Size and Electrophoretic Mobility of C14 TASal Micelles in Aqueous Media

Toyoko Imae* and Takashi Kohsaka

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan (Received: March 30, 1992; In Final Form: August 5, 1992)

Spinnable, viscoelastic solutions of tetradecyltrimethylammonium salicylate ($C_{14}TASal$) with and without sodium salicylate (NaSal) have been examined by static, dynamic, and electrophoretic light scattering. In aqueous solutions without NaSal, $C_{14}TASal$ molecules associate into short rodlike micelles at temperatures below 25 °C. Since the external interference effect indicating the intermicellar correlation is strong, short rodlike micelles may pseudolink with each other. While the intermicellar correlation decreases with addition of NaSal, rodlike micelles lengthen and reach 800–1600 nm in 0.1 M NaSal, resulting in the formation of entangled rodlike micelles. Further addition of NaSal diminishes the micelle size, as manifested by a result that micelles in 1 M NaSal are spherical. Electrophoretic mobility examination indicates that, with addition of NaSal, net micelle surface charge is converted from positive to negative through neutral at ~0.1 M NaSal. This manifests that specific adsorption and penetration of salicylate ions dominate micelle size and solution behavior such as spinnability and viscoelasticity.

Introduction

Viscoelastic polymer solutions often exhibit the Weissenberg effect, which results in the spinnability phenomenon.¹⁻⁴ The spinnability phenomenon has also been reported for aqueous solutions of surfactants such as alkyltrimethylammonium salicylates (C_n TASal, n = 14, 16) and alkyldimethylamine oxides,⁵⁻⁷ and the strong correlation with viscoelasticity has been confirmed.^{7.8} The viscoelasticity for aqueous C_n TASal solutions⁸⁻¹¹ can be compared with that for aqueous solutions of alkyltrimethylammonium bromide/NaSal mixture.^{12,13}

Aqueous C_nTASal solutions displayed spinnability and viscoelasticity even at dilute concentrations, although the rheological behavior for $C_{14}TASal$ developed at higher surfactant concentrations than that for $C_{16}TASal$.^{6,8} The spinnability behaved like "ductile failure" or "cohesive fracture failure", depending on surfactant and NaSal concentrations and temperatures. The cohesive fracture failure spinnability could be connected with gellike viscoelasticity, and the ductile failure spinnability was concerned with Maxwell-like and polymer-like viscoelasticity. The rheological character disappeared on excess addition of NaSal.

Electrophoretic light scattering is one of useful methods to examine surface potential and charge of colloidal particles which are essential for the stability of particles in solutions. This is especially beneficial for small particles such as micelles. However, electrophoretic mobility of micelles was reported for only a few cases.¹⁴⁻¹⁶ The electrophoretic light scattering for aqueous $C_{16}TASal$ solutions was recently investigated with static and dynamic light scattering, and the positive mobility was obtained in an aqueous solution without salt.¹⁵ The mobility decreased with NaSal concentration and was almost null at 0.1 M NaSal.

In this work, light scattering is measured for aqueous $C_{14}TASal$ solutions with and without NaSal, and size and electrophoretic mobility of $C_{14}TASal$ micelles are evaluated. Especially the mobility is measured for solutions up to 0.5 M NaSal concentrations in order to obtain the information for solutions at high NaSal concentrations. The results are discussed in relation to the surface potential and the rheological behavior. The solution aspect is compared with that for aqueous $C_{16}TASal$ solutions.

The specific affection of salicylate counterions for cationic micelles was not necessarily clarified in the past work, although the characteristic rheological behavior of C_n TASal micelles was estimated to be carried by salicylate ions. When it is assumed that salicylate ions exhibit specific adsorption and penetration ability, the electric structure such as electrophoretic mobility, surface potential and electron double layer, and, as a result, the micelle structure may change remarkably. Therefore, the purpose of this investigation is to confirm the role of salicylate ions on the micelle formation and the rheological properties by the aid of the electric properties.

