probe outside the micellar surface, where the hydrophobic tail of the surfactant molecules were suggested to have a radial distribution to achieve a small density of the methyl groups near the center of the micelle (Figure 13a of ref 6).

The possibility of a nonspherical shape of the micelles has also been investigated in the present case. The incorporation of iron porphyrin might lead to a prolate ellipsoidal shape of the micelles with short semiaxis of 17.4 Å (radius of the spherical micelle) and long semiaxis of 30.8 Å. Figure 10 shows the variation in the average value of the short semiaxes ($R_a$) of the ellipsoids containing the micellar atoms. The average value of $(1/R_a)$ for the ellipsoid was evaluated by numerical integration of eq 11 over the ellipsoid using Gaussian quadrature formula. Two different situations were considered: (i) both the micellar carbon and the iron center form ellipsoids inside the micelles with short semiaxes $R_a$ and $R_b$, respectively (Figure 10a) and (ii) the iron center makes a sphere while the micellar carbon forms ellipsoid around it (Figure 10b). The values of $R_a$ for the case (i) were found to be 9.2 and 9.3 Å for aquahydroxy- and bis(cyanohem), respectively, while in the second case (ii), $R_a$ was 15.3 Å for aquahydroxy- and 14.7 Å for the bis(cyanohem) complex.

Figure 10 shows that the overall nature of the distribution of micellar carbons inside the micelles is very similar to that observed with a spherical model of the micelles (Figure 9). The iron center of the porphyrin in all these models is quite embedded inside the micellar core. Moreover, similar results were obtained with a spherical micellar shape of radius 15.8 Å. This indicates that the relative distribution of the micellar atoms inside the micelles containing the heme does not depend on the actual size or shape of the micelles, and in all these models the heme iron resides at the side of the micellar core. The position of the heme complex inside the micelles was found to depend on the type of the model considered. The iron atom in the porphyrin ring resides $\sim 5 \text{ Å}$ inside the micellar radius for the spherical model, while this distance is not constant for the ellipsoidal models. However, in all the models considered, the iron porphyrin moiety is definitely embedded inside the hydrophobic micellar core. The total error in determination of the radial distances of different carbons from the center of the micelle was $\pm 10\%$, estimated from the experimental errors and the subsequent approximations in correlation times made in the calculations.

Conclusions

The structural disposition of the ferric porphyrins inside aqueous detergent micelles determined in this paper suggests that these complexes are embedded inside the micellar Stern layer, with the hydrophilic propionate side chains of the porphyrin ring directed toward the polar surface of the micelles. We have assumed a smooth surface of the micelles and a uniform probability distribution of the detergent and heme centers so that the average value of $(1/R_a)$ could be evaluated by simple integration of the micelle. A spherical micelle with larger aggregation number ($N$) has been suggested to be a very suitable model for this system. Since the critical micellar concentration of the micelles does not show any drastic change on addition of the ferric heme complex, the assumption of spherical micelles seems to be valid under the experimental conditions. The structural parameters were deduced in the present study from the average distances between the surfactant carbons and the heme iron center, which gave only a statistically averaged picture of the micelles rather than the exact structure of the aggregate. A detailed analysis of the experimental results for different ellipsoidal structures showed that although the absolute values of the distance parameters depend on the radius and shape of the micelles the relative distribution of the micellar atoms inside the micellar core is more or less independent of the type of model. Thus, the assumption made in using an average value of aggregation number does not affect the overall picture of the heme inside micelles. Since the distance parameters were evaluated from $T_{IM}$ by using the Solomon–Bloembergen equation (eqs 9 and 10), the small errors because of the neglect of $K_D$ and simplification of $\tau_C$ in the evaluation of $T_{IM}$ do not essentially affect the final results.

Acknowledgment. The NMR work reported here was done at the 500-MHz FT NMR National Facility. The author thanks Mr. V. Subrahmanyan, D. G. Maharana, and Dr. O. K. Medhi for help and Prof. Samaresh Mitra for encouragement and advice.

