

Size of Spherical Micelles of 1-Decylpyridinium Iodide in Aqueous NaI Solutions

by

Katsuhiko FUJIO^{*1} and Masaya WATANABE²

¹*Department of Chemistry, School of Science, Tokai University
4-1-1 Kitakaname, Hiratsuka-shi, Kanagawa, 259-1292, Japan*

²*Department of Chemistry, Faculty of Science, Shinshu University
Matsumoto, Nagano, 390-8621, Japan*

^{*}Corresponding author: E-mail: kfujio@tokai.ac.jp

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Abstract

The static light scattering was measured on aqueous NaI solutions of 1-decylpyridinium iodide (DePI) at 25°C and the dependence of its micelle molecular weight on NaI concentration was studied. As a result, it was shown that DePI micelle does not undergo any salt-induced shape transition and therefore remains normal spherical over the whole NaI concentration range from 0 to 0.080 mol dm⁻³, as opposed to 1-dodecylpyridinium iodide micelle reported to undergo the salt-induced sphere-rod transition at 0.007 mol dm⁻³ NaI. At 0.050–0.080 mol dm⁻³ NaI, however, the second virial coefficients were observed to be negative, and it was suggested that the interaction between spherical micelles of DePI would be attractive and therefore the molecular weight of DePI micelle would increase with increasing NaI concentration.

Keywords: alkylpyridinium halide surfactant; added salt effect on micelle size; salt-induced shape transition; normal spherical micelle

1 Introduction

Most ionic surfactants whose hydrophobic chain is longer than the decyl one can form rod-like micelles in aqueous salt solutions, when the simple salt with a common counterion is added to a concentration exceeding a certain threshold [1]. We have previously reported that 1-dodecylpyridinium chloride (DPC) [2] and bromide (DPB) [3] and 1-tetradecylpyridinium (TPC) and 1-hexadecylpyridinium chlorides (CPC) [4] form spherical micelles alone even in a saturated solution of the corresponding sodium halide at 25°C, whereas 1-dodecylpyridinium iodide (DPI) forms rodlike micelles above 0.007 mol dm⁻³ NaI at the same temperature [5]. DPC, TPC and CPC form the normal spherical micelles above 0.05×10^{-3} , 0.015×10^{-3} and 0.0034×10^{-3}

mol dm^{-3} NaCl, respectively, but only the loosely packed spherical micelles at the lower NaCl concentrations [2, 4]. Consequently, micelles of these alkylpyridinium chlorides undergo the salt-induced shape transition from the loosely packed spherical micelle to the normal spherical micelle at threshold NaCl concentrations mentioned above. DPB forms the normal spherical micelles below 0.30 mol dm^{-3} NaBr, but the special spherical micelles having a constant aggregation number of 70.7, called the constant size spherical micelle in this article, at NaBr concentrations from 0.30 to 6.00 mol dm^{-3} [3]. Such constant size spherical micelle was reported by Anacker [6] for CPC in aqueous NaCl solutions at 30°C .

In this study, we measured static light scattering on aqueous NaI solutions of 1-decylpyridinium iodide (DePI) at 25°C and studied the dependence of its micelle molecular weight on NaCl concentration in order to confirm whether DePI micelle undergoes some salt-induced shape transition and whether DePI form the loosely packed or the constant size spherical micelles.

2 Experimental

Materials. 1-Decylpyridinium iodide (DePI) was synthesized from 1-iododecane and pyridine. ACROS Organics 1-iododecane was used without any purification. Pyridine was purchased from Nacalai Tesque, Inc. and dried over molecular sieve 3A before use. A mixture of 1-iododecane (102.6 g, 0.38 mol) and dry pyridine (64.5 g, 0.79 mol) was refluxed at 120°C for 7 h. After the mixture was cooled in an ice-water bath, the precipitates obtained were recrystallized three times from acetone-diethyl ether (1 : 2 v/v) mixture. The desired surfactant (64.8 g, 49% yield) was obtained as a pale-yellow crystal.

As shown in Fig. 1, the surface tension of aqueous solutions of the DePI sample shows no minimum around its critical micelle concentrations (cmc), $2.23 \times 10^{-2} \text{ mol dm}^{-3}$. This cmc value of DePI is in good agreement with the literature value of $2.25 \times 10^{-2} \text{ mol dm}^{-3}$ [7].

