Light Scattering from Spinnable, Viscoelastic Solutions of Alkyldimethylamine Oxides

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Light scattering was measured for spinnable, viscoelastic solutions of tetradecyl- and hexadecyltrimethylamine oxides (C_{14}DAO, C_{16}DAO). Dilute aqueous solutions of C_{14}DAO and C_{16}DAO displayed strong intermicellar correlation, while that in aqueous C_{14}DAO solutions diminished by the addition of 0.2 M NaCl. Aqueous C_{14}DAO solutions in 0.2 M NaCl belonged to the semidilute regime at micelle concentrations above 0.5 \times 10^{-2} \text{ g cm}^{-3}. The micellar contour length between pseudonetwork meshes formed by entangled rodlike micelles in the semidilute regime was longer at degree of ionization of 0.2\sim 0.45. The pseudonetwork by more flexible rodlike micelles may be concluded to induce ductile failure spinnability and polymer-like viscoelasticity.

1 Introduction

The spinnability, thread-forming property of a liquid, is related to the non-Newtonian behavior in viscosity and the Weissenberg effect in viscoelasticity. The spinnability of aqueous surfactant solutions was reported for few cases\(^1\sim^3\) : we investigated for aqueous solutions of alkyltrimethylammonium salicylates (C\(_n\)TASal)\(^2\) and alkyl- and oleyldimethylamine oxides (C\(_n\)DAO, ODAO)\(^3\).

The aqueous C\(_n\)TASal solutions presented the cohesive fracture failure spinnability and the gel-like viscoelasticity\(^2\), if the pseudolinkages between short rodlike micelles were formed\(^4\),\(^5\). On the other hand, when long rodlike micelles entangled with each other, the solutions provided the ductile failure (or capillary ductile failure) spinnability and the Maxwell or polymer-like viscoelasticity.

The aqueous solutions of C\(_n\)DAO and ODAO were divided into two groups in their rheological properties\(^3\). One group exhibited the cohesive fracture failure spinnability with the gel-like viscoelasticity. This behavior originated in the interacting platelike assemblies\(^6\),\(^7\). Second group presented the ductile failure spinnability with the polymer-like viscoelasticity. This aspect was assumed to be based on the existence of rodlike micelles.

In this work, we report light scattering of aqueous C\(_n\)DAO solutions and discuss the relation between micelle formation and rheological properties.

2 Experimental

The samples of C\(_n\)DAO are same as previously used\(^3\). Water and NaCl were purified by a routine method. Light scattering and specific refractive index increment, respectively, were measured on a dynamic light scattering spectrophotometer DLS-700 and a differencial refractometer RM-102, manufactured by Otsuka Electronics, Co. Ltd., Osaka. The experimental procedure and the numerical analysis are described elsewhere in detail\(^4\). Numerical values of the specific refractive index increment are listed for various temperatures and different NaCl concentrations C\(_s\) in Table-1, where the critical micelle concentration C\(_0\) are also included. The C\(_0\) value for aqueous C\(_{14}\)DAO solutions agrees with the value previously reported\(^8\).

3 Results and Discussion

3.1 Aqueous C\(_{16}\)DAO solutions

The light scattering was measured for aqueous C\(_{16}\)DAO solutions at 25\sim 45\textdegree C. Fig. -1 represents the angular dependence of
static light scattering. The reciprocal angular envelop of light scattering for the solutions of $0.038 \times 10^{-2}$ g cm$^{-3}$ increases with scattering angle $\theta$ at low angles, while it keeps constant or decreases at high angles. On the other hand, the reciprocal angular envelop decreases with increasing scattering angle for the solutions of $0.069 \times 10^{-2}$ g cm$^{-3}$ at 30 to 45°. Such abnormal angular dependence is emphasized with temperature but diminishes with further increase in micelle concentration. This behavior may be due to the strong effect of structure factor $S(\theta, c)$, arising from the external interference, i.e., the intermicellar correlation, in an equation of

$$R_{0}^{-1} - R_{0}^{-1} = K(c-c_0)MP(\theta)S(\theta, c) \quad (1)$$

where $R_0 - R_0$ represents the reduced scattering intensity of micelles, $K$ is the optical constant, $c$ is the total surfactant concentration, $M$ is the molecular weight, and $P(\theta)$ is the particle scattering factor. The effect of structure factor on the reciprocal envelop of light scattering is schematically illustrated in Fig.-2. Similar behavior was previously reported for aqueous solutions of oleyl-dimethylamine oxide$^9$ and hexadecyltrimethylammonium salicylate$^4$.