TABLE I: Cmc and Specific Refractive Index Increment (in cm³ g⁻¹) for Aqueous C_{14} TASal Solutions at Various NaSal Concentrations and Temperatures

	$10^{2}c_{m}$	<i>T</i> , °C						
<i>C</i> ,, M	g cm ⁻³	7	15	25	35	45		
0	0.037	0.178	0.176	0.175	0.175	0.172		
0.1	0.014		0.181	0.183	0.174	0.158		
1.0	<0.001		0.158	0.140	0.136	0.131		

Experimental Section

Samples of $C_{14}TASal$ and NaSal are the same as previously prepared and used.^{6,8}

Measurements were carried out on a dynamic light-scattering spectrophotometer (DLS-700), a differential refractometer (RM-102), and an electrophoretic light-scattering spectrophotometer (ELS-800). While the static and dynamic light scattering was measured at scattering angles of 20–150°, the electrophoretic light-scattering measurement was performed at 15°. A 2 × 10 × 17 mm electrophoretic rectangular cell was used for NaSal concentrations below 0.1 M and the 1 × 5 × 17 mm cell was for 0.2–0.5 M NaSal concentrations. Details of the experimental procedure are described elsewhere.^{14,17,18} Numerical values of specific refractive index increment are given for various NaSal concentrations C_s and temperatures in Table I with those of critical micelle concentration (cmc, c_0). The cmc value (0.94 mM) for an aqueous C₁₄TASal solution without NaSal was close to that from surface tension method.⁸

Results

Light Scattering for Aqueous Solutions without NaSal. Figure 1 represents the angular dependence of static light scattering for aqueous C_{14} TASal solutions without NaSal at various micelle concentrations and temperatures. While the reciprocal angular envelop of light scattering at low micelle concentrations is independent of scattering angle, at high concentrations it decreases gradually or goes through a maximum with the scattering angle. The unusual behavior may result from the strong effect of the external interference, i.e., the intermicellar correlation, as already estimated for aqueous solutions of oleyl- and alkyldimethylamine oxides^{19,20} and C₁₆TASal.¹⁵ The effect is emphasized with increasing micelle concentration.

On the basis of the equation

$$\lim_{\substack{\theta \to 0 \\ c = C_{0} \to 0}} K(c - c_{0})/(R_{0} - R_{0}^{\circ}) = 1/M$$
(1)

where K is the optical constant and $R_{\theta} - R_{\theta}^{\circ}$ is the reduced scattering intensity at micelle concentration $c - c_0$ and scattering angle θ , micelle molecular weight M and aggregation number m



Figure 1. Angular dependence of static light scattering for aqueous C_{14} TASal solutions without NaSal at various micelle concentrations and temperatures. Micelle concentration $(10^{-2} \text{ g cm}^{-3})$: O, 0.11; \triangle , 0.27; \square , 0.46; \oplus , 0.76; \triangle , 1.19.

TABLE II: Characteristics of $\rm C_{14}TASal$ Micelles in Water at Various Temperatures

<i>T</i> , °C	10 ⁻⁴ M, g mol ⁻¹	m	$10^7 D_0,$ cm ² s ⁻¹	R _H , nm	L _c , nm
7	21.9	557	1.40	10.2	75
15	21.9	557	2.22	8.37	57
25	13.3	339	4.81	5.06	27
35	4.26	108			
45	1.80	46			

= M/393.6 are evaluated for dilute solutions without angular dependence and listed in Table II. Table II includes diffusion coefficient D_0 and hydrodynamic radius $R_{\rm H}$, which are evaluated from a relation of

$$\lim_{\Theta \to 0} D_{o} = K_{B}T/6\pi\eta_{o}R_{H}$$
(2)
$$\theta \to 0$$
$$c-c_{0} \to 0$$

where D is mutual diffusion coefficient, $k_{\rm B}$ is the Boltzmann constant, T is absolute temperature, and η_0 is the viscosity of solvent.