Light Scattering of Spinnable, Viscoelastic Solutions of Hexadecyltrimethylammonium Salicylate

Toyoko Imae

Department of Chemistry, Faculty of Science. Nagoya University, Chikusa, Nagoya 464, Japan

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Static, dynamic, and electrophoretic light scattering were measured for spinnable, viscoelastic solutions of hexadecyltrimethylammonium salicylate with and without sodium salicylate (NaSal) at various temperatures. While short rodlike micelles are formed in aqueous solutions without NaSal, the length of rodlike micelles increases with an increase in NaSal concentration and reaches 2000–3000 nm in 0.1 M NaSal. However, the size decreases below 0.5 M NaSal, and small micelles exist in 1 M NaSal. The external interference effect indicating a strong intermicellar correlation is quite apparent in aqueous solutions without NaSal, but it decreases with addition of NaSal and is imperceptible above 0.001 M NaSal. The electrophoretic mobility changes sign from positive to negative with addition of 0.1 M NaSal, indicating the reversal of the net micelle charge. The pseudolinkages between short rodlike micelles, in which salicylate ions participate, would be constructed in aqueous solutions without or with a small amount of NaSal, and the entanglement of long rodlike micelles exists, besides the pseudolinkages, in aqueous solutions with a medium amount of NaSal.

Introduction

The thread-forming property of a liquid, i.e., its "spinnability", is a phenomenon that is frequently observed for native and synthetic polymers. Similar characteristics have been observed for aqueous solutions of cationic surfactants with certain kinds of aromatic counterions, and many investigations have been reported, mainly regarding solution viscoelasticity. Nevertheless,
Solutions

derlich, interface differential experimental plotted two ammonium of surfactant

TABLE 3
Water (10⁻² g cm⁻³): A, 0.017; Δ, 0.034; B, 0.049; O, 0.066; Δ, 0.094; M, 0.200; O, 0.302; Δ, 0.448; G, 0.600; G, 0.987.

the mechanism for the spinnability and viscoelasticity of aqueous surfactant solutions has not been clearly identified.

Recently, we have quantitatively measured the spinnability of aqueous salt solutions of tetradecl- and hexadecyltrimethylammonium salicylates (C₁₆TASal and C₁₆TASal). There were two types of spinnability, which exhibited three extremes when plotted against NaSal concentration.

In this paper, we present light scattering studies from spinnable, viscoelastic solutions of C₁₆TASal, and the size and structure of micelles in aqueous solutions with and without NaSal are discussed in connection with a proposed mechanism for the spinnable behavior.

Experimental Section
The sample of C₁₆TASal is the same as previously prepared and used. Commercial NaSal was used without any purification.

Water was prepared by a routine method.

Light scattering intensity, mutual diffusion coefficient, specific refractive index increment, and electrophoretic drift velocity were measured on dynamic light scattering spectrophotometer DLS-700, differential refractometer RM-102, and electrophoretic light scattering spectrophotometer ELS-800, all of which were manufactured by Otsuka Electronics, Co. Ltd., Osaka. The details of the experimental procedure are described elsewhere. Numerical values of the specific refractive index increment are given in Table I for various NaSal concentrations Cné and temperatures.

Results
Light Scattering for Aqueous Solutions without NaSal. The light scattering was measured for aqueous solutions of C₁₆TASal without NaSal at 15-45 °C. The critical micelle concentration Ccm above which the reduced scattering intensity increases, was determined as 0.006 × 10⁻² g cm⁻³ (1.5 × 10⁻⁴ M), which is consistent with that previously reported.

Figure 1 represents the angular dependence of static light scattering for aqueous solutions of C₁₆TASal without NaSal. The reciprocal angular envelope of light scattering increases with the scattering angle, θ, for dilute solutions of (0.017–0.025) × 10⁻² g cm⁻³, according to the relation of

$$ K(c - c_0)/(R_0 - R_e^0) = 1/MP(θ) + 2B_2(c - c_0) $$

with

$$ 1/P(θ) = 1 + (1/3)R_0^2μ^2 $$

where K is the optical constant. R and R₀ represent the reduced scattering intensities at the surfactant concentration, c, and the critical micelle concentration, c₀, respectively. M is the molecular weight, R₀ is the radius of gyration, B₂ is the second virial coefficient, P(θ) is the particle scattering factor originating in the internal interference effect, and μ is the magnitude of scattering vector.

