Aqueous Sodium Halide Solutions of Cationic Surfactants with Consolute Phase Boundary. Viscosity Behavior in Semidilute Regime

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The effect of temperature on viscosity has been investigated for aqueous sodium halide solutions of hexadecyldimethylammonium chloride ($C_{16}DAC$), tetradecyldimethylammonium chloride and bromide ($C_{14}DAC$, $C_{14}DAB$), and dodecylammonium chloride ($C_{12}AC$) in semidilute regime. If the relative viscosity, depending on shear rate, is extrapolated to zero shear rate and is plotted against the micelle concentration, the scaling law $\eta_{rel}^0 \sim (c - c_0)^x$ holds. The exponent, x, for alkyldimethylammonium halides amounts to 1.2–1.8 within temperatures up to the lower consolute phase boundary, independent of the sort of surfactant. On the other hand, the reduced viscosity at zero shear rate of $C_{16}DAC$ in 1.4 M NaCl is considerably higher than those of $C_{14}DAC$ in 2.6 and 2.8 M NaCl and $C_{14}DAB$ in 4.3 M NaBr. The viscosity of $C_{12}AC$ in 0.3 M NaCl is low but scaled with the x values from 1.3 to 2.3, which slightly increase with a rise in temperature.

Introduction

If molecules of surfactants can associate into rodlike micelles in aqueous solutions, rodlike micelles overlap and entangle with one another at micelle concentrations above a certain threshold value, that is, in semidilute regime. The solution behavior of overlapped and entangled micelles in semidilute regime may be described by the scaling laws, such as proposed for solutions of polymers.[1]

The application of the scaling laws to aqueous micellar solutions has first been performed by Candau et al.[2,3] They reported that light scattering results from semidilute solutions of hexadecyltrimethylammonium bromide ($C_{16}TAB$) obeyed the scaling laws, which were theoretically predicted for real polymer chains in good solvent,[1] but viscometric results did not obey them.

Imae and Ikeda[4,5] evaluated the characteristic exponent on the scaling laws in dilute and semidilute regimes for aqueous sodium halide solutions of hexadecyl- and tetradecyltrimethylammonium chloride and bromide ($C_{16}TAC$, $C_{14}TAC$, $C_{14}TAB$) from light-scattering measurements. The characteristic exponent was lower than that for oleyldimethylamine oxide in dilute solutions.[6]

The behavior of semidilute solutions was investigated even for rodlike micelles of oligo(oxyethylene) alkyl ethers (C_nE_m). Kato et al.[7] reported that the slope on the double logarithmic plot of mutual diffusion coefficient vs $C_{12}E_5$ concentration was close to a theoretical value for entangled polymer chains in good solvent. Imae[8] measured the static and dynamic light scattering for aqueous NaCl solutions of $C_{16}E_7$ and $C_{14}E_7$ and reported the solution behavior in dilute and semidilute regimes which obeyed the scaling laws.

The viscosity in semidilute regime was investigated for aqueous sodium halide solutions of $C_{16}TAC$, $C_{16}TAB$, and $C_{14}TAB$.[9] According to the reptation model and the scaling laws,[1,10] the relative viscosity at the zero shear rate for semidilute solutions followed the scaling law against

micelle concentration with an exponent of 2.2–3.0. The exponent values of the viscosity for aqueous NaCl solutions of $C_{16}E_7$, $C_{14}E_7$, and $C_{12}E_7$ in semidilute regime changed from 1.1 to 4.8, depending on the temperature.[11]

The aqueous C_nE_m solutions are often subject to the liquid–liquid phase separation with a rise in temperature, and several workers investigated the solution behavior at different temperatures up to the lower consolute boundary.[7,12–21] Imae et al.[22] have recently reported that aqueous solutions of alkyldimethylammonium chlorides and bromides (C_nDAC, C_nDAB) and dodecylammonium chloride ($C_{12}AC$) separate into two liquid phases, if the salt is added to surfactant solutions. While aqueous $C_{14}DAC$, $C_{14}DAB$, and $C_{12}DAC$ solutions exhibited the lower critical solution temperature (LCST) just like aqueous C_nE_m solutions, aqueous $C_{16}DAC$ and $C_{12}DAB$ solutions displayed closed loop profiles. On the other hand, the upper critical solution temperature (UCST) was observed for aqueous $C_{12}AC$ solutions.