The aggregation number decreases from 557 to 46 with increasing temperature, as expected for ionic micelles, and micelles may be elliptic or rodlike at temperatures below 25 °C. If a rigid rod is assumed, the contour length L_c can be calculated from a relation of²¹

$$R_{\rm H} = \frac{L_{\rm c}}{\left[2 \ln (L_{\rm c}/r) - 0.19 - 8.24 / \ln (L_{\rm c}/r) + 12 / \left[\ln (L_{\rm c}/r)\right]^2\right]}$$
(3)

where a cross section radius r of rod is taken as 1.85 nm. As shown in Table II, the rod length is, at most, 27–75 nm and is consistent with the value previously reported.²²

Light Scattering for Aqueous Solutions with 0.1 M NaSal. The angular dependence of static and dynamic light scattering for aqueous C_{14} TASal solutions with 0.1 M NaSal at 25 °C is given in Figure 2. With increasing $\sin^2(\theta/2)$, the reciprocal angular envelope and the diffusion coefficient increase linearly or with upward convex curvature. This behavior is characteristic to long rodlike micelles in dilute and semidilute solutions and observed even at different temperatures of 7-45 °C.

The reciprocal scattering intensity and the mutual diffusion coefficient extrapolated to zero scattering angle are plotted in Figure 3. Then, in a dilute regime

$$\lim_{\theta \to 0} K(c - c_0)/(R_{\theta} - R_{\theta}^{\circ}) = K(c - c_0)/(R_0 - R_0^{\circ}) = 1/M + 2B_2(c - c_0)$$
(4)

$$\lim_{\substack{D \to 0 \\ k_D = 2B_2M - k_1 - \overline{v}}} D = D_c = D_o[1 + k_D(c - c_o)]$$

where B_2 , k_D , and k_f are the second virial coefficient, the hydrodynamic virial coefficient, and the frictional virial coefficient, respectively, and σ is the partial specific volume.

It may be noted from Figure 3 that apparent micelle size increases remarkably with increasing micelle concentration in dilute regime up to 0.1×10^{-2} g cm⁻³ which is a crossover con-



Figure 2. Angular dependence of static and dynamic light scattering for aqueous C_{14} TASal solutions with 0.1 M NaSal at 25 °C. Micelle concentration (10^{-2} g cm⁻³): \bigcirc , 0.018; \triangle , 0.063; \square , 0.097; \bigoplus , 0.19; \triangle , 0.29; \square , 0.60; \bigoplus , 0.99.



Figure 3. Reciprocal scattering intensity and diffusion coefficient at zero scattering angle and electrophoretic mobility as a function of micelle concentration for aqueous $C_{14}TASal$ solutions with 0.1 M NaSal. Temperature (°C): 0, 15; \oplus , 25; \square , 35; \oplus , 45.

TABLE III: Characteristics of Rodlike C14TASal Micelles in 0.1 M NaSal at Various Temperatures

<i>T</i> , ⁰C	10 ⁻⁴ M, g mol ⁻¹	m	R _G , nm	$10^7 D_0,$ cm ² s ⁻¹	R _H , nm	ρ	$10^5 B_2,$ mol cm ³ g ⁻²	$k_{\rm f},$ cm ³ g ⁻¹	$k_{\rm D},$ cm ³ g ⁻¹	L _c , nm	<i>a</i> , nm	$10^2(c-c_0)^*_{obs},$ g cm ⁻³	$10^{2}(c-c_{0})^{*}_{w},$ g cm ⁻³
15	1590	40 500	232	0.136	131	1.77	3.39	1120	-42	1640	122	0.097	0.084
25	1280	32 500	222	0.200	117	1.89	4.23	1080	2	1310	156	0.097	0.065
35	897	22800	176	0.340	87.8	2.00	1.73	396	-86	922	160	0.138	0.074
45	738	18 8 00	152	0.546	68.4	2.22	1.28	236	-47	758	156	0.138	0.085

TABLE IV: Characteristics of Small C14TASal Micelles in 1 M NaSal at Various Temperatures