On the basis of the equation

$$ \lim_{θ→0} K(c - c_0)/(R_0 - R_e^0) = K(c - c_0)/(R_0 - R_e^0) = 1/M + 2B_2(c - c_0) + 3B_3(c - c_0)^2 $$

and

$$ M_{app} = 1/M $$

where B₂ is the third virial coefficient, the apparent molecular weight, M_{app} at 0.017 × 10⁻² g cm⁻³ (5 × 10⁻⁴ M) was evaluated as 3.2 × 10⁶, 3.7 × 10⁶, and 1.8 × 10⁴ at 15, 25, and 35 °C, respectively. These molecular weights correspond to aggregation numbers of 740, 880, and 440, respectively, indicating that short rodlike micelles are formed in aqueous solutions of C₁₆TASal without NaSal.

The virial coefficients where
\[ g_{cn}T_3(\Theta_d) \]
are solutions of the equation
\[ (24) \]
where \( g_{c0} \) is the coefficient.

\[ \text{Figure 3. Angular dependence of dynamic light scattering for 0.1 M NaSal solutions of C_{16}TASal at 15 and 45 °C. The symbols represent the same micelle concentrations as in Figure 2.} \]

\[ \text{Figure 4. } K(c - c_0)/(R_g - R_0^2) \text{ and } D_e \text{ values plotted against micelle concentration for 0.1 M NaSal solutions of C_{16}TASal. Temperature (°C): } 15; \text{ O, 25; D, 35; M, 45.} \]

\[ \theta^\circ \text{ is drawn in Figure 2. A similar angular dependence was observed at 25 and 35 °C. The reciprocal angular envelope of static light scattering barely depends on temperature.} \]

\[ \text{Different from aqueous solutions of C_{16}TASal without NaSal, the reciprocal angular envelope is for 0.1 M NaSal solutions always increases with } \sin^2(\theta/2) \text{ at micelle concentrations of } (0.014-0.20) \times 10^{-2} \text{ g cm}^{-3} \text{ examined here. Moreover, the reciprocal angular envelope has an upward convex curvature at high micelle concentrations above } 0.070 \times 10^{-2} \text{ g cm}^{-3}, \text{ indicating the formation of rodlike micelles.} \]

\[ \text{The upward convex curvature of mutual diffusion coefficient against } \sin^2(\theta/2) \text{ was observed simultaneously, as shown in Figure 3. This is characteristic of rodlike micelles in dilute and semidilute solutions and suggests that there is a contribution of rotational diffusion, besides translational diffusion, on the mutual diffusion coefficient.} \]

\[ \text{The angular dependence of the mutual diffusion coefficient increases slightly with temperature.} \]

\[ \text{Same concluding remarks can be obtained from Figure 4, where the mutual diffusion coefficient, } K(c - c_0)/(R_g - R_0^2), \text{ and the mutual diffusion coefficient, } D_e, \text{ extrapolated to zero scattering angle are plotted. Then} \]

\[ \lim_{\theta \to 0} D = D_e = D_0 [1 + k_D(c - c_0)] \]

\[ \text{with} \]

\[ k_D = 2B_2M - k_1 - \theta \]

TABLE II: Characteristics of Spherical Micelles of C_{16}TASal in 1 M NaSal Solutions at Various Temperatures

<table>
<thead>
<tr>
<th>T, °C</th>
<th>10^2(c - c_o)</th>
<th>10^4M</th>
<th>10^2D_o</th>
<th>R_H, nm</th>
<th>V, mm</th>
<th>10^2B_H</th>
<th>10^2B_o</th>
<th>k_0</th>
<th>k_0</th>
<th>k_D</th>
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<tbody>
<tr>
<td>0</td>
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<td>118</td>
<td>5.25</td>
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<tr>
<td>0.40</td>
<td>4.89</td>
<td>116</td>
<td>4.34</td>
<td>2.89</td>
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<td></td>
<td></td>
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<tr>
<td>0.70</td>
<td>5.54</td>
<td>131</td>
<td>4.11</td>
<td>3.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1.01</td>
<td>6.31</td>
<td>150</td>
<td>3.83</td>
<td>3.43</td>
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<td></td>
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<tr>
<td>25</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.70</td>
<td>88</td>
<td>7.50</td>
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<td>35</td>
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<td>2.80</td>
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<td>9.90</td>
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<tr>
<td>0.19</td>
<td>2.34</td>
<td>67</td>
<td>11.7</td>
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<tr>
<td>0.40</td>
<td>3.33</td>
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<td>9.92</td>
<td>2.50</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>0.70</td>
<td>4.14</td>
<td>98</td>
<td>7.29</td>
<td>3.40</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1.01</td>
<td>4.85</td>
<td>115</td>
<td>7.02</td>
<td>3.53</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Calculated from the \( K(c - c_o)/(R_9 - R_s) \) and \( D_o \) values extrapolated to zero micelle concentration.