In the present work, the viscosity as a function of micelle concentration is measured at temperatures up to the lower consolute boundary for aqueous sodium halide solutions of $C_{16}DAC$, $C_{14}DAC$, and $C_{14}DAB$. The viscosity measurement is also carried out for aqueous NaCl solutions of $C_{12}AC$, which have a lower NaCl concentration than the critical value for the liquid–liquid phase separation. The viscosity behavior for semidilute solutions of these surfactants is discussed in relation to the liquid–liquid phase separation and is compared to that for C_nTAC, C_nTAB, and C_nE_7.

Experimental Section

Samples of $C_{16}DAC$, $C_{14}DAC$, $C_{14}DAB$, and $C_{12}AC$ are the same as previously prepared and used.[22] NaCl and NaBr were ignited

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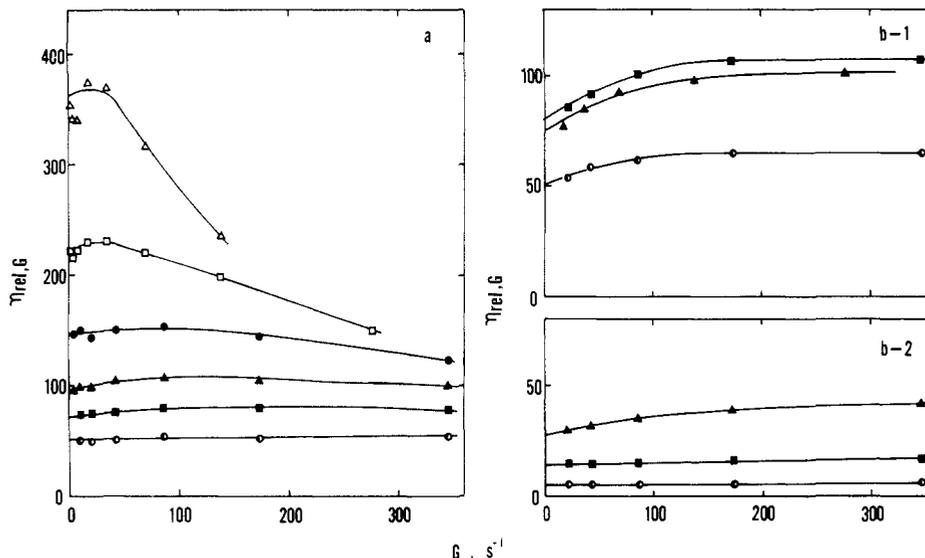
Figure 1. Relative viscosity as a function of the shear rate. (a) 2.6 M NaCl solutions of $C_{14}DAC$ at a micelle concentration of 3 $\times$ 10^{-2} g cm^{-3}. (b) 0.3 M NaCl solutions of $C_{12}AC$ at 7 $\times$ 10^{-2} g cm^{-3} (1) and 3 $\times$ 10^{-2} g cm^{-3} (2). Temperature (°C): $\triangle$, 20; $\square$, 25; $\bullet$, 30; $\blacktriangle$, 35; $\blacksquare$, 40; $\mathbf{O}$, 45.

for 1 h, and water was redistilled from alkaline KMnO$_4$.

The 1.4 M NaCl solutions of $C_{16}DAC$, 2.6 and 2.8 M NaCl solutions of $C_{14}DAC$, and 4.3 M NaBr solutions of $C_{14}DAB$ were prepared with surfactant concentrations of (0.1–10) $\times$ 10^{-2} g cm^{-3}. The LCST of solutions described above was 35 °C at 0.3 wt %, 37 and 30 °C at 0.5 wt % and 35 °C at 0.2 wt %, respectively.[22] To aqueous $C_{12}AC$ solutions, 0.3 M NaCl was added. The 0.3 M NaCl solutions of $C_{12}AC$ were homogeneous at temperatures above the Krafft boundary in the vicinity of 20 °C, while aqueous $C_{12}AC$ solutions exhibited the UCST above the Krafft boundary on the addition of 0.33 M NaCl.[22]

On the basis of light-scattering results,[23,24] the surfactant and salt concentrations of solutions prepared in this work are higher by far than the critical micelle concentration and the threshold salt concentration of the sphere–rod transition, respectively, assuring dominant formation of rodlike micelles in these solutions.

