

The Shape Transition of Micelles of 1-Tetradecyl- and 1-Hexadecylpyridinium Chlorides in Aqueous NaCl Solutions

by

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(Received on Oct. 14, 2024; accepted on Dec. 6, 2024)

Abstract

We measured static light scattering on aqueous NaCl solutions of 1-tetradecylpyridinium chloride (TPC) and 1-hexadecylpyridinium chloride (CPC) at 25°C and investigated the dependence of their micelle molecular weight on NaCl concentration. As a result, it was shown that TPC and CPC micelles undergo the salt-induced shape transition from the loosely packed spherical micelle to the normal spherical micelle at $0.015 \times 10^{-3} \text{ mol dm}^{-3}$ and $0.0034 \times 10^{-3} \text{ mol dm}^{-3}$ NaCl, respectively. This observation is consistent with our previous result on 1-dodecylpyridinium chloride (DPC)-NaCl system, in which DPC micelle underwent the salt-induced shape transition at 0.05 mol dm^{-3} NaCl. The phenomena that the spherical micelle molecular weight does not depend on the added salt concentration, as reported for CPC-NaCl system at 30°C and for 1-dodecylpyridinium bromide (DPB)-NaCl system at 25°C, was not observed.

Keywords: alkylpyridinium halide surfactant; salt-induced shape transition; loosely packed spherical micelle; constant size spherical micelle

1 Introduction

Most ionic surfactants having an alkyl chain longer than the decyl one can form rodlike 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 observed that 1-dodecylpyridinium chloride (DPC) [2] and bromide (DPB) [3] form spherical micelles alone even in a saturated solution of the corresponding sodium halide, whereas 1-dodecylpyridinium iodide (DPI) forms rodlike micelles above $0.007 \text{ mol dm}^{-3}$ NaI [4]. DPC forms the normal spherical micelles above

0.05 mol dm⁻³ NaCl, but only the loosely packed spherical micelles at the lower NaCl concentrations [2]. Consequently, DPC micelle undergoes the salt-induced shape transition from the loosely packed spherical micelle to the normal spherical micelle at 0.05 mol dm⁻³ NaCl. 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 at NaBr concentrations from 0.30 to 6.00 mol dm⁻³ [3]. Such phenomena that aggregation number of spherical micelles does not depend on salt concentration was reported by Anacker [5] for 1-hexadecylpyridinium chloride, which is popular by the trivial name of 1-cethylpyridinium chloride (CPC), in aqueous NaCl solutions at 30°C.

In this study, we measured static light scattering on aqueous NaCl solutions of 1-tetradecylpyridinium chloride (TPC) and CPC at 25°C and investigated the dependence of their micelle molecular weight on NaCl concentration in order to confirm whether these surfactant micelles undergo some salt-induced shape transition and whether these surfactants form the loosely packed spherical micelles or the special spherical micelles with a constant aggregation number.

2 Experimental

Materials. 1-Tetradecylpyridinium chloride (TPC) was synthesized from 1-chlorotetradecane and pyridine. 1-Chlorotetradecane was obtained from Merck Co., Inc. and distilled in vacuo. Pyridine purchased from Nacalai Tesque, Inc. was dried over molecular sieve 3A. A mixture of freshly distilled 1-chlorotetradecane (130.2 g, 0.56 mol) and dry pyridine (132.3 g, 1.67 mol) was refluxed at 120°C for 8 h. After the mixture was cooled in an ice-water bath, the precipitates obtained were recrystallized four times from acetone-ethanol (25 : 1 v/v) mixture (77% yield).

1-Hexadecylpyridinium chloride (CPC) was obtained from Nacali Tesque, Inc. and recrystallized three times from acetone-ethanol (70 : 1 v/v) mixture.

The surface tension of aqueous solutions of the TPC and CPC samples did not show any minimum around their critical micelle concentrations (cmc), 4.16 and 1.02×10^{-3} mol dm⁻³, respectively, as shown in Fig. 1. This value of cmc of CPC is in good agreement with the literature value of 0.9×10^{-3} mol dm⁻³ [6].

Apparatus. Light scattering was measured at 488 nm on a Laser Light Scattering Photometer DLS-700 with a 6-mW argon ion laser, manufactured by Otsuka Denshi Co., Inc., Japan. The incident light was vertically polarized, 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 water of constant temperature from a Julabo F10-VC Thermostat. Solutions and solvents for light scattering measurements were filtered four or five 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°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 NaCl solutions at 488 nm and 25°C was calculated from tabulated values at other wavelengths [7] with the method described previously [3].

