

ORIGINAL

Light Scattering from Spinnable, Viscoelastic Solutions of Alkyldimethylamine Oxides

Toyoko IMAE

Department of Chemistry, Faculty of Science, Nagoya University
(Furo-cho, Chikusa-ku, Nagoya-shi, 464)

Light scattering was measured for spinnable, viscoelastic solutions of tetradecyl- and hexadecyldimethylamine 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 $0.5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$. The micellar contour length between pseudonetwork meshes formed by entangled rodlike micelles in the semidilute regime was longer at degree of ionization of 0.2~0.45. 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)~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 viscoelasticity²⁾, 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 properties³⁾. 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 used³⁾. 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 differential refractometer RM-102, manufactured by Otsuka Electronics, Co. Ltd., Osaka. The experimental procedure and the numerical analysis are described elsewhere in detail⁴⁾. 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 reported⁸⁾.

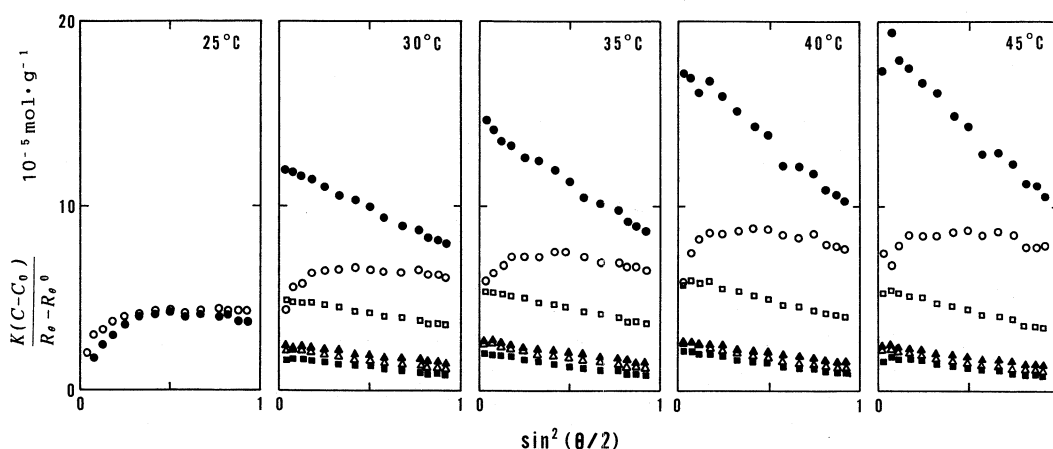
3 Results and Discussion

3.1 Aqueous C_{16} DAO solutions

The light scattering was measured for aqueous C_{16} DAO solutions at 25~45°C. Fig. -1 represents the angular dependence of

Table-1 Specific refractive index increment for aqueous C_n DAO solutions (in units of $\text{cm}^3 \cdot \text{g}^{-1}$).

	C_s , M	$c_0, 10^{-2}$ $\text{g} \cdot \text{cm}^{-3}$	$T, ^\circ\text{C}$						
			7	15	25	30	35	40	45
C_{16} DAO	0	<0.001			0.126	0.144	0.145	0.149	0.141
C_{14} DAO	0	0.004	0.161	0.158	0.156		0.154		0.150
	0.2	<0.001			0.151				



Micelle concentration ($10^{-2} \text{g} \cdot \text{cm}^{-3}$): \circ , 0.038; \bullet , 0.069; \square , 0.10; \blacksquare , 0.15; \triangle , 0.22; \blacktriangle , 0.30
Fig.-1 Angular dependence of static light scattering for aqueous C_{16} DAO solutions at various temperatures.

static light scattering. The reciprocal angular envelop of light scattering for the solutions of $0.038 \times 10^{-2} \text{g} \cdot \text{cm}^{-3}$ increases with scattering angle θ 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 $0.069 \times 10^{-2} \text{g} \cdot \text{cm}^{-3}$ at 30 to 45°C . 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

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

where $R - R^0$ 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 oxide⁹⁾ and hexadecyltrimethylammonium salicylate⁴⁾.