The viscosity measurement was carried out on a capillary viscometer for solutions with low viscosity. The viscosity under the shear rate, G, for the other solutions was measured on a Haake Rotovisco RV 12 concentric cylinder rotational viscometer, equipped with the coaxial double-cylinder sensor system NV. When the temperature was varied from 20 to 45 °C, solutions were kept for 1 h at each temperature before measurement. The procedure for using the rotational viscometer is described elsewhere in detail.[9,11]

Results

The viscosity of aqueous surfactant solutions displays the shear rate dependence. Figure 1a illustrates the shear rate dependence of the relative viscosity for 2.6 M NaCl solutions of $C_{14}DAC$ at a micelle concentration of 3 $\times$ 10^{-2} g cm^{-3}. As the shear rate increases, the relative viscosity, $\eta_{rel,G}$, at 20 °C increases slightly at low shear rates and decreases greatly at high shear rates. With increasing temperature, the magnitude of the relative viscosity decreases and the shear rate for the maximum relative viscosity shifts higher. At 45 °C, the relative viscosity is constant and only slightly increases at high shear rates. An increase in the micelle concentration affects the shear rate dependence of the relative viscosity in a similar way to the lowering of the temperature.

The shear rate dependence of the relative viscosity of $C_{14}DAC$ in 2.8 M NaCl is very similar to that of $C_{14}DAC$

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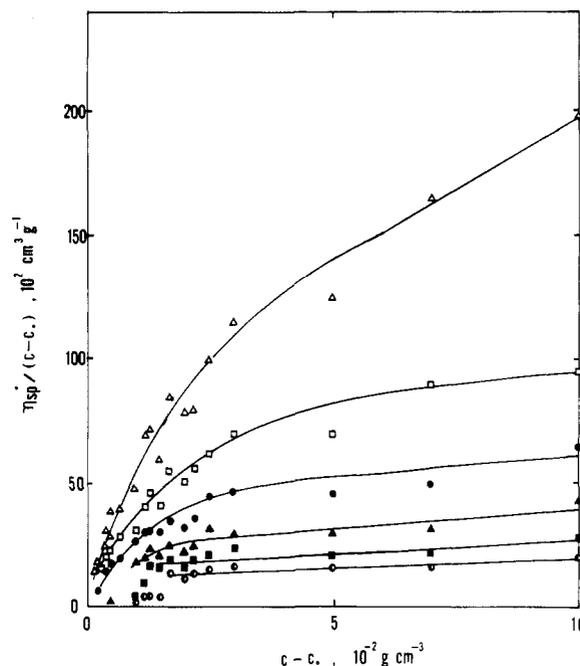
Figure 2. Reduced viscosity at zero shear rate as a function of micelle concentration for 2.6 M NaCl solutions of $C_{14}DAC$. The symbols represent the same temperatures as in Figure 1.

in 2.6 M NaCl. A similar temperature dependence is also observed for $C_{14}DAB$ in 4.3 M NaBr. The relative viscosity of $C_{16}DAC$ in 1.4 M NaCl exhibits the maximum at low shear rates even at high temperatures and low micelle concentrations. On the other hand, as seen in parts b-1 and b-2 of Figure 1, the relative viscosity of $C_{12}AC$ in 0.3 M NaCl displays gradual shear thickening over all temperatures and micelle concentrations. The relative viscosity under the shear rate is extrapolated to zero shear rate in order to obtain the relative viscosity at zero shear rate, η_{rel}^{0}.