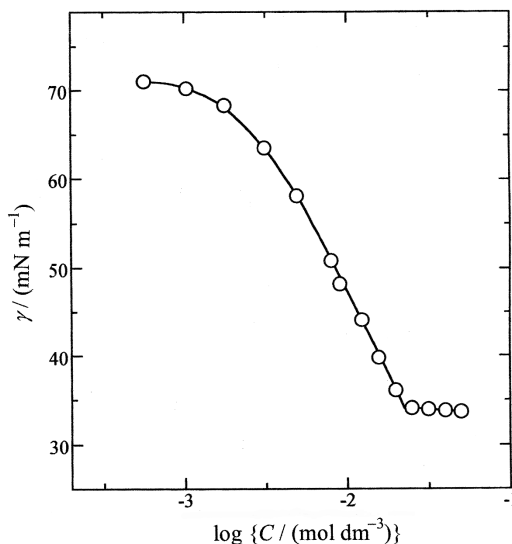


Fig. 1 Relationship between surface tension, γ , and logarithm of concentration, C , for aqueous solutions of DePI at 25°C . Surface tensions were measured by the drop weight method.

Apparatus. Light scattering was measured on a Laser Light Scattering Photometer DLS-700 manufactured by Otsuka Denshi Co., Inc., Japan. The incident light was vertically polarized light of 488 nm generated by a 7 mW argon ion laser, and both vertical and horizontal components of the scattered light were collected. The photometer was calibrated with purified benzene, as previously described [3]. The temperature was regulated to $25 \pm 0.2^\circ\text{C}$, by circulating constant temperature water from a Julabo F10-VC Thermostat. Solutions and solvents for light scattering measurements were filtered 4 or 5 times through a Millipore filter with a 0.10 or 0.22 μm pore size.

The specific refractive index increment was also measured at 488 nm and $25 \pm 0.1^\circ\text{C}$ on a Differential Refractometer RM-102 with a 50 W iodine lamp, manufactured by Otsuka Denshi Co., Inc. Its calibration method was also described previously [3].

The refractive index of aqueous NaI solutions at 488 nm and 25°C was evaluated from the concentration dependence of the difference of refractive index between NaI solution and water, measured by the above differential refractometer. We calculated the refractive index of water at 488 nm and 25°C from tabulated values at other wavelengths [8].

3 Results and Discussion

Excess reduced scattering intensities, $R_{90} - R_{90}^0$, of aqueous NaI solutions of DePI are shown in Fig. 2 as a function of surfactant concentration, c (g cm^{-3}) at various NaI concentrations, C_S (mol dm^{-3}). They are almost zero below the critical micelle concentration, c_0 (g cm^{-3}), but increase with increasing surfactant concentration above c_0 .

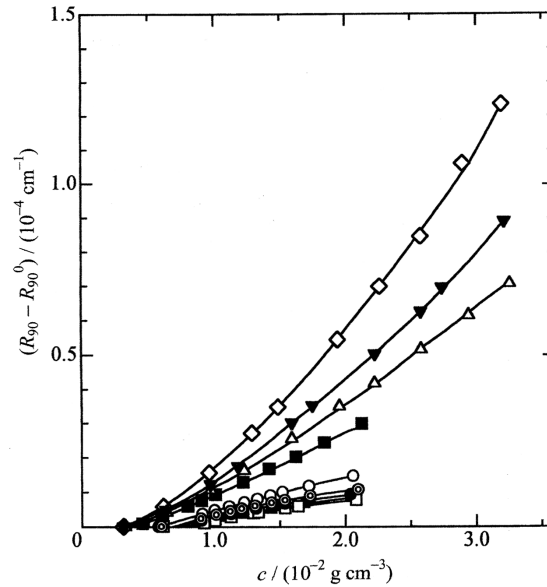


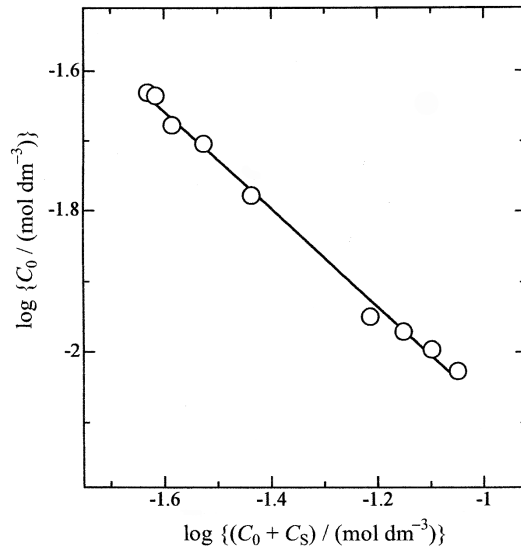
Fig. 2 Excess reduced intensity of scattered light from aqueous NaI solutions of DePI. C_S / (mol dm^{-3}): $\circ$, 0; $\blacktriangle$, 0.001; $\square$, 0.005; $\bullet$, 0.010; $\odot$, 0.020; $\blacksquare$, 0.050; $\triangle$, 0.060; $\blacktriangledown$, 0.070; $\diamond$, 0.080.