where \( D_o \) is the total translational diffusion coefficient and \( k_0 \) is the hydrodynamic virial coefficient. It is noticed that an apparent micellar size increases remarkably at micelle concentrations up to \( 0.1 \times 10^{-2} \) g cm\(^{-3} \), while it changes scarcely at \( (0.1-0.2) \times 10^{-2} \) g cm\(^{-3} \).

Light Scattering for 1 M NaSal Solutions. Despite that the critical micelle concentration of C_{16}TASal in 1 M NaSal is less than \( 10^{-3} \) g cm\(^{-3} \) as well as that in 0.1 M NaSal, the reciprocal scattering intensity and the mutual diffusion coefficient for 1 M NaSal solutions of C_{16}TASal are larger than those for 0.1 M NaSal solutions. Moreover, they are independent of scattering angle.

The reciprocal scattering intensity and the mutual diffusion coefficient at zero scattering angle, which are represented in Figure 5, decrease with increasing micelle concentration. The decrease is more gradual at lower temperature and more rapid at higher temperature.

Molecular weight and hydrodynamic radius, \( R_H \), of micelles can be calculated by

\[
\lim_{c \to 0} K(c - c_o)/(R_9 - R_s) = 1/M
\]

and

\[
\lim_{c \to 0} D = D_o = k_0 T/6 \pi \eta_o R_H
\]

where \( k_0 \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \eta_o \) is the viscosity of solvent. From numerical values that are given in Table II, it can be interpreted that molecules of C_{16}TASal in 1 M NaSal associate into small micelles. The aggregation number, \( m (=M/421.6) \), increases from 61 at 45 °C to 118 at 15 °C, and the hydrodynamic radius ranges from 2.2 to 4.4 nm, indicating the variation of micellar shape from sphere to ellipsoid.

Light Scattering for Aqueous Solutions with Various NaSal Concentrations. The light scattering for aqueous solutions of

Figure 5. \( K(c - c_o)/(R_9 - R_s) \) and \( D_o \) values plotted against micelle concentration for 1 M NaSal solutions of C_{16}TASal. The symbols represent the same temperatures as in Figure 4.

Figure 6. Angular dependence of static light scattering for aqueous NaSal solutions of C_{16}TASal at 25 °C, \( c = 0.2 \times 10^{-2} \) g cm\(^{-3} \). NaSal concentration (M): \( \Theta, 0; \Delta, 0.0001; \Xi, 0.0005; \Phi, 0.001; \Delta, 0.005; \Psi, 0.01; \Theta, 0.05; \Delta, 0.1; \Xi, 0.2; \Phi, 0.5; \Psi, 1.0 \).

Figure 7. Angular dependence of dynamic light scattering for aqueous NaSal solutions of C_{16}TASal at 25 °C, \( c = 0.2 \times 10^{-2} \) g cm\(^{-3} \). The symbols represent the same NaSal concentrations as in Figure 6.
Spinnable, Viscoelastic Solutions of C_{14}TASal

Figure 8. Double logarithmic plots of $K(c-c_0)/(R_0-R_g)$, $R_{phot}$ and $D_v$ vs $c_0$ for aqueous NaSal solutions of C_{14}TASal at 25 °C and schematic models of typical micelle structures. $c_0 = 0.2 \times 10^{-2}$ g cm$^{-3}$, $\Omega$, $K(c-c_0)/(R_0-R_g)$; $\Omega$, $R_{phot}$, $D_v$. The contribution of external interference effect is included in the region of dotted lines.