	10²-										
Τ,	$(c-c_0),$	10 ⁻⁴ M,		$10^7 D_0$,			10 ⁴ <i>B</i> ₂ ,	10 ³ B ₃ ,	k _f ,	$k_{\rm D}$,	
°C	g cm ⁻³	g mol ⁻¹	m	$cm^2 s^{-1}$	R _H , nm	<i>b</i> , nm	mol cm ³ g ⁻²	mol cm ⁶ g ⁻³	$cm^{3} g^{-1}$	$cm^{3} g^{-1}$	
25	0ª		77		1.85						-
	0.62	3.32	84	7.53	2.22	3.20	1.01	0.21	5.5	0.38	
	1.00	3.51	89	6.71	2.47	4.40	1.24	0.34	7.1	0.49	
	2.02	4.12	105	5.86	2.83	6.62	1.35	0.47	9.1	0.63	
	6.06	6.75	172	4.58	3.62	13.86	1.05	0.47	11.6	0.80	
	9.98	7.39	188	4.38	3.79	15.91	1.01	0.47	12.2	0.84	
35	0 ^a		77		1.85						
	0.62	3.42	87	9.16	2.30	3.56	1.06	0.24	5.9	0.41	
	1.00	3.29	84	10.04	2.11	2.74	0.88	0.16	4.8	0.33	
	2.02	3.51	89	8.64	2.45	4.30	1.20	0.32	6.9	0.47	
	6.06	5.42	138	6.82	3.11	8.79	1.04	0.37	9.2	0.63	
	9.98	5.63	143	6.58	3.22	9.75	1.07	0.40	9.8	0.68	
45	0 ^a		77		1.85						
	6.06	3.74	95	11.97	2.21	3.15	0.78	0.14	4.8	0.33	
	9.98	4.41	112	9.62	2.74	6.01	1.07	0.31	7.7	0.53	

^a Calculated from $K(c - c_0)/(R_0 - R_0^{\circ})$ and D_c values extrapolated to zero micelle concentration.





Figure 4. Reciprocal scattering intensity and diffusion coefficient at zero scattering angle, aggregation number, and hydrodynamic radius as a function of micelle concentration for aqueous C_{14} TASal solutions with 1 M NaSal. Temperature (°C): \oplus , 25; \square , 35; \blacksquare , 45.

centration from dilute to semidilute regimes. The size decreases with an increase in concentration above the crossover point, indicating that the "size" in the semidilute regime corresponds to the correlation length between network meshes.²³

The analysis method for light scattering data at a finite micelle concentration in dilute regime²⁴ is applied for an aqueous C_{14} TASal solution of $(0.097-0.138) \times 10^{-2}$ g cm⁻³ in 0.1 M NaSal, and numerical values of micelle parameters and their virial coefficients are evaluated, as shown in Table III, by the aid of the procedure described previously.^{25,26}

Aggregation number and contour length decrease from 40 500 to 18 800 and from 1640 to 760 nm, respectively, with rising temperature. Although $C_{14}TASal$ micelles can be regarded as semiflexible rods from a $\rho = R_G/R_H$ value of 1.8-2.2, where R_G is a radius of gyration, the persistence length *a* of 120-160 nm implies a more rigid semiflexible character of $C_{14}TASal$ micelles. The persistence length is equal to those of $C_{16}TASal$ and oleyl-dimethylamine oxide micelles but is about 2 times longer than those of alkyltrimethylammonium halide, alkyldimethylammonium halide, and oligooxyethylene alkyl ether micelles.¹⁵ The second virial coefficient is as small as 10^{-5} mol cm³ g⁻², but the frictional virial coefficient is large.

coefficient is a result of the compensation between $2B_2M$ and k_f values. The observed crossover concentration between dilute and semidilute regimes $(c - c_0)_{obs}^*$ is consistent with that calculated, $(c - c_0)_w^*$, which is based on the theoretical approach for wormlike chains.²⁷ The consistency between observed and calculated crossover concentrations was also reported for other micellar systems.¹⁵

Light Scattering for Aqueous Solutions with 1 M NaSal. Aqueous C_{14} TASal solutions with 1 M NaSal do not display any angular dependence on reciprocal scattering intensity and diffusion coefficient, which is different from aqueous solution with 0.1 M NaSal. Figure 4 plots their values at zero scattering angle as a function of micelle concentration. The micelle aggregation number, which can be evaluated from the extrapolation to zero micelle concentration of reciprocal scattering intensity, is only 77, suggesting the formation of small (spherical) micelles in infinite dilution.