The critical micelle concentration, C_0 (mol dm^{-3}), of DePI decreases with increasing NaI concentrations, as given in Tables 1. It follows the Corrin-Harkins equations:

$$\log \{C_0 / (\text{mol dm}^{-3})\} = -0.693 \log \{(C_0 + C_S) / (\text{mol dm}^{-3})\} - 2.77 \quad (1)$$

Table 1 Critical micelle concentration, specific refractive index increment, and optical constant of aqueous NaI solution of DePI and refractive index of solvent.

$C_S/$ (mol dm ⁻³)	$\tilde{n}_0$	$c_0/$ (10 ⁻³ g cm ⁻³)	$C_0/$ (10 ⁻² mol dm ⁻³)	$(\partial\tilde{n}/\partial c)_{C_S}$ /(cm ³ g ⁻¹)	$K/$ (10 ⁻⁷ mol cm ² g ⁻²)
0	1.3367	8.12	2.34	0.1681	5.836
0.001	1.3367	8.04	2.32	0.1679	5.822
0.005	1.3368	7.30	2.10	0.1680	5.830
0.010	1.3369	6.86	1.98	0.1676	5.803
0.020	1.3371	5.78	1.66	0.1678	5.819
0.050	1.3378	3.90	1.12	0.1676	5.797
0.060	1.3380	3.71	1.07	0.1674	5.799
0.070	1.3383	3.50	1.01	0.1674	5.803
0.080	1.3385	3.26	0.94	0.1671	5.783

**Fig. 3** The Corrin-Harkins plot for DePI micelle in aqueous NaI solutions.

for DePI, as shown in Fig. 3. The slope of Corrin-Harkins plot, -0.693 , agrees well with the literature value for DPI, -0.703 [5]. On the other hand, the intercept, -2.77 , is larger than the one for DPI, -3.837 [5], as reflects the less hydrophobicity of DePI than DPI.

Fig. 4 shows Debye plots for micellar solutions of DePI. They give straight lines with positive slopes at 0.001 – 0.020 mol dm⁻³ NaI. At 0 mol dm⁻³ NaI, the reduced intensity increases with increasing surfactant concentration, but the rate of its increase gradually decreases. Such behavior was observed on light scattering from aqueous solutions of some other ionic surfactants [3–5, 9]. It has been attributed to changes in the degree of counterion binding [9, 10]. At the higher NaI concentrations, 0.050 – 0.080 mol dm⁻³, the reduced intensity decreases with increasing surfactant concentration, as observed for DPI which undergoes the salt-induced sphere-rod transition [5]. However, it continues to decrease and does not have a minimum observed for DPI [5]. Therefore, at the NaI concentrations observed, DePI micelles remains spherical and does not undergo the sphere-rod transition.

The linear relationship between reduced intensity and surfactant concentration follows the equa-

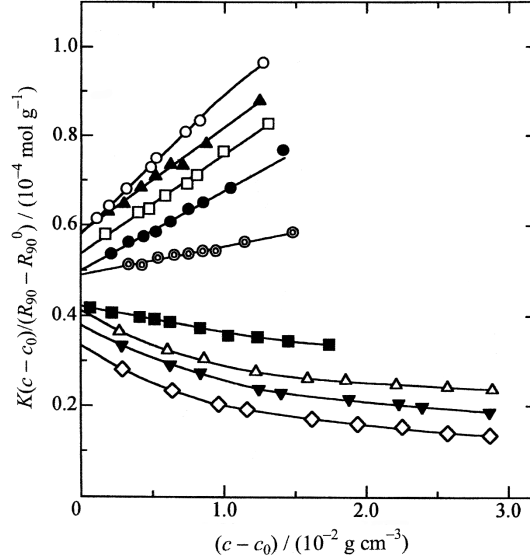


Fig. 4 Debye plots for aqueous NaI solutions of DePC. C_S / (mol dm^{-3}): $\circ$, 0; $\blacktriangle$, 0.001; $\square$, 0.005; $\bullet$, 0.010; $\odot$, 0.020; $\blacksquare$, 0.050; $\triangle$, 0.060; $\blacktriangledown$, 0.070; $\diamond$, 0.080.