TABLE III: Electrophoretic Light Scattering Data of C_{14}TASal Micelles at 25 °C ($c = 0.855 \times 10^{-2}$ g cm$^{-3}$)

<table>
<thead>
<tr>
<th>$c_0$, M</th>
<th>$\theta$, deg</th>
<th>$E$, V cm$^{-1}$</th>
<th>$10^2v_c$, cm s$^{-1}$</th>
<th>$10^2U_0$, cm V$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>49.8</td>
<td>2.16</td>
<td>4.34</td>
</tr>
<tr>
<td>0.01</td>
<td>20</td>
<td>29.6</td>
<td>0.48</td>
<td>1.62</td>
</tr>
<tr>
<td>0.10</td>
<td>20</td>
<td>33.4</td>
<td>-0.063</td>
<td>-0.19</td>
</tr>
</tbody>
</table>

C_{14}TASal at 0.20 $\times 10^{-2}$ g cm$^{-3}$ (0.005 M) with various NaSal concentrations was measured at 25 °C and plotted in Figures 6 and 7. It may be noted from Figure 6 that the contribution of external interference effect inducing the unusual angular dependence of static light scattering diminishes with an addition of NaSal and cannot be detected at NaSal concentrations above 0.001 M. While the usual angular dependence of static light scattering with an upward convex curvature is observed in the presence of 0.005-0.5 M NaSal, the static light scattering for 1 M NaSal solution is independent of scattering angle.

The mutual diffusion coefficient measured in an addition of 0.005-0.2 M NaSal increases with an upward convex curvature with an increase of $\sin^2(\theta/2)$, as seen in Figure 7, while for 0.5 M NaSal solutions it increases linearly with $\sin^2(\theta/2)$.

Double logarithmic plots of $K(c-c_0)/(R_0-R_g)$ and $D_v$ vs $c_0$ are given in Figure 8, which includes values of apparent radius of gyration, $R_{phot}$ evaluated from the equation

$$K(c-c_0)/(R_0-R_g) = (1/M_{phot})(1+(1/3)R_{phot}^2\mu^2)$$

Around 0.05 M NaSal, the $K(c-c_0)/(R_0-R_g)$ and $D_v$ values exhibit minima and the $R_{phot}$ values present a maximum, suggesting the formation of longest rodlike micelles.

Electrophoretic Light Scattering. When the electric field, $E$, was applied, the electrophoretic drift velocity, $v$, which is evaluated from a Doppler shift value on the light scattering power spectrum, was measured for aqueous NaSal solutions of C_{14}TASal of 0.055 $\times 10^{-2}$ g cm$^{-3}$ at 25 °C. Then the electrophoretic mobility, $U$, is calculated by

$$U = v/E$$

and listed in Table III with numerical values of related parameters. The mobility, which is $4.34 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for aqueous solution without NaSal, decreases with an addition of NaSal; it converts the sign to negative in the presence of 0.1 M NaSal.

It can be mentioned that C_{14}TASal micelles in water exhibit positive electrostatic potential. The electrostatic potential decreases with an addition of NaSal, owing to the strong adsorption of salicylate ions on a Stern layer surface of micelle. The excess adsorption of salicylate ions occurs above 0.1 M NaSal, inducing the negative electrostatic potential at a sliding plane, i.e., the negative $\delta$ potential.

Discussion

When NaSal was added to aqueous solutions of C_{14}TASal, the size of micelles increased with an addition of NaSal up to 0.05 M, while it diminished at higher NaSal concentrations. This salt effect of NaSal was very different from that of NaCl and NaBr. The addition of the latter salts always promoted the formation of larger micelles. While NaCl or NaBr always produces the salting-out effect, large amounts of NaSal affect C_{14}TASal micelles differently due to the specific binding behavior of salicylate ion. When large amounts of salicylate counterion bind to a micelle, and the net surface charge varies sign, if the counterion binding is excess. Electrophoretic light scattering measurement confirmed that the $\delta$ potential of C_{14}TASal micelle already changed its sign in an addition of 0.1 M NaSal.

Different from bromide ions which bind electrostatically on a micelle surface, salicylate ions penetrate into a micelle. While NaCl or NaBr always produces the salting-out effect, large amounts of NaSal affect C_{14}TASal micelles differently due to the specific binding behavior of salicylate ion. When large amounts of salicylate counterion bind to a micelle, and the net surface charge varies sign, if the counterion binding is excess. Electrophoretic light scattering measurement confirmed that the $\delta$ potential of C_{14}TASal micelle already changed its sign in an addition of 0.1 M NaSal.