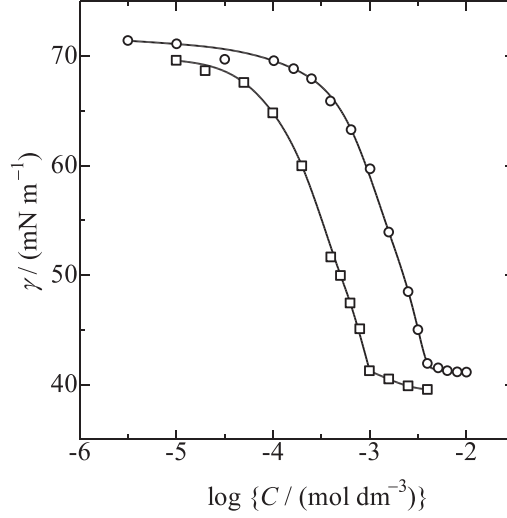


Fig. 1 Relationship between surface tension, γ , and logarithm of concentration, C , for aqueous solutions of TPC (○) and CPC (□) at 25°C.

3 Results and Discussion

Excess reduced scattering intensities, $R_{90} - R_{90}^0$, of aqueous NaCl solutions of TPC and CPC are shown in Fig. 2 and 3, respectively, as a function of surfactant concentration, c (g cm^{-3}) at various NaCl concentrations, C_S (mol dm^{-3}). Above the critical micelle concentration, c_0 (g cm^{-3}), they suddenly increase with increasing surfactant concentration.

The critical micelle concentrations, C_0 (mol dm^{-3}), of TPC and CPC decrease with increasing

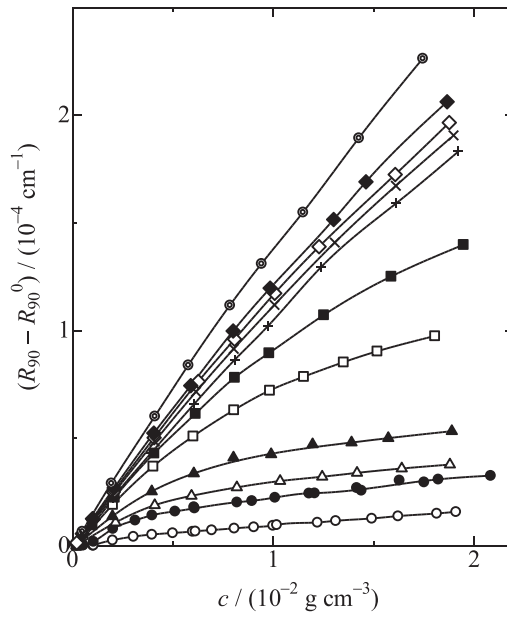


Fig. 2 Excess reduced intensity of scattered light from aqueous NaCl solutions of TPC. $C_S/(\text{mol dm}^{-3})$: ○, 0; ●, 0.005; △, 0.010; ▲, 0.015; □, 0.050; ■, 0.100; ◇, 0.500; ◆, 1.00; ◎, 1.50; ×, 2.00; +, 2.60.

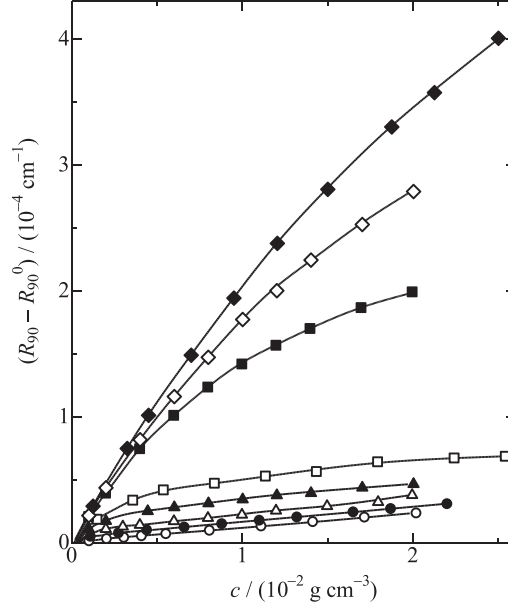


Fig. 3 Excess reduced intensity of scattered light from aqueous NaCl solutions of CPC. $C_S/(\text{mol dm}^{-3})$: $\circ$, 0; $\bullet$, 0.0010; $\triangle$, 0.0025; $\blacktriangle$, 0.0050; $\square$, 0.0100; $\blacksquare$, 0.0500; $\diamond$, 0.100; $\blacklozenge$, 0.250.