As seen in Figure 4, the reciprocal scattering intensity and the diffusion coefficient depend on micelle concentration with a different manner as a result of the competition of the contributions of micelle growth and virial coefficient. Then, according to the previous analytical procedure of light scattering for small micelles



Figure 5. Angular dependence of static light scattering at 25 °C for aqueous C_{14} TASal solutions of 0.8×10^{-2} g cm⁻³ with various NaSal concentrations. NaSal concentration (M): O, 0; \triangle , 0.0001; \square , 0.0005; \square , 0.001; \triangle , 0.005; \square , 0.01; \square , 0.005; \square , 0.01; \square , 0.005; \square , 1.0.



Figure 6. Angular dependence of dynamic light scattering at 25 °C for aqueous C_{14} TASal solutions of 0.8×10^{-2} g cm⁻³ with various NaSal concentrations. NaSal concentration (M): **B**, 0.01; **O**, 0.05; **A**, 0.1; **D**, 0.5.

at each concentration,^{15,18} micelle parameters and the virial coefficients can be evaluated, as listed in Table IV, where b is the long axis of a prolate ellipsoid when the short axis is 1.85 nm, and B_3 is the third virial coefficient. In Figure 4, the calculated aggregation number and the hydrodynamic radius are plotted as a function of micelle concentration.

Micelle growth with an increase in micelle concentration is remarkable, especially at low temperatures. On the other hand, the positive contribution of the third, frictional, and hydrodynamic virial coefficients slightly increases with increasing micelle concentration and with decreasing temperature, while the second virial coefficient scarcely depends on concentration and temperature.

Light Scattering for Aqueous Solutions with Various NaSal Concentrations. Figures 5 and 6 show angular dependence of light scattering at 25 °C for aqueous $C_{14}TASal$ solutions of 0.8×10^{-2} g cm⁻³ with various NaSal concentrations. As seen in Figure 5, unusual angular dependence of static light-scattering resulting from the external interference effect diminishes with addition of NaSal, and reciprocal angular envelope for solutions with NaSal



Figure 7. Light-scattering and rheological properties as a function of ionic strength for aqueous C_nTASal solutions at 25 °C. Surfactant: a-d, $C_{14}TASal$; e-h, $C_{16}TASal$. Surfactant concentration $(10^{-2} \text{ g cm}^{-3})$: a, b, 0.8; c, d, 1.6; e, h, 0.2; f, 0.055; g, 1. a, e: O, $K(c - c_0)/(R_0 - R_0^\circ)$; \Box , D_c . Broken lines represent the contribution of external interference. b, f: O, U. c, g: O, η_0 ; \Box , G_N ; Δ , τ . d: O, $\Delta L_0/\Delta v$. h: O, $1/L_{0,c}$.

above 0.005 M increases linearly with $\sin^2(\theta/2)$, except a solution of 1 M NaSal which displays angular independency. The relation is given by

$$K(c-c_0)/(R_{\theta}-R_{\theta}^{\circ}) = (1/M)(1+R_{\rm G}^2\mu^2/3) + 2B_2(c-c_0)$$
(6)

where μ is the magnitude of scattering vector.