Molecules of C_{14}TASal associate into rodlike micelles in aqueous solutions without NaSal. According to the procedure previously reported,33 and utilizing the aggregation number, 61, and the radius, 2.2 nm, of spherical micelles, the length of rodlike micelles can be estimated as 29 and 34 nm in aqueous solutions of C_{14}TASal of 0.017 $\times 10^{-2}$ g cm$^{-3}$ (5 $\times 10^{-4}$ M) at 1.5 and 25 °C, respectively. Rehahe and Hoffmann4 calculated the lengths of rodlike micelles of C_{14}TASal at 38.5 and 46.0 nm for solutions of 0.001 and 0.002 M, respectively, at 20 °C from viscosity data on the basis of the theory of Doi and Edwards for stiff rods. The lengths estimated here are not inconsistent with values by Rehahe and Hoffmann.

For 0.1 M NaSal solutions of C_{14}TASal where long rodlike micelles are formed, the analysis method35 was applied for light scattering data at a finite micelle concentration and the numerical values of micellar size and micellar interaction were obtained for micellar solutions of 0.099 $\times 10^{-2}$ g cm$^{-3}$, as shown in Table IV.

It is noteworthy that the temperature dependence of numerical values is not remarkable. Aggregation number, radius of gyration, and hydrodynamic radius are comparable with or slightly larger than those for tetradecyltrimethylammonium chloride (C_{14}DAC) in 2.6 M NaCl and tetradeaclylammonium bromide (C_{12}DAB) in 4.3 M NaBr.35 Since a kind of flexibility parameter, $p = R_g/R_w$, ranges from 1.6 to 1.8, rodlike micelles of C_{14}TASal can be regarded as semiflexible as well as rodlike micelles of C_{14}DAC, C_{14}DAB, and heptaoxyethylene alkyl ethers (C_{14}EO).33 The second virial coefficient and the frictional virial coefficient are larger than those for C_{14}DAC, C_{12}DAB, and C_{14}EO, suggesting that there is stronger interaction or correlation between C_{14}TASal micelles. The hydrodynamic virial coefficient is smaller than the frictional virial coefficient owing to the compensation between large 2$\beta_M$ and $k_t$ values.

On the basis of the equation

$$R_g/a^2 = L_0/3a + 1 - (2a/L_0)[1 - (a/L_0)(1 - e^{-L_0/a})]$$

and with the use of the obtained values of molecular weight and radius of gyration, the persistence length, $\alpha$, of semiflexible rodlike micelles in 0.1 M NaSal was evaluated. The contour length, $L_c$, is related to molecular weight by

$$L_c = M/M_L$$

where $M_L$ is the molecular weight per contour length and was calculated according to the method described previously.33 The threshold micelle concentration of overlap, that is, the

TABLE IV: Characteristics of Rodlike Micelles of C16TASal in 0.1 M NaSal Solutions at Various Temperatures (c − c*) = 0.999 × 10⁻³ g cm⁻³

<table>
<thead>
<tr>
<th>T. °C</th>
<th>10⁻²M</th>
<th>m</th>
<th>R₀, nm</th>
<th>10⁻²D₀, cm² s⁻¹</th>
<th>Rₑ, nm</th>
<th>10⁻²Dₑ, mol cm⁻³ g⁻²</th>
<th>kₑ, cm² g⁻¹</th>
<th>kₑ, cm² g⁻¹</th>
<th>Lₑ, nm</th>
<th>a, nm</th>
<th>Lₑ/2a</th>
<th>10⁻²(c − c*)</th>
<th>g⁻³ cm⁻³</th>
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<tr>
<td>15</td>
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<td>1.61</td>
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crossover concentration between dilute and semidilute regimes, (c − c*)⁰⁺, was, in turn, evaluated from the relation

\[(c − c*)⁰⁺ = \frac{2/3M_c}{[(aL)²/3]N_A}\] (14)

for wormlike chains.\(^{36}\) The numerical values are listed in Table IV with values of \(L_{c2}/a\).