### 3.2 Aqueous C$_{14}$DAO solutions

The angular dependence of static light scattering for aqueous C$_{14}$DAO solutions at 7~45°C is shown in Fig.-3. The abnormal angular dependence of scattering intensity is observed at low micelle concentrations, although it is weaker than that for aqueous C$_{16}$DAO solutions. The abnormality increases with temperature as well as for aqueous C$_{16}$DAO solutions, while it is undistinguishable at micelle concentrations above $10^{-2}$ g cm$^{-3}$, where there are no angular dependence of scattering intensity. The strong external interference effect also affects the mutual diffusion coefficient from dynamic light scattering$^9$.

#### Table-1 Specific refractive index increment for aqueous C$_n$DAO solutions (in units of cm$^3$ g$^{-1}$)

<table>
<thead>
<tr>
<th>C$_n$</th>
<th>$c_0$, 10$^{-2}$</th>
<th>T, °C</th>
<th>7</th>
<th>15</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{16}$DAO</td>
<td>0</td>
<td>&lt;0.001</td>
<td>0.126</td>
<td>0.154</td>
<td>0.149</td>
<td>0.141</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_{14}$DAO</td>
<td>0.004</td>
<td>0.161</td>
<td>0.158</td>
<td>0.156</td>
<td>0.154</td>
<td>0.150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>&lt;0.001</td>
<td>0.151</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

### Fig.-1 Angular dependence of static light scattering for aqueous C$_{16}$DAO solutions at various temperatures.

### Table-1 Specific refractive index increment for aqueous C$_n$DAO solutions (in units of cm$^3$ g$^{-1}$).

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</tbody>
</table>

#### Micelle concentration (10$^{-2}$ g cm$^{-3}$): ○, 0.038 ; ●, 0.069 ; □, 0.10 ; ■, 0.15 ; △, 0.22 ; ▲, 0.30

### Fig.-1 Angular dependence of static light scattering for aqueous C$_{16}$DAO solutions at various temperatures.
sufficient at 25°C as a function of micelle concentration $c-c_0$ above $10^{-2}$ g·cm$^{-3}$, where the mutual diffusion coefficient can be measured only at low scattering angles and the values are averaged. They display the gradual increase with micelle concentration.

### 3.3 Aqueous C$_{14}$DAO solutions in 0.2 M NaCl

The light scattering measurement was carried out for aqueous C$_{14}$DAO solutions in 0.2 M NaCl at 25°C. The addition of 0.2 M NaCl suppresses the external interference effect, and the normal angular dependence of reciprocal scattering intensity and mutual diffusion coefficient is observed, as illustrated in Fig.-5.

Then the reciprocal scattering intensity $K/R (c-c_0)/(R_0-R_0^0)$ and the mutual diffusion coefficient $D$ are written by

\[ K(c-c_0)/(R_0-R_0^0) = 1/\theta + 2B_2(c-c_0) \]

\[ 1/P(\theta) = 1 + R_G^2 \mu^2/3 \]  

and

\[ D = D_0(1 + AR_G^2 \mu^2)[1 + k_D(c-c_0)] \]

\[ = D_e(1 + AR_G^2 \mu^2) \]

\[ D_0 = k_B T/6 \pi \eta_0 R_H \]  

respectively, where $B_2$ is the second virial coefficient, $R_G$ is the radius of gyration, and $\mu$ is the magnitude of scattering vector. $D_0$ is the total translational diffusion coefficient, $A$ is a constant ($=2/15$), $k_D$ is the hydrodynamic virial coefficient, $D_e$ is the mutual diffusion coefficient at zero scattering, $k_B$ is the Boltzmann constant, $T$ is absolute temperature, $\eta_0$ is the solvent viscosity, and $R_H$ is the hydrodynamic radius.

The reciprocal scattering intensity and the mutual diffusion coefficient at zero scattering angle are plotted in Fig.-5 and compared with those in water. They exhibit minima at $0.5 \times 10^{-2}$ g·cm$^{-3}$ and increase highly with further increasing micelle concentration, although those in 0.2 M NaCl...
are smaller than those in water, indicating the larger size.