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

$C_S/$ (mol dm^{-3})	$\tilde{n}_0$	$c_0/$ ($10^{-3} \text{ g cm}^{-3}$)	$C_0/$ ($10^{-3} \text{ mol dm}^{-3}$)	$(\partial\tilde{n}/\partial c)_{C_S}$ ($\text{cm}^3 \text{ g}^{-1}$)	$K/$ ($10^{-7} \text{ mol cm}^2 \text{ g}^{-2}$)
0	1.3367	1.10	3.52	0.1828	6.904
0.005	1.3367	0.75	2.40	0.1800	6.691
0.010	1.3368	0.70	2.24	0.1827	6.898
0.015	1.3368	0.56	1.80	0.1814	6.794
0.050	1.3372	0.40	1.28	0.1824	6.880
0.100	1.3377	0.31	0.99	0.1823	6.874
0.500	1.3418	0.13	0.42	0.1808	6.805
1.00	1.3467	0.10	0.32	0.1751	6.425
1.50	1.3514	0.09	0.29	0.1722	6.258
2.00	1.3561	0.09	0.29	0.1670	5.924
2.60	1.3616	0.07	0.22	0.1571	5.286

NaCl concentrations, as given in Tables 1 and 2, respectively. They follow the Corrin-Harkins equations:

$$\log \{C_0/(\text{mol dm}^{-3})\} = -0.409 \log \{(C_0 + C_S)/(\text{mol dm}^{-3})\} - 3.453 \quad (1)$$

for TPC and

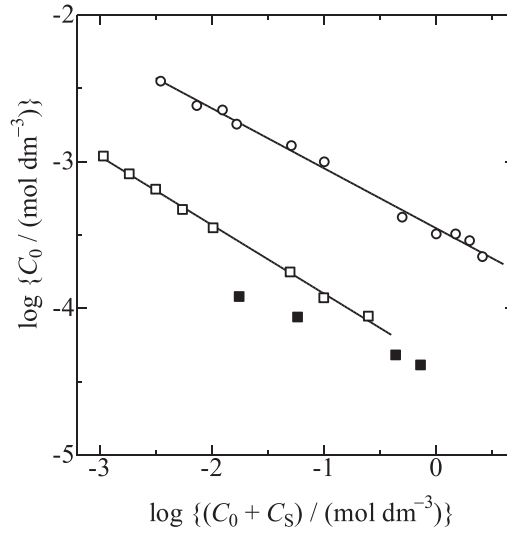
$$\log \{C_0/(\text{mol dm}^{-3})\} = -0.468 \log \{(C_0 + C_S)/(\text{mol dm}^{-3})\} - 4.367 \quad (2)$$

for CPC, as shown in Fig. 4. This figure includes Anacker's data for CPC-NaCl system at 30°C , which are somewhat smaller than our data because of different measurement temperature.

Figs. 5 and 6 show Debye plots for micellar solutions of TPC and CPC, respectively. They give straight lines with positive slopes except below $0.015 \times 10^{-3} \text{ mol dm}^{-3}$ NaCl for TPC and below

Table 2 Critical micelle concentration, specific refractive index increment, and optical constant of aqueous NaCl solution of CPC and refractive index of solvent.

$C_s /$ (mol dm ⁻³)	$\tilde{n}_0$	$c_0 /$ (10 ⁻³ g cm ⁻³)	$C_0 /$ (10 ⁻⁴ 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	0.37	10.9	0.1853	7.092
0.0010	1.3367	0.28	8.24	0.1845	7.034
0.0025	1.3367	0.22	6.47	0.1832	6.931
0.0050	1.3367	0.16	4.71	0.1835	6.954
0.0100	1.3368	0.12	3.53	0.1851	7.080
0.0500	1.3372	0.06	1.77	0.1842	7.016
0.100	1.3377	0.04	1.12	0.1830	6.924
0.250	1.3392	0.03	0.88	0.1835	6.980


Fig. 4 The Corrin-Harkins plots for TPC (○) and CPC (□) micelles in aqueous NaCl solutions. Anacker's data [5] for CPC in aqueous NaCl solutions are also plotted (■).