Although the contour length ranges from 2000 to 3000 nm and is in agreement with those for C₁₄DAC in 2.6 M NaCl and C₁₂DB in 4.3 M NaBr,\(^{37}\) the persistence length of 100–150 nm is 2 times longer than those of C₁₂DAC and C₁₂DB micelles\(^{37}\) and is close to that of oleyldimethylamine oxide micelle,\(^{39}\) indicating the more rigid semiflexible character of C₁₆TASal micelles. The calculated \((c − c*)⁰⁺\) values agree with the observed one. Since the threshold micelle concentration of overlap is around \(0.1 \times 10⁻²\) g cm⁻³, the threshold concentration of entanglement must be around \(0.2 \times 10⁻²\) g cm⁻³ (ca. 2 times larger).\(^{31,32,33}\) For 1 M NaSal solutions of C₁₆TASal, the decrease of reciprocal scattering intensity and mutual diffusion coefficient with an increase in micelle concentration indicates the increase in micellar size. This includes the variation of virial coefficients. Therefore, the analytical procedure of light scattering for small micelles at each micelle concentration was presented.\(^{21}\) That procedure was applied to 1 M NaSal solutions of C₁₆TASal.

Table II shows the numerical values evaluated by using the value of 6.55⁵⁹ for the constant, \(k₀\), in the equation

\[k_ₑ = k₀N_A[(4/3)nRₑ²]/M\] (15)

In Table II, \(b\) is the long axis, when a prolate ellipsoid is assumed as the micelle shape instead of a sphere and 2.2 nm is taken as a value of the short axis.

The size of micelles increases obviously with an increase in micelle concentration, but it depends slightly on temperature in a different way depending on micelle concentration. The second and third virial coefficients are \((0.7–2.5) \times 10⁻⁴\) mol cm⁻³ g⁻² and \((0.1–4) \times 10⁻³\) mol cm⁻³ g⁻³, respectively, and the frictional virial coefficient and the hydrodynamic virial coefficient ranges are 5–17 cm² g⁻¹ and 0.3–1.1 cm² g⁻¹, respectively. The numerical values of these coefficients are consistent with those for small micelles of C₁₂E₅.\(^{21}\)

The spinnability was observed even for aqueous solutions of C₁₆TASal without salt,\(^{18}\) in which micelles take a short rod shape but the intermicellar correlation is very strong. When the micelle concentration is diluted, micelles are short and few, and the intermicellar correlation is rather weak. Then the loose pseudonetwork composed of short rodlike micelles must be formed in micellar solutions. Such a loose pseudonetwork structure can induce the spinnability with type D behavior where the drawing length is proportional to the drawing velocity.\(^{18}\) The type D spinnability was observed for solutions where the viscous flow overcomes the elastic deformation.

As the micelle concentration increases, micelles lengthen, and the amount of micelles and the intermicellar correlation increase. Therefore, the pseudonetwork would tighten and such structure induces the type C spinnability, where the drawing length decreases with the drawing velocity or is independent of it and where the elastic deformation is predominant.\(^{18}\) As the temperature is raised, micelles shorten. Then the pseudonetwork loosens so that the spinnability converts into type D. The possible structures of

(36) Ying, Q.; Chu, B.; Macromolecules 1987, 20, 362.
Selective Reduction at the Single-Crystal Surface of All Mobile Cations In Zeolite A.
Structures of Dehydrated \(\text{Ag}_2\text{Ca}_5\)-A and \(\text{Ag}_2\text{Cs}_{10}\)-A

Yang Kim,* Seong Hwan Song,
Chemistry Department, Pusan National University, Pusan 609-735, Korea
and Karl Seff*
Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822-2275 (Received: November 6, 1989; In Final Form: February 8, 1990)