The feature of the concentration dependence of light scattering with a minimum is common to the solutions of entangled rodlike micelles: the micelles entangle with each other at the micelle concentrations above a minimum. The micelle concentration region above a minimum is called the semidilute regime, where entangled rodlike micelles behave like entangled linear polymers\(^\text{12),13)}\).

When the analytical procedure previously developed\(^\text{12)}\) is applied to a solution of \(0.5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}\), the following micelle parameters and virial coefficients are evaluated; \(M = 591,000\), aggregation number \(m = 2300\), \(R_C = 30.7 \text{ nm}\), \(R_h = 15.9 \text{ nm}\), \(B_2 = 2.66 \times 10^{-4} \text{ mol} \cdot \text{cm}^3 \cdot \text{g}^{-2}\), and \(k_D = 121 \text{ cm}^3 \cdot \text{g}^{-1}\).

3.4 Aqueous C\(_{14}\)DAO solutions in 0.2 M NaCl at various HCl concentrations

Fig.-6 shows the reciprocal scattering intensity and the mutual diffusion coefficient at zero scattering angle for aqueous C\(_{14}\)DAO solutions of \(5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}\) in 0.2 M NaCl as a function of \(C_a/C\) ratio, where \(C_a\) and \(C\) are mole concentrations of HCl and surfactant, respectively. Both values exhibit minima at \(C_a/C = 0.2 \sim 0.45\), which correspond to pH = 6.5 \sim 4.5 or degree of ionization \(\alpha = 0.2 \sim 0.45\). This indicates that micellar contour length between pseudonetwork meshes formed by entangled rodlike micelles is longer at \(\alpha = 0.2 \sim 0.45\), since micelle concentration of \(5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}\) belongs to the semidilute
regime and the scattering intensity is a measure of a contour length between pseudonetwork meshes.

The longer contour length can be expected owing to the formation of hydrogen bonded pair of amine oxide molecule and N-hydroxyammonium ion at moderate degree of ionization\(^{14}\). Then rodlike micelles may be more flexible, as illustrated in Fig.-7 (a). Hydrated nonionic micelles and ionic micelles are formed at lower and higher degree of ionization, respectively, and the micellar contour length between resultant pseudonetwork meshes can be shorter and less flexible [Fig.-7 (b)].

3.5 The relation between micelle formation and rheological properties

Aqueous C\(_{14}\)DAO solutions in 0.2 M NaCl revealed the remarkable rheological properties when HCl was added\(^ {3,15}\). Fig.-6 includes the data of ductile failure spinnability as a function of C\(_a\)/C at a micelle concentration of 5\(\times\)10\(^{-2}\) g\(\cdot\)cm\(^{-3}\)\(^{3}\). The spinnability had a maximum at C\(_a\)/C\(\approx\)0.3. The polymer-like viscoelasticity increased up to \(\alpha = 0.25\), and did not change almost at \(\alpha = 0.25 \sim 0.61\)\(^ {15}\).

It may be noted that the rheological behavior is more remarkable at the C\(_a\)/C value where the contour length between pseudonetwork meshes of rodlike micelles is longer. This suggests that the network illustrated in Fig.-7 (a) reveals viscous behavior rather than elastic one, and then induces the ductile failure spinnability and the polymer-like viscoelasticity.

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References

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アルキルジメチルアミンオキシドの
えい(曳)系性を示す粘弾性溶液の光散乱

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テトラデシル-, ヘキサデシルジメチルアミンオキシド (C₁₄DAO, C₁₆DAO) のえい系性を示す粘弾性水溶液に対して光散乱を測定した。C₁₄DAO と C₁₆DAO の
希薄な水溶液は強いミセル間相互を示すが、相関は
C₁₄DAO 水溶液に 0.2 M NaCl を添加することにより消失する。0.2 M NaCl を添加した C₁₄DAO 水溶液は
0.5×10⁻² g·cm⁻³ 以上のミセル濃度では準希薄領域に
属する。準希薄領域中の絡まった棒状ミセルによって形
成された擬銅目構造中綱目を構成するミセル長は、イオン化度が 0.2 〜 0.45 のとき、最長である。擬銅目構造が
比較的屈曲した棒状ミセルによって構築される時、溶液
は線形高分子の挙動に似た粘弾性と共に延性破損型えい
系性を引き起こすと推論できる。