3-2 Aqueous C_{14} DAO solutions

The angular dependence of static light scattering for aqueous C_{14} DAO solutions at $7 \sim 45^\circ\text{C}$ 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 $10^{-2} \text{g} \cdot \text{cm}^{-3}$, where there are no angular dependence of scattering intensity. The strong external interference effect also affects the mutual diffusion coefficient from dynamic light scattering⁴⁾.

Fig.-4 represents the reciprocal scattering intensity and the mutual diffusion coef-

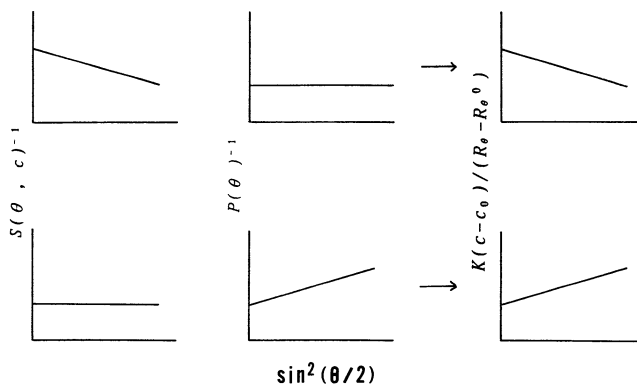
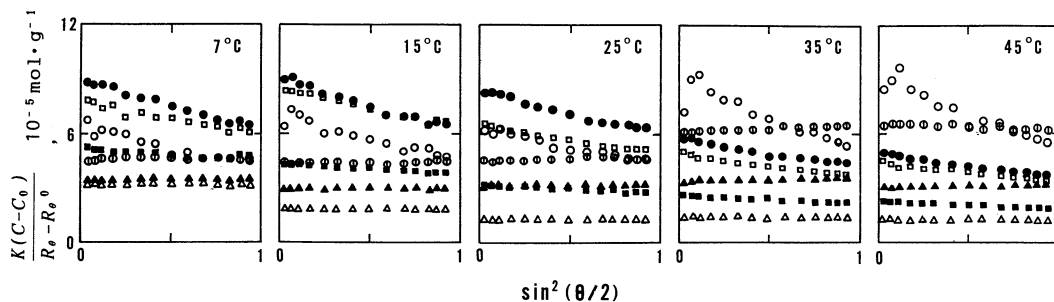


Fig.-2 The schematic representation of the effect of structure factor on the reciprocal angular envelop of light scattering.



Micelle concentration ($10^{-2} \text{ g}\cdot\text{cm}^{-3}$): \circ , 0.048; \bullet , 0.093; \square , 0.20; \blacksquare , 0.50; \triangle , 2.48; \blacktriangle , 7.49; \oplus , 9.98.
Fig.-3 Angular dependence of static light scattering for aqueous C_{14}DAO solutions at various temperatures.

ficient at 25°C as a function of micelle concentration $c-c_0$ above $10^{-2} \text{ g}\cdot\text{cm}^{-3}$, 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 $K(c-c_0)/(R_\theta-R_\theta^0)$ and the mutual diffusion coefficient D are written by

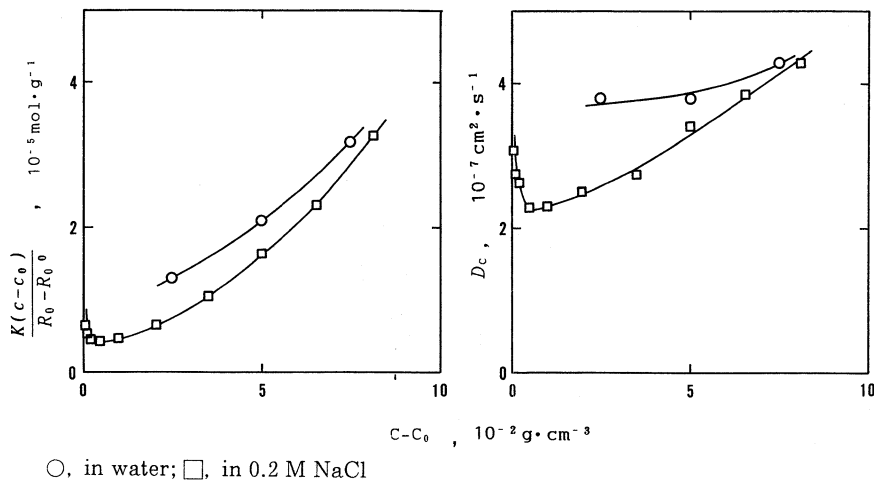
$$\begin{aligned} K(c-c_0)/(R_\theta-R_\theta^0) &= 1/MP(\theta) + 2B_2(c-c_0) \\ 1/P(\theta) &= 1 + R_G^2 \mu^2/3 \end{aligned} \quad (2)$$