tion

$$\frac{K(c - c_0)}{R_{90}^0 - R_{90}^0} = \frac{1}{M} + 2B(c - c_0) \quad (2)$$

where M is the micelle molecular weight and B is the second virial coefficient. The optical constant, K , for the vertically polarized incident light is given by

$$K = \frac{4\pi^2 \tilde{n}_0^2 (\partial \tilde{n} / \partial c)_{C_S}^2}{N_A \lambda^4} \quad (3)$$

where N_A is Avogadro constant, λ the wavelength of the incident light, $\tilde{n}_0$ the refractive index of the solvent, and $(\partial \tilde{n} / \partial c)_{C_S}$ the specific refractive index increment of solution. At the NaI concentrations of 0 and 0.050–0.080 mol dm^{-3} , although the Debye plot is not linear, its adequate extrapolation to the infinite dilution of micelle is possible. It has been assumed that Eq. (2) would hold in the limit of zero micelle concentration.

Table 2 gives values of micelle molecular weight and second virial coefficient, together with those of micelle aggregation number, m , which calculated by dividing M by surfactant molecular weight, for DePI. The micelle molecular weight and aggregation number also indicate that DePI micelles are spherical at all NaI concentrations investigated.

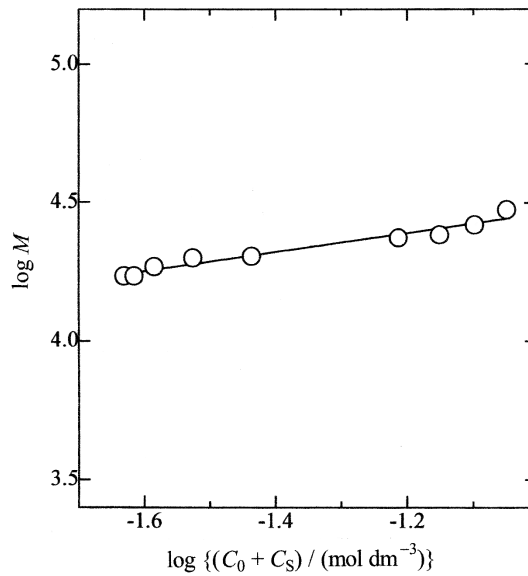
The salt-induced shape transition of ionic micelles is most clearly revealed by plotting the logarithm of micelle molecular weight against the logarithm of ionic strength or counterion concentration [1]. The ionic strength is given by concentrations of the surfactant monomer and the added salt, $C_0 + C_S$, because the monomer concentration remains almost constant above cmc. Fig. 5 shows such double logarithmic plot for DePI micelles in aqueous NaI solutions. The plot gives a straight line, expressed by

$$\begin{aligned} \log M &= 0.343 \log \{(C_0 + C_S) / (\text{mol dm}^{-3})\} + 4.81 \\ 0 &\leq C_S / (\text{mol dm}^{-3}) \leq 0.080. \end{aligned} \quad (4)$$

The coefficient of $\log (C_0 + C_S)$ was reported to be 0.305 for normal spherical DPI micelle and

Table 2 Molecular weight, aggregation number, and second virial coefficient of DePI micelles in aqueous NaI solution.

$C_S / (\text{mol dm}^{-3})$	$M/10^4$	m	$B/(10^{-3} \text{ mol cm}^3 \text{ g}^{-1})$
0	1.72	49.5	1.57
0.001	1.72	49.5	1.18
0.005	1.86	53.6	1.10
0.010	2.00	57.6	0.88
0.020	2.03	58.5	0.31
0.050	2.37	68.2	-0.29
0.060	2.43	70.0	-0.88
0.070	2.64	76.0	-1.68
0.080	2.99	86.1	-1.97

**Fig. 5** The double logarithmic plot of molecular weight against ionic strength for DePI micelle in aqueous NaI solutions.

1.885 for rodlike DPI micelle [5]. Judging by the aggregation number and the increasing rate of micelle molecular weight with increasing ionic strength, that is coefficient of $\log (C_0 + C_S)$ in Eq. (4), the straight line would correspond to the normal spherical micelle. However, the negative second virial coefficients observed at the higher NaI concentrations suggest that the attractive interaction would work between spherical DePI micelles and the molecular weight of DePI micelle would increase with increasing DePI concentration and therefore does not eliminate the possibility that DePI could form rodlike micelles. At least, in the concentration ranges investigated of NaI and DePI, we conclude that DePI forms only the normal spherical micelles.

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