Figure 2 shows the reduced viscosity extrapolated to zero shear rate, $(\eta_{rel}^{0} - 1)/(c - c_0) \equiv \eta_{sp}^{0}/(c - c_0)$, for 2.6 M NaCl solutions of $C_{14}DAC$ at various temperatures as a function of micelle concentration, $c - c_0$, where c is the total surfactant concentration and c_0 is the critical micelle concentration. The reduced viscosity increases with a curvature with increasing micelle concentration but decreases

Figure 3. Double logarithmic plot of the relative viscosity vs the micelle concentration for 2.6 M NaCl solutions of C_{14}DAC. The symbols represent the same temperatures as in Figure 1.

with an increase in the temperature.

The reduced viscosity of C_{16}DAC in 1.4 M NaCl, C_{14}DAC in 2.8 M NaCl, and C_{14}DAB in 4.3 M NaBr also increases nonlinearly with micelle concentration and decreases with temperature, similar to the viscosity behavior for C_{14}DAC in 2.6 M NaCl. Whereas the numerical values of the reduced viscosity for C_{14}DAC in 2.6 M NaCl are almost the same as those for C_{14}DAC in 2.8 M NaCl, those for C_{16}DAC in 1.4 M NaCl and C_{14}DAB in 4.3 M NaBr are 10 and 2 times, respectively, larger than those for C_{14}DAC.

The reduced viscosity of C_{12}AC in 0.3 M NaCl is at most 1200 cm^3 g^{-1} and decreases through the maximum with an increase in micelle concentration at 35 and 40 °C, while the reduced viscosity at 45 °C increases gradually but nonlinearly. Similar to that for C_{16}DAC, C_{14}DAC, and C_{14}DAB, the viscosity for C_{12}AC decreases with an increase in temperature.

It should be noted that, above temperatures slightly lower than the lower consolute boundary, the reduced viscosity of alkyldimethylammonium halides and C_{12}AC decreases remarkably.

The nonlinear relation between the reduced viscosity and the micelle concentration is characteristic of the semidilute solutions, as already demonstrated on the viscosity behavior for entangled rodlike micelles of C_nE_7.[11]

According to the reptation model and the scaling law for viscosity behavior of entangled polymer chains,[1,10] the relative viscosity at the zero shear rate in semidilute regime relates to the micelle concentration by

$$\eta_{\text{rel}}^0 \sim (c - c_0)^x \qquad (1)$$

with

$$x = 3\nu_\eta/(3\nu_\eta - 1) \qquad (2)$$

ν_η is a characteristic exponent defined by a scaling law of

$$\xi_\eta \sim m_\eta^{\nu_\eta} \qquad (3)$$

where ξ_η is the viscometric correlation length of entangled rodlike micelles and m_η is the aggregation number within the correlation length, ξ_η. The exponent x can be evaluated from the slope of the straight line, when the relative vis-
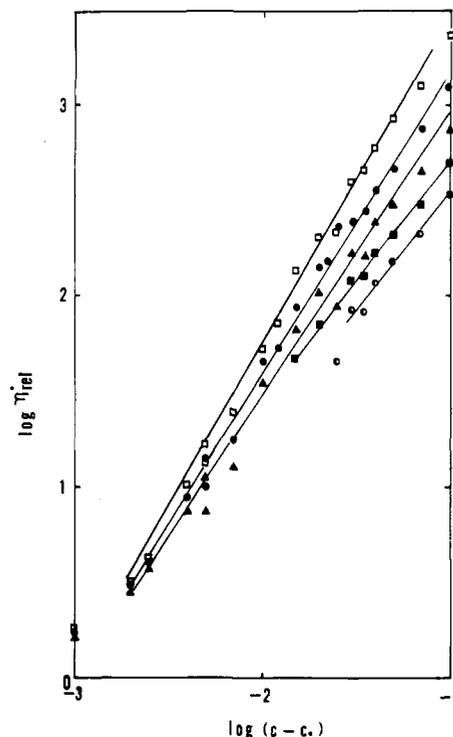
Figure 4. Double logarithmic plot of the relative viscosity vs the micelle concentration for 4.3 M NaBr solutions of C_{14}DAB. The symbols represent the same temperatures as in Figure 1.
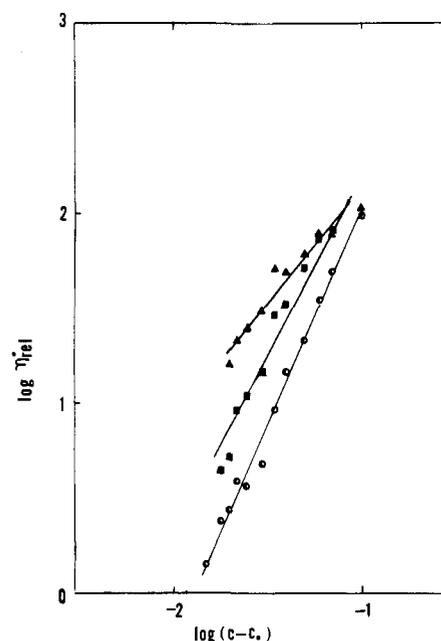
Figure 5. Double logarithmic plot of the relative viscosity vs the micelle concentration for 0.3 M NaCl solutions of C_{12}AC. The symbols represent the same temperatures as in Figure 1.