and

$$\begin{aligned} D &= D_0(1 + AR_G^2 \mu^2)[1 + k_D(c-c_0)] \\ &= D_c(1 + AR_G^2 \mu^2) \\ D_0 &= k_B T/6\pi\eta_0 R_H \end{aligned} \quad (3)$$

respectively, where B_2 is the second virial coefficient, R_G is the radius of gyration, and μ is the magnitude of scattering vector. D_0 is the total translational diffusion coefficient, A is a constant ($=2/15$)^{10,11}, k_D is the hydrodynamic virial coefficient, D_c is the mutual diffusion coefficient at zero scattering, k_B is the Boltzmann constant, T is absolute temperature, η_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.-4 and compared with those in water. They exhibit minima at $0.5 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$ and increase highly with further increasing micelle concentration, although those in 0.2 M NaCl



○, in water; □, in 0.2 M NaCl
 Fig.-4 Reciprocal scattering intensity and mutual diffusion coefficient at zero scattering angle for aqueous C_{14} DAO solutions with and without NaCl at 25°C.

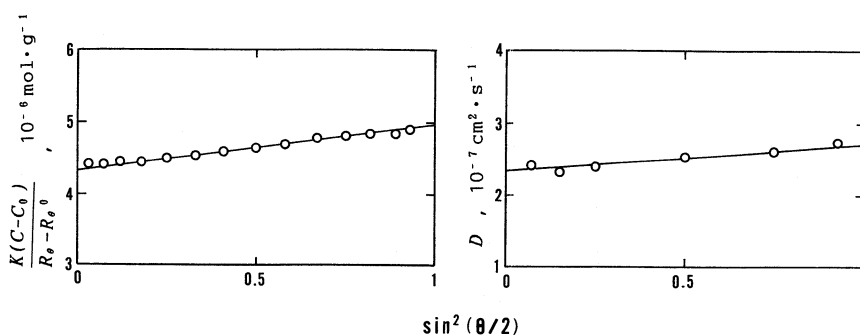


Fig.-5 Angular dependence of static and dynamic light scattering for an aqueous C_{14} DAO solution of $0.50 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$ in 0.2 M NaCl at 25°C.

are smaller than those in water, indicating the larger size.

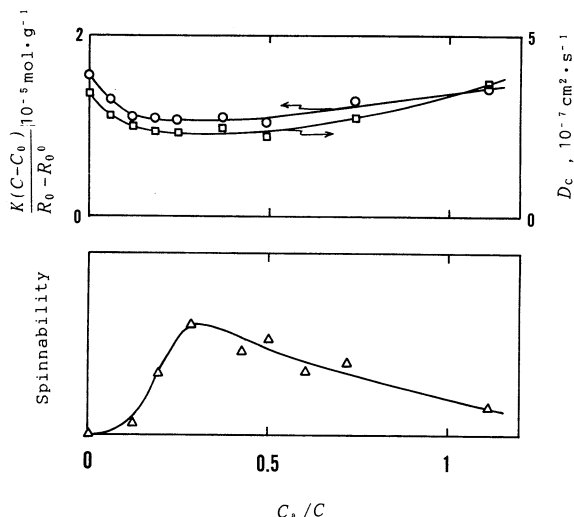
The feature of the concentration dependence of light scattering with a minimum is common to the solutions of entangled rodlike micelles: the micelles entangle with each other at the micelle concentrations above a minimum. The micelle concentration region above a minimum is called the semidilute regime,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

When the analytical procedure previously developed¹²⁾ 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 $m = 2300$, $R_G = 30.7 \text{ nm}$, $R_H = 15.9 \text{ nm}$, $B_2 = 2.66 \times 10^{-4} \text{ mol} \cdot$

$\text{cm}^3 \cdot \text{g}^{-2}$, 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 $\text{pH} = 6.5 \sim 4.5$ 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



Spinnability data were taken from Ref. 3.

