) mixed systems at 30 °C. Total concentration is 1.0 × 10^{-2} M. (Broken lines were drawn for ideal behavior, i.e. no interaction)

Ito et al. have reported that the intrinsic viscosity according to Einstein's equation should be 2.5[23]. Since a colloidal particle has a hydrated layer around it with an electrical surface charge, the intrinsic viscosity of the usual particle is larger than 2.5. Therefore, the viscosity is mainly affected by two parameters: the hydration of the colloidal particle surface, and the electroviscous effect. It is known that the electroviscous effect can be suppressed by the addition of an electrolyte[24]. The relative viscosities of the SDS - $C_{12}POE_{23}$systems were measured in the presence of 0.1 M NaCl as a function of the mole fraction of SDS as shown in Figure 5. The electroviscous effect on viscosity declined with the decrease in the surface charge of the micelle. As shown in Figure 5, the relative viscosity was considerably decreased by the addition of NaCl and behaved almost ideally. The electrolyte provides counter-ions near the micelle surface and suppresses the dissociation of the anionic surfactants in the mixed micelles thereby decreasing the surface change.

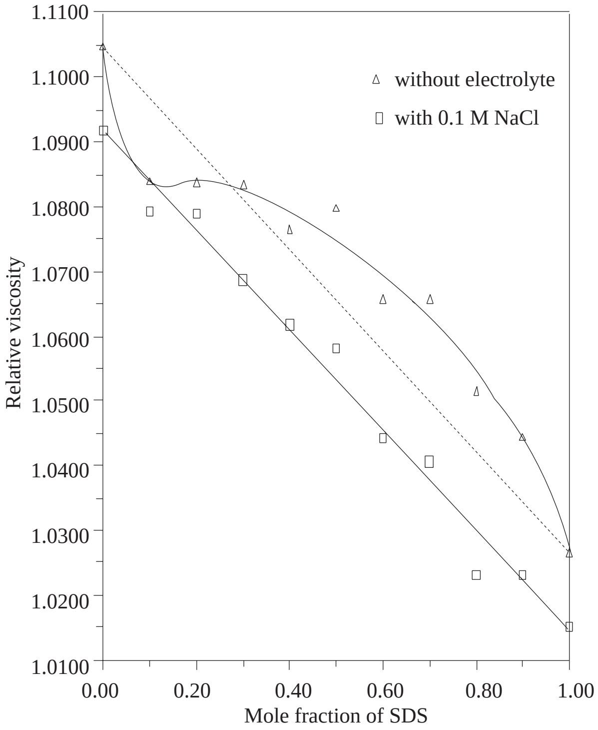

Figure 5. Effect of 0.1 M NaCl on the relative viscosity of the SDS + $C_{12}POE_{23}$ mixed system as a mole fraction of SDS at 30 °C.

In conclusion, the relative viscosity in the mixed surfactant solutions is greater than that in a single surfactant solution. The variation in the relative viscosity of mixed surfactant solutions is attributed to the repulsion between similarly changed head groups and to the interaction between the hydrophilic group of two surfactants. The extent of interaction increases with a rise in the number of members of the oxyethylene group. Viscosity measurements showed the deviation from the ideal behavior because of the electroviscous effect. If the mixed micelles form easily, the electroviscous effect will be large. This effect was greater in mixed surfactant systems than in single surfactant systems and could be reduced by the addition of an electrolyte for industrial applications.

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