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Size of Micelles of 1-Dodecylpyridinium Chloride in Aqueous NaCl Solutions

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Static light scattering has been measured on aqueous NaCl solutions of 1-dodecylpyridinium chloride over the NaCl concentrations from 0 to 4.00 M at 25 °C, and the micelle molecular weight has been estimated by means of the Debye equation. In aqueous solution the molecular weight is as small as 5280, corresponding to the aggregation number, 18.6. With increasing NaCl concentration up to 0.05 M the molecular weight increases sharply, reaching 12350. The small micelles would not be so compact as the common spherical micelles but would be porous except for their core. With increasing NaCl concentration beyond 0.05 M the micelle molecular weight increases only gradually, similar to growth of the common spherical micelles, and reaches 20410 in 4.00 M NaCl.

Most of ionic surfactants having a dodecyl group as hydrophobic part can form rodlike micelles in aqueous solutions when simple salts such as NaCl or NaBr are present to concentrations beyond a certain threshold, while they associate into spherical micelles in water and dilute salt solutions.[1] These surfactants are sodium dodecyl sulfate, dodecylammonium chloride, and dodecyldimethylammonium chloride or bromide. Only dodecyltrimethylammonium chloride is an exception, and its spherical micelles are stable even in saturated NaCl solutions.[2] However, dodecyltrimethylammonium bromide forms rodlike micelles when NaBr is present to concentrations higher than 1.80 M (1 M=1 mol dm^{-3}).[3]

In the previous work[4] we have shown by static light scattering that 1-dodecylpyridinium bromide (DPB) does not form rodlike micelles even in the presence of NaBr up to 6.00 M; DPB forms only spherical micelles in aqueous NaBr solutions. Since it has been observed that Br$^-$ ion is more effective than Cl$^-$ ion for converting spherical micelles into rodlike micelles,[2,3,5] we can except that 1-dodecylpyridinium chloride (DPC) remains to form spherical micelles alone even in the presence of NaCl up to the saturation. In the present work we will aim to confirm the stability of spherical micelles of DPC in aqueous NaCl solutions.

Generally, spherical micelles of ionic surfactants gradually grow with increasing concentration of simple salt added. The size of spherical micelles increases by 1.2 to 1.9 times when the salt concentration increases up to the threshold salt concentration for the sphere-rod transition or up to the saturation of salt.[1] Nevertheless, we have previously[4] found a distinct property of the spherical micelles of DPB. The aggregation number of spherical micelles of DPB increases from 46.0 to 70.7 with increasing NaBr concentration from 0 to 0.30 M, but it remains constant at NaBr concentrations from 0.30 to 6.00 M. Then we might suppose that such a maximum and constant size can also be reached by spherical micelles of DPC when NaCl is present beyond a certain threshold concentration; such a threshold NaCl concentration would be much higher than 0.30 M. It is our second aim of the present work to examine whether spherical micelles of DPC have such a maximum size at NaCl concentrations higher than a certain threshold.

Ford et al.[6] measured static light scattering on aqueous KCl solutions of DPC in the presence of KCl from 0 to 0.08 M and found that its micelle molecular weight increased rather sharply with increasing KCl concentration. However, their results suggest that the micelles of DPC are small and also appear to show the presence of such a maximum micelle size.

In the present work we perform static light scattering measurements on aqueous NaCl solutions of DPC at 25 °C, of which the NaCl concentration is varied from 0 to 4.00 M.

Experimental

Materials. 1-Dodecylpyridinium chloride monohydrate purchased from Aldrich Chemical Co., was recrystallized three times from acetone.

Surface tension of aqueous solution of DPC was measured by the drop weight method and did not show any minimum near the critical micelle concentration, 16.6×10^{-3} M, as shown in Fig. 1. The molecular area at the critical micelle concentration was calculated to be 64.8 Å^2 molecule^{-1}. It should be noticed that the surface tension has a clear tendency to decrease with increasing DPC concentration beyond the critical micelle concentration. This suggests formation of very small micelles.

Apparatus. Light scattering was measured on a laser light scattering photometer DLS-700 with a 7 W argon ion laser, manufactured by Otsuka Denshi Co., Inc., Osaka, Japan, in which the vertically polarized light is incident to solutions. Specific refractive index increment was measured on a differential refractometer RM-102 with a 50 W iodine lamp, made by the same company. Both of them were determined at 488 nm and at 25 °C, and the methods of their determination were described previously.[4]

The refractive index of aqueous solutions of NaCl was calculated at 488 nm and at 25 °C by first interpolating tabulated values at other wavelengths[7] to 488 nm and then interpolating or extrapolating them to a desired NaCl concentration.