0.010 × 10⁻³ mol dm⁻³ NaCl for CPC. At the lower NaCl concentrations, 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, 4, 8]. It has been attributed to changes in the degree of counterion binding [8, 9].

The linear relationship between reduced intensity and surfactant concentration follows the equation

$$\frac{K(c - c_0)}{R_{90} - R_{90}^0} = \frac{1}{M} + 2B(c - c_0) \quad (3)$$

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

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

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 lower NaCl concentrations, although the Debye plot is not linear, its adequate extrapolation to the infinite

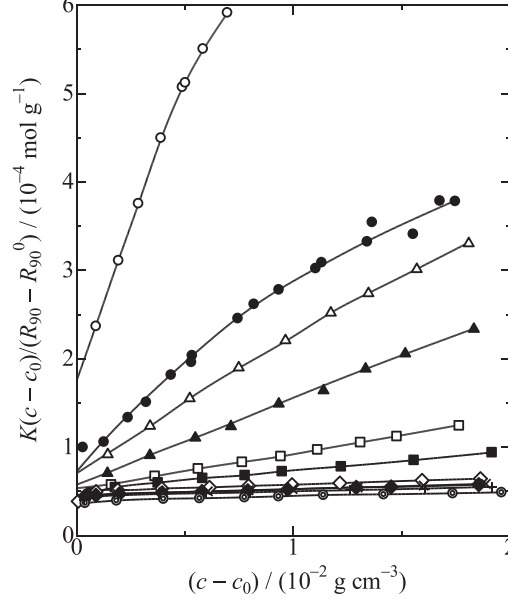


Fig. 5 Debye plots for aqueous NaCl solutions of TPC. $C_S/(\text{mol dm}^{-3})$: $\circ$, 0; $\bullet$, 0.005; $\triangle$, 0.010; $\blacktriangle$, 0.015; $\square$, 0.050; $\blacksquare$, 0.100; $\diamond$, 0.500; $\blacklozenge$, 1.00; $\odot$, 1.50; $\times$, 2.00; $+$, 2.60.

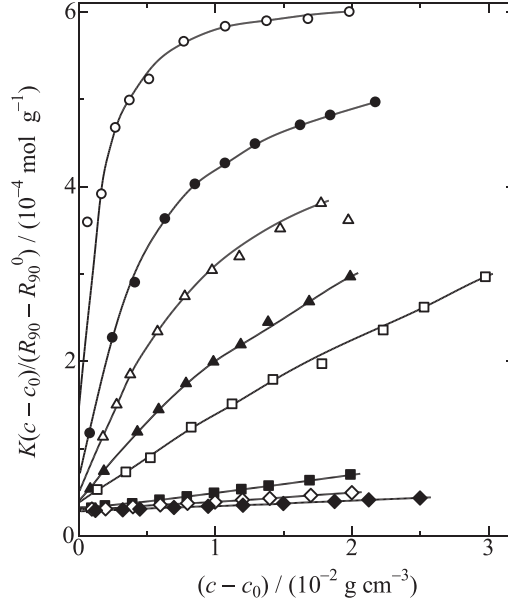


Fig. 6 Debye plots for aqueous NaCl solutions of CPC. $C_S/(\text{mol dm}^{-3})$: $\circ$, 0; $\bullet$, 0.0010; $\triangle$, 0.0025; $\blacktriangle$, 0.0050; $\square$, 0.0100; $\blacksquare$, 0.0500; $\diamond$, 0.100; $\blacklozenge$, 0.250.

dilution of micelle is possible. It has been assumed that the equation (3) would hold in the limit of zero micelle concentration.

Tables 3 and 4 give 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 TPC and CPC, respectively. The micelle molecular weight and aggregation number indicate that TPC and CPC micelles are spherical at all NaCl 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 concentra-

Table 3 Molecular weight, aggregation number, and second virial coefficient of TPC micelles in aqueous NaCl solution.