cosity is plotted against the micelle concentration in a double logarithmic scale.

Figures 3 and 4 illustrate the double logarithmic plots of the relative viscosity vs the micelle concentration for 2.6 M NaCl solutions of C_{14}DAC and 4.3 M NaBr solutions of C_{14}DAB. The linear relation holds above the micelle concentration of 0.2×10^{-2} g cm^{-3} at all temperatures for both solutions. The straight lines are almost parallel and shift to lower viscosity with the temperature. The similar behavior of the relative viscosity against the micelle concentration is also obtained for C_{16}DAC in 1.4 M NaCl and C_{14}DAC in 2.8 M NaCl.

Table I. Viscometric Characteristics of Rodlike Micelles of Cationic Surfactants in Aqueous Sodium Halide Solutions

	T, °C	$\eta_{sp}^0/(c-c_0)$,[a] 10^2 cm^3 g^{-1}	x	ν_η
C_{16}DAC in 1.4 M NaCl	35	40.0	1.51	1.00
	40	28.0	1.36	1.07
	45	18.0	1.29	1.11
C_{14}DAC in 2.6 M NaCl	20	17.5	1.62	0.95
	25	13.5	1.46	1.02
	30	9.2	1.36	1.07
	35	8.0	1.35	1.07
	40	5.6	1.39	1.05
	45	4.2	1.37	1.06
C_{14}DAC in 2.8 M NaCl	20	18.0	1.47	1.01
	25	14.0	1.33	1.09
	30	10.5	1.27	1.12
	35	6.8	1.27	1.12
C_{14}DAB in 4.3 M NaBr	25	19.0	1.76	0.90
	30	16.0	1.64	0.94
	35	13.0	1.43	1.03
	40	9.1	1.21	1.16
	45	6.0	1.26	1.13
C_{12}AC in 0.3 M NaCl	35		1.31	1.10
	40		2.05	0.82
	45		2.29	0.77

[a] At $c - c_0 = 0.2 \times 10^{-2}$ g cm^{-3}.

The double logarithmic plot of the relative viscosity vs the micelle concentration for C_{12}AC in 0.3 M NaCl is given in Figure 5. Although the logarithmic relative viscosity increases linearly with the logarithmic micelle concentration and decreases with the temperature, similar to aqueous sodium halide solutions of alkyldimethylammonium halides, the slope of the straight lines increases with the temperature.

The x and ν_η values evaluated from the double logarithmic plot of the relative viscosity against the micelle concentration are listed in Table I. Table I also includes the numerical values of the reduced viscosity of alkyldimethylammonium halides at the micelle concentration of 0.2×10^{-2} g cm^{-3}. The values were obtained by the extrapolation or interpolation on the straight lines of plots of log η_{rel}^0 vs log $(c - c_0)$.

Discussion

From the comparison of the reduced viscosity at the micelle concentration of 0.2×10^{-2} g cm^{-3} as shown in Table I, it can be recognized that an increase in NaCl concentration from 2.6 to 2.8 M scarcely influences the viscosity of C_{14}DAC, suggesting no change in micelle character, although the LCST decreases by 7 °C.[22] This result indicates that the addition of NaCl at high NaCl concentrations plays mainly a role of the salting-out effect and, eventually, causes the liquid–liquid phase separation.