Fig.-6 Light scattering and spinnability as a function of C_a/C ratio for aqueous C_{14} DAO solutions of $5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$ in 0.2 M NaCl at 25°C.

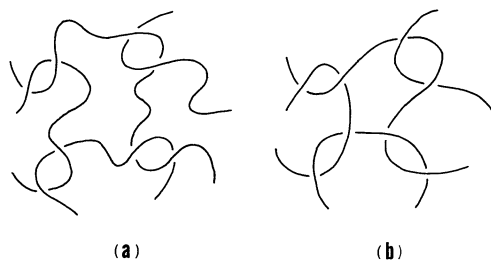
regime and the scattering intensity is a measure of a contour length between pseudonetwork meshes.

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 ionization¹⁴). 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 $5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$ 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



(a), by more flexible rodlike micelles; (b), by less flexible rodlike micelles.

Fig.-7 Schematic representation of pseudonetworks formed by entangled rodlike micelles.

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.

(Received Jan. 28, 1992)

References

- 1) S. Gravsholt, *J. Colloid Interface Sci.*, **57**, 575 (1976).
- 2) T. Imae, K. Hashimoto, and S. Ikeda, *Colloid Polym. Sci.*, **268**, 460 (1990).
- 3) K. Hashimoto and T. Imae, *Langmuir*, **7**, 1734 (1991).
- 4) T. Imae, *J. Phys. Chem.*, **94**, 5953 (1990).
- 5) K. Hashimoto, T. Imae, and K. Nakazawa, *Colloid Polym. Sci.*, in press.
- 6) T. Imae and B. Trend, *J. Colloid Interface Sci.*, **145**, 207 (1991).
- 7) T. Imae and T. Iwamoto, submitted for publication.
- 8) H. Hoffmann, G. Oetter, and B. Schwandner, *Progr. Colloid Polym. Sci.*, **73**, 95 (1987).
- 9) T. Imae and S. Ikeda, *J. Colloid Interface Sci.*, **98**, 363 (1984); *Colloid Polym. Sci.*, **263**, 756 (1985); *Surfactants in Solution*, Ed. K.L. Mittal, *Plenum*, **7**, 455 (1989).
- 10) W. Burchard, M. Schmidt, and W. H. Stockmayer, *Macromolecules*, **13**, 580 (1980).
- 11) W. Burchard, *Adv. Polym. Sci.*, **48**, 1 (1983).
- 12) T. Imae, *J. Phys. Chem.*, **92**, 5721 (1988); *Langmuir*, **5**, 205 (1989).
- 13) T. Imae, *Colloid Polym. Sci.*, **267**, 707 (1989).

- 14) T. Imae and S. Ikeda, *J. Colloid Interface Sci.*, 113, 449 (1986).
 15) M. Sasaki, M.Sc. Thesis, Nagoya University (1989).

アルキルジメチルアミノキシドの
えい(曳)糸性を示す粘弾性溶液の光散乱

今米 東洋子

名古屋大学理学部化学科 (〒464 名古屋市千種区不老町)

テトラデシル-, ヘキサデシルジメチルアミノキシ

ド (C_{14} DAO, C_{16} DAO) のえい糸性を示す粘弾性水溶液に対して光散乱を測定した。 C_{14} DAOと C_{16} DAOの希薄な水溶液は強いミセル間相関を示すが、相関は C_{14} DAO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 C_{14} DAO水溶液は $0.5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$ 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網目構造中網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。擬網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糸性を引き起こすと推論できる。

《新刊図書案内》

書 名 : "Refining and Reformulation : The Challenge of
Green Motor Fuels"
 編 集 者 : Adam Seymour
 発 行 所 : Ms Susan Millar, Oxford Institute for Energy
Studies, 57 Woodstock Road, Oxford, OX2 6FA, UK
(Fax : 0865-310527)
 発 行 年 : 1992年
 価 格 : £ 16.00 (送料込)