A single crystal of dehydrated \(\text{Ag}_2\text{Ca}_5\)-A (\(\text{Ag}^+\)- and \(\text{Ca}^{2+}\)-exchanged zeolite A) was treated with 0.01 Torr of Cs vapor at 200 °C for 2 h, and another such crystal was treated with 0.1 Torr of Cs vapor at 250 °C for 48 h. The product structures were determined at 21 °C by X-ray diffraction techniques in the cubic space group \(Pm3m\). The composition of first crystal was \(\text{Ag}_2\text{Ca}_5\text{A} (a = 12.294 (1) \text{Å})\), indicating no reaction, while that of the second crystal, \(\text{Ag}_2\text{Cs}_{10}\text{A} (a = 12.166 (1) \text{Å})\), indicated that all \(\text{Cs}^{+}\) ions were reduced by Cs vapor and replaced by \(\text{Cs}^+\) ions. Full-matrix least-squares refinements of \(\text{Ag}_2\text{Ca}_5\text{A}\) and \(\text{Ag}_2\text{Cs}_{10}\text{A}\) converged to the final error indices, \(R_1 = 0.041\) and \(R_2 = 0.048\) with 227 reflections, and \(R_3 = 0.114\) and \(R_4 = 0.120\) with 167 reflections, respectively, for which \(I > 3\sigma(I)\). In \(\text{Ag}_2\text{Ca}_5\text{A}\), both \(\text{Ag}^+\) and \(\text{Cs}^{2+}\) ions lie on threefold-axis sites near 6-ring centers. In \(\text{Ag}_2\text{Cs}_{10}\text{A}\), both \(\text{Ag}^+\) ions are found near 6-ring centers as before, and the 10 \(\text{Cs}^+\) ions occupy 4 crystallographic sites: 3 \(\text{Cs}^+\) ions lie at the centers of the 8-rings at sites of \(D_4h\) symmetry; 6 \(\text{Cs}^+\) ions lie on the threefold axes of the unit cell, 4 deep in the large cavity and 2 in the sodalite cavity; one \(\text{Cs}^+\) ion is found in the large cavity near a 4-ring. It is striking, considering the electrochemical potentials involved, to observe no reaction at all between \(\text{Ag}^+\) and \(\text{Cs}^+\) while simultaneously the reaction of \(\text{Ca}^{2+}\) and \(\text{Cs}^+\) has gone to completion. It must therefore be true that \(\text{Cs}^+\) atoms are too large to enter the 8-ring channels at 250 °C and that \(\text{Ag}^+\) ions lack the mobility to migrate to the crystal surface for reaction. \(\text{Cs}^{2+}\) ions must have this mobility at 250 °C, as must the \(\text{Cs}^+\) ions formed by reaction, which must therefore have occurred only at the surface of the zeolite single crystal.

Introduction

In 1956, Breck et al. reported that \(\text{Cs}^+\) ion exchange into zeolite A with a 100% excess of \(\text{Cs}^+\) (0.14 M aqueous solution at 90 °C) resulted in the replacement of only 31% the \(\text{Na}^+\) ions in the zeolite A structure.1 Brearley et al. increased the level of \(\text{Cs}^+\) exchange to 45% by exposing the zeolite to successive concentrated aqueous solutions at 25 °C.2 Subsequently, during the past decade, the levels of \(\text{Cs}^+\) exchange into zeolite A were gradually increased from 7/12 to 11/12 by various ion-exchange strategies.3-5 In 1987, Seff and Heo succeeded in preparing fully dehydrated, fully \(\text{Cs}^+\)-exchanged zeolite A by the reduction of all \(\text{Na}^+\) ions in \(\text{Na}_{12}\text{A}\) with cesium vapor. Complete reaction of the \(\text{Na}^+\), \(\text{K}^+\), \(\text{Ca}^{2+}\), and \(\text{Cs}^{2+}\) ions in dehydrated zeolite A with Cs vapor is readily achieved at 250 °C or higher.6,7,8 However, when dehydrated \(\text{Ag}_{12}\text{A}\) (an ill-defined material) was exposed to ca. 0.1 Torr of Cs vapor at 220 °C, the resulting crystal showed no single-crystal diffraction pattern, indicating that the crystallinity of the zeolite A structure had been lost.9 

\(\text{Ag}^+\) ions in zeolite A can be reduced by heating, by reaction with reducing agents, or by sorption of metal atoms.10,11 In the structure of dehydrated \(\text{Ag}_5\text{Na}_{17}\text{A}\), treated with 50 Torr of \(\text{H}_2\) at room temperature, 1.27 (\(\text{Ag}^+\)) clusters and 0.7 (\(\text{Ag}^{2+}\)) clusters per unit cell were found in the large cavity.10 In the structure of \(\text{Ag}_{46}\text{Na}_{45}\text{A}\), vacuum dehydrated and treated with \(\text{H}_2\) at 350 °C, (\(\text{Ag}^+\))1 clusters of low symmetry were found in the large cavity.11 

Barrer and Whiteman reported that large quantities of mercury vapor could be sorbed by \(\text{Ag}^{2+}\)-exchanged zeolite X without damaging the zeolite structure.12 However, the uptake of mercury vapor by single crystals of \(\text{Ag}^+\)-exchanged zeolite A at both 70