On the other hand, in spite of low NaCl concentration, the reduced viscosity of C_{16}DAC in 1.4 M NaCl is higher than that of C_{14}DAC in 2.6 and 2.8 M NaCl, indicating the effect of alkyl chain length to the viscosity. The viscosity of C_{14}DAB in 4.3 M NaBr is only slightly larger than that of C_{14}DAC in 2.6 and 2.8 M NaCl, although the salt concentration is different. This is comparable to the fact that diagrams of the liquid–liquid phase separation for these solutions resemble one another.

The values of the exponent x in eq 1 are plotted in Figure 6 as a function of the temperature. The x values of C_{14}DAC in 2.6 M NaCl amount to 1.4–1.6 within temperatures from 20 to 45 °C. The x values of C_{14}DAC in 2.8 M NaCl are very close to those of C_{14}DAC in 2.6 M NaCl. The x values of C_{16}DAC in 1.4 M NaCl and C_{14}DAB in 4.3 M NaBr are in the range 1.3–1.5 and 1.2–1.8, respectively. The range of the x values from 1.2 to 1.8 of
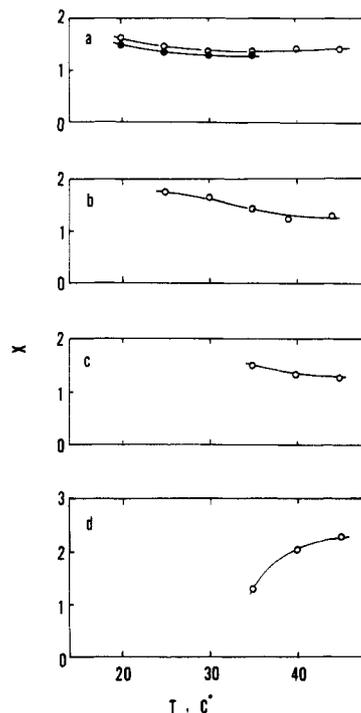
Figure 6. Temperature dependence of the exponent, x. (a) C_{14}DAC in 2.6 M NaCl (O) and 2.8 M NaCl (●). (b) C_{14}DAB in 4.3 M NaBr. (c) C_{16}DAC in 1.4 M NaCl. (d) C_{12}AC in 0.3 M NaCl.

alkyldimethylammonium halides corresponds to ν_η values of 0.90–1.1, scarcely dependent on the temperature.

While the viscosity of alkyldimethylammonium halides was mainly measured at temperatures lower than the lower consolute boundary, the viscosity measurement of C_{12}AC should be carried out at a temperature higher than the upper consolute boundary, because the UCST of C_{12}AC in 0.3 M NaCl should be less than 20 °C, even if there is the UCST. If this assumption is valid, it can be stated that, as the temperature rises beyond the upper consolute boundary, the x values for C_{12}AC slightly increase from 1.3 to 2.3 and the ν_η values decrease from 1.1 to 0.8.

Imae et al.[9] measured the viscosity at 25 °C for aqueous sodium halide solutions of C_{16}TAC, C_{16}TAB, and C_{14}TAB. The exponent x on the scaling law of the relative viscosity against the micelle concentration of alkyltrimethylammonium halides in semidilute solutions ranged between 2.2 and 3.0, scarcely dependent on the alkyl chain length, the salt concentration, and the sort of counterion, Cl$^-$ or Br$^-$. The corresponding ν_η values were 0.80–0.67.

The temperature dependence of the viscosity in semidilute regime was investigated for aqueous NaCl solutions of C_{16}E$_7$, C_{14}E$_7$, and C_{12}E$_7$.[11] The exponent x on the scaling law of the relative viscosity decreased from 4.8 to 1.1, remarkably, with a rise in temperature and decreased slightly with an increase in NaCl concentration. This change of the x values corresponded to the variation of the ν_η value from 0.54 to 1.3.