With increasing $\sin^2(\theta/2)$, the diffusion coefficient shown in Figure 6 increases linearly for solutions with 0.01 and 0.5 M NaSal and with upward convex curvature for solutions with 0.05 and 0.1 M NaSal. This suggests that, besides translational diffusion, rotational diffusion contributes on the mutual diffusion coefficient in a latter case.²⁸

Double logarithmic plots of reciprocal scattering intensity and diffusion coefficient at zero scattering angle as a function of ionic strength $C_0 + C_s$ are given in Figure 7a. The plots show minima at ionic strength around 0.1 M, manifesting that longer rodlike micelles are formed there.

Electrophoretic Light Scattering. Electrophoretic drift velocity v at applied electric field E was measured at 25 °C for aqueous $C_{14}TASal$ solutions of 0.8×10^{-2} g cm⁻³ with various NaSal concentrations. The electrophoretic mobility U calculated from U = v/E is listed in Table V and plotted in Figure 7b. The mobility decreases with addition of NaSal and changes sign around 0.1 M NaSal. The mobility for aqueous $C_{14}TASal$ solutions with 0.1 M NaSal is independent of surfactant concentration c of $(0.05-0.80) \times 10^{-2}$ g cm⁻³, as seen in Table V and Figure 3.

Discussion

 C_{14} TASal molecules in water associate into elliptic or short rodlike micelles at 25 °C. The micelles exhibit a positive net charge and strong intermicellar interaction. Figure 8 illustrates

TABLE V: Electrophoretic Mobility of C14TASal Micelles at 25 °C



Figure 8. Light-scattering and rheological properties as a function of micelle concentration for aqueous C₁₄TASal solutions without NaSal. a, 25 °C: O, $K(c - c_0)/(R_0 - R_0^\circ)$; D, D_c . b, 25 °C: O, η_0 ; D, G_N ; Δ , τ . c, $\Delta L_0/\Delta v$: O, 20 °C; D, 30 °C.

the reciprocal scattering intensity and diffusion coefficient at zero scattering angle as a function of micelle concentration for aqueous C_{14} TASal solutions without NaSal at 25 °C. The abrupt increase in reciprocal scattering intensity and diffusion coefficient at micelle concentrations above 10^{-3} g cm⁻³ implies an increase in intermicellar interaction.

In Figure 8, light-scattering results are compared with rheological results previously reported.^{6,8} While relaxation time τ is almost independent of micelle concentration, zero shear viscosity η_0 , plateau modulus G_N , and ductile failure spinnability $\Delta L_0/\Delta \nu$ (drawing length/drawing velocity) increase at micelle concentration above 10^{-3} g cm⁻³. The spinnability changes from ductile failure to cohesive fracture failure at 4×10^{-2} g cm⁻³ micelle concentration, namely, from viscous response to elastic deformation. These behaviors can be explained as a result that loose pseudolinkages composed of short rodlike micelles as drawn in Figure 9(1) are formed in dilute solutions. The pseudolinkages between micelles increase with micelle concentration and tighten in concentrated solutions.





Figure 9. Schematic representation of characteristics of $C_{14}TASal$ micelles at different NaSal concentration regions. NaSal concentration region: (1) ~0 M; (2) ~0.1 M; (3) ~1 M. (A) micelle size and structure; (B) molecular arrangement on micelle surface and surface potential. @---, surfactant ion; \oplus , salicylate ion adsorbed on micelle surface; \ominus , salicylate ion penetrated into a micelle.

In Figure 7, light-scattering results are compared with rheological results as a function of ionic strength for aqueous $C_{14}TASal$ solutions at 25 °C.^{6,8} Characteristics of $C_{14}TASal$ micelles at different NaSal concentration regions are illustrated in Figure 9. With the addition of NaSal, while intermicellar correlation diminishes owing to the electric shielding by excess salt, the micelle size or rod length increases at NaSal concentrations up to ~0.1 M, and long rodlike micelles entangle with each other in ~0.1 M NaSal (Figure 9(2)). Besides that, some salicylate ions are adsorbed on a Stern layer of micelle surface, some other salicylate ions can penetrate into micelles, which is different from simple salts such as NaCl and NaBr. Therefore, net surface charge of micelles decreases from positive to zero.