$C_S/(\text{mol dm}^{-3})$	$M/10^3$	m	$B/(10^{-3} \text{ mol cm}^3 \text{ g}^{-1})$
0	5.53	17.7	33.7
0.005	11.5	36.9	9.60
0.010	14.0	44.7	7.19
0.015	17.5	56.2	4.84
0.050	19.3	61.8	2.05
0.100	19.6	62.7	1.12
0.500	20.0	64.0	0.39
1.00	21.8	69.8	0.32
1.50	25.2	80.7	0.24
2.00	21.6	69.4	0.33
2.60	22.4	71.7	0.27

Table 4 Molecular weight, aggregation number, and second virial coefficient of CPC micelles in aqueous NaCl solution.

$C_S/(\text{mol dm}^{-3})$	$M/10^3$	m	$B/(10^{-3} \text{ mol cm}^3 \text{ g}^{-1})$
0	6.67	19.6	67.5
0.0010	12.1	35.6	26.1
0.0025	19.8	58.2	17.9
0.0050	25.0	73.5	9.08
0.0100	28.6	84.1	4.96
0.0500	33.5	98.5	0.99
0.100	34.0	100	0.50
0.250	35.6	105	0.31

tion [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. 7 shows such double logarithmic plot for TPC and CPC micelles in aqueous NaCl solutions. In both cases of TPC and CPC, the plot consists of two straight lines, expressed by

$$\begin{aligned} \log M &= 0.716 \log \{(C_0 + C_S) / (\text{mol dm}^{-3})\} + 5.527 \\ 0 &\leq C_S / (\text{mol dm}^{-3}) \leq 0.015 \end{aligned} \quad (5)$$

and

$$\begin{aligned} \log M &= 0.037 \log \{(C_0 + C_S) / (\text{mol dm}^{-3})\} + 4.328 \\ 0.015 &< C_S / (\text{mol dm}^{-3}) \leq 2.60 \end{aligned} \quad (6)$$

for TPC micelle and

$$\begin{aligned} \log M &= 1.014 \log \{(C_0 + C_S) / (\text{mol dm}^{-3})\} + 6.838 \\ 0 &\leq C_S / (\text{mol dm}^{-3}) \leq 0.0034 \end{aligned} \quad (7)$$

and

$$\begin{aligned} \log M &= 0.089 \log \{(C_0 + C_S) / (\text{mol dm}^{-3})\} + 4.620 \\ 0.0034 &\leq C_S / (\text{mol dm}^{-3}) \leq 0.250 \end{aligned} \quad (8)$$

for CPC micelle. 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 equations (5)–(8), straight lines at the higher NaCl concentrations would correspond to the normal spherical micelle. Because aggregation number of micelles expressed by straight lines at the lower NaCl concentrations is too small to form the normal spherical micelle, these micelles would be the loosely packed spherical micelle like DPC micelle at the lower NaCl concentrations [2]. Fig. 7 also includes Anacker’s data of CPC micelles in aqueous NaCl solutions at 30°C, based on which he concluded that the size of CPC micelles does not depend on NaCl concentration [5]. But his data also shows the same dependence of micelle molecular weight on ionic strength. The spherical micelle having constant molecular weight observed for DPB at the higher NaBr concentrations [3] is not detected for TPC and CPC micelles.

We thank Dr. Toyoko Imae for the use of a light scattering instrument.

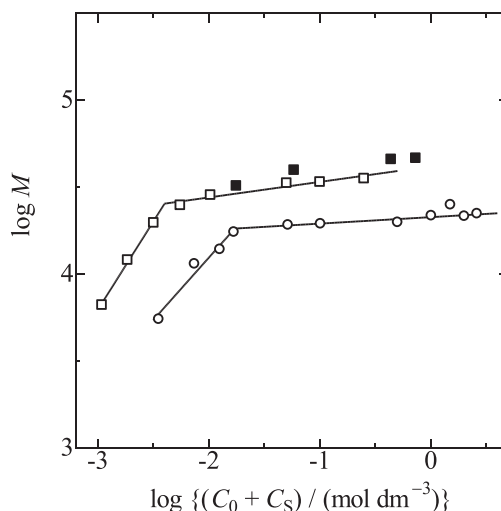


Fig. 7 The double logarithmic plots of molecular weight against ionic strength for TPC (○) and CPC (□) micelles in aqueous NaCl solutions. Anacker’s data [5] for CPC in aqueous NaCl solutions are also plotted (■).

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