If the ν_η value can be regarded as a measure of rigidity or expansion of rodlike micelles,[9] the evaluated values of ν_η may suggest that rodlike micelles of C_{16}DAC, C_{14}DAC, and C_{14}DAB expand more than those of C_{16}TAC, C_{16}TAB, and C_{14}TAB. Since the viscosity of alkyldimethylammonium halides is higher than those of alkyltrimethylammonium halides, longer rodlike micelles of alkyldimethylammonium halides are formed, and they expand more by the intramicellar excluded volume effect.

The ν_η values of rodlike micelles of C_nE_7 increase remarkably with an increase in the temperature up to the

consolute phase boundary.[11] However, the ν_η values increase slightly for $C_{12}AC$ but scarcely for $C_{16}DAC$, $C_{14}DAC$, and $C_{14}DAB$, as the temperature approaches the consolute boundary of the liquid–liquid phase separation. Therefore, the rigidity or expansion of rodlike micelles is not necessarily related to the liquid-liquid phase separation.

The difference in the rigidity or expansion of rodlike micelles seems to manifest itself in the shear rate dependence of the viscosity. The shear thickening phenomenon was observed for almost all of aqueous sodium halide solutions of $C_{16}DAC$, $C_{14}DAC$, $C_{14}DAB$, and $C_{12}AC$, rodlike micelles of which may have more expanded character: the relative viscosity shows the shear thickening at low shear rates, before the shear thinning occurs. The expanded long rodlike micelles entangle further at low shear rates, and then entangled micelles are aligned or destructed at high shear rates. On the other hand, shear-induced association may occur for shorter rodlike micelles of $C_{12}AC$.

The strong shear thinning or pseudoplastic behavior happened for solutions of more flexible rodlike micelles of $C_{16}TAC$, $C_{16}TAB$, and $C_{14}TAB$.[9] The entanglement of such flexible micelles can be aligned or destructed easily, if the shear stress is applied. The same discussion can be applicable to the shear rate dependence on the viscosity of aqueous NaCl solutions of C_nE_7. As the rigidity or expansion of rodlike micelles increased with a rise in temperature, the relative viscosity changed from shear thinning to shear thickening.[11]

The shear rate dependence on the viscosity was reported for aqueous NaBr solutions of alkylpyridinium salicylate, aqueous solutions of tetradecyltrimethylammonium salicylate, and their mixture.[25,26] The possibility of the shear-induced phase transition was suggested for these solutions.

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Excited-State Resonance Raman Spectroscopy as a Probe of Alumina–Sodium Dodecyl Sulfate Hemimicelles

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Excited-state resonance Raman spectroscopy has been shown to be a sensitive technique to monitor the formation of hemimicelles. The alumina–sodium dodecyl sulfate hemimicelles are examined by excited-state Raman spectroscopy, for the first time, by observing the Raman spectrum of tris(2,2′-bipyridyl)ruthenium(II)* incorporated in the solid–liquid interface under in situ equilibrium conditions. The study clearly shows several transitions are sensitive to the evolution and structure of hemimicelles.

Introduction

Adsorption of ionic surfactants on alumina from aqueous solutions results in the aggregation of surfactant molecules on the solid–water interface forming two-dimensional surfactant structures called hemimicelles. Hemimicelles tend to change the surface properties of solids and are exploited in many technologically important processes such as flotation, flocculation, and oil recovery.[1]

The internal structure of hemimicelles formed by sodium dodecyl sulfate on alumina was recently studied by fluorescence[2] and electron spin resonance[3] spectroscopic methods. These results substantiated the earlier observations involving bulk property measurements.[4] Microscopic properties like polarity and viscosity as well as aggregation number for different regions in the adsorption isotherm were determined[5] by these spectroscopic measurements. These studies indicated that hemimicellar micropolarity is comparable to that in a micellar environment; but the hemimicellar microviscosity showed marked increase which was about 10 times more than the micellar viscosity. Here, the alumina–SDS system is investigated by excited-state resonance Raman spectroscopy, which is convenient in an aqueous environment as in the present system. Tris(2,2′-bipyridyl)ruthenium(II) chloride, $Ru(bpy)_3^{2+}$, was chosen as the reporter molecule. It has been shown that ruthenium polypyridyl complexes serve as excellent photophysical probes for biopolymers like

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