At NaSal concentrations above 0.1 M, excess adsorption and penetration of salicylate ions induce negative net charge of micelles. Simultaneously micelle size decreases to small (spherical) micelles in 1 M NaSal (Figure 9(3)) because of electrostatic repulsion in "anionic" micelles. Generally, simple salts such as NaCl and NaBr affect only to increase micelle size even at 1 M and higher salt concentrations. Therefore, the destruction of rodlike C_n TASal micelles by 1 M NaSal to form small micelles is unusual. This type of "structural transition" has never been reported in any other surfactant systems up to date.

Surface potentials ψ for micelles at different NaSal concentration regions are drawn in Figure 9 with molecular arrangement on micelle surface. The surface potentials at a Stern layer ψ_s are positive, zero, and negative at ~0, ~0.1, and ~1 M NaSal, respectively, depending on adsorption and penetration of salicylate ions. The net micelle surface charge is already low even in a solution without salt because of the specific adsorption and penetration of salicylate ions for micelles. The added NaSal affects to promote the specific adsorption and penetration and to decrease the electric double layer. Thus, 0.1 M NaSal must be enough to reach to zero thickness of electric double layer.

As seen in Figure 7, while the plateau modulus is independent of ionic strength, the zero shear viscosity, relaxation time, and ductile failure spinnability increase with the addition of a small amount of NaSal, where the intermicellar correlation diminishes and rodlike micelles lengthen. On further addition of NaSal, the zero shear viscosity and the spinnability decrease through a second maximum and a shoulder, respectively, at ~ 0.1 M NaSal, where micelle size is maximum and net surface charge of micelle is converted the sign.

The relation between light-scattering and rheological results was also observed for aqueous C16 TASal solutions as seen in Figure 7. In Figure 7, $1/L_{0,c}$ (1/intrinsic drawing length) values are plotted as a measure of the cohesive fracture failure spinnability, which is more dominant than the ductile failure spinnability in aqueous C₁₆TASal solutions. The intermicellar correlation disappeared above 0.001 M ionic strength, and the reciprocal scattering intensity and diffusion coefficient had minima around 0.1 M NaSal, where the net surface charge of micelles changed sign. On the other hand, zero shear viscosity had two maxima. The corresponding maxima around 0.1 M NaSal were also obtained on relaxation time and cohesive fracture failure spinnability. These properties of C_{16} TASal solutions are identical with those of C_{14} TASal solutions.

Conclusion

In relation to micelle structure and the situation in solutions, the variation of rheological behavior for aqueous C_nTASal solutions with addition of NaSal can be explained as follows:

(1) In aqueous C_nTASal solutions without NaSal, since short rodlike micelles interact with each other to form pseudolinkages, the linked micelles form a pseudonetwork structure and, therefore, induce the strong rheological behavior.

(2) Since an addition of a small amount of NaSal stimulates the growth of rodlike micelles by the salting-out effect, the rheological character is slightly emphasized.

(3) The further addition of NaSal destroys the intermicellar correlation and the pseudolinkages owing to the electric shielding effect. As a result, the rheological character diminishes in opposition to micelle growth.

(4) Salicylate ions can penetrate into micelles besides their specific adsorption at a Stern layer of micelle surface. The specific adsorption and penetration are promoted by the addition of excess NaSal. As a result, rodlike micelles have no net surface charge in the presence of ~ 0.1 M NaSal. This accelerates the growth of rodlike micelles, and long rodlike micelles entangle with each other in solutions. Therefore, the rheological behavior slightly increases for rodlike micelles in semidilute region at ~ 0.1 M NaSal concentrations. Then, while the pseudonetwork composed of pseudolinkages presents a rather elastic rheology character, the pseudonetwork by entanglement has more viscous rheology character.

(5) At further higher NaSal concentrations, excess adsorption and penetration of salicylate ions allow for micelles to charge negative and to diminish destructively to smaller sizes, e.g., spherical, in 1 M NaSal because of the electrostatic repulsion in a micelle. Then the rheology behavior is lost.

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