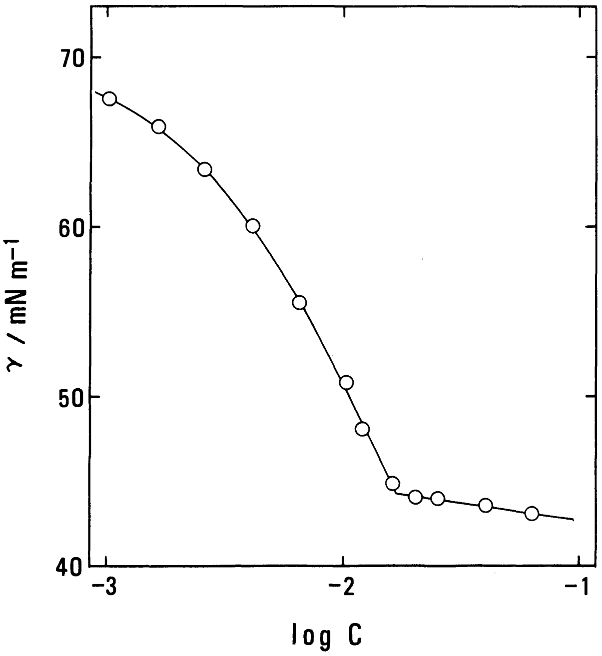

Fig. 1. Relationship between surface tension and logarithm of concentration for aqueous solution of DPC at 25 °C.

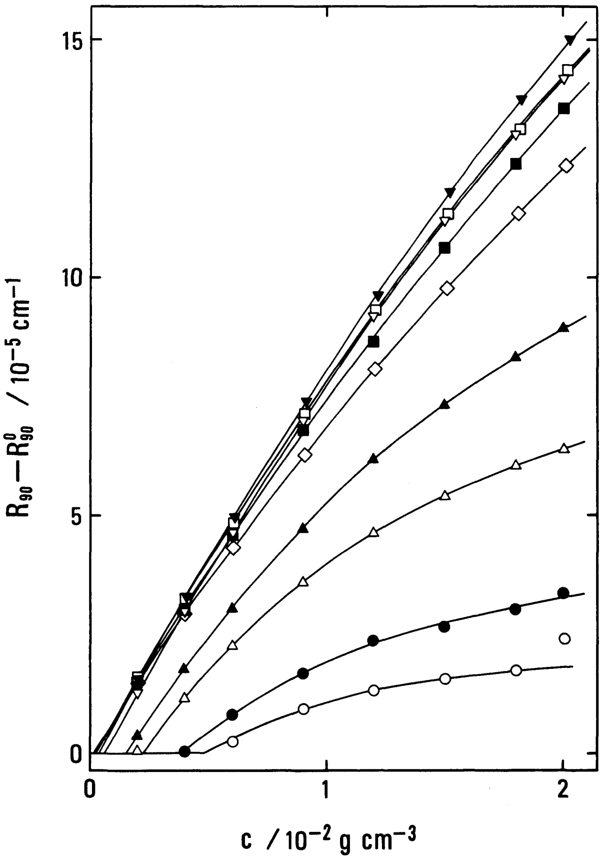

Fig. 2. Excess reduced intensity of scattered light from aqueous NaCl solutions of DPC. C_S (M): ○, 0; ●, 0.01; △, 0.05; ▲, 0.10; ▽, 0.50; ▼, 1.00; □, 2.00; ■, 3.00; ◇, 4.00.

Results

Excess reduced intensity of light scattered from aqueous NaCl solutions of DPC, $R_{90}-R_{90}^{\circ}$, at different NaCl concentrations is given in Fig. 2 as a function of DPC concentration, c (g cm^{-3}). Above the critical micelle concentration, c_0 (g cm^{-3}), the reduced intensity increases with increasing DPC concentration. The increase is convex upward. The reduced intensity is stronger but the rate of its increase is larger, as the NaCl concentration is increased. The excess reduced intensity reaches a maximum at 1.00 M NaCl, and it decreases with a further increase in NaCl concentration. This phenomena is quite similar to that observed for aqueous NaBr solutions of DPB, for which the maximum intensity is attained at 0.50 M NaBr.

The critical micelle concentration, C_0 (M), decreases with increasing NaCl concentration, as given in Table 1. It follows the Corrin–Harkins equation:

$$\log C_0 = -0.593 \log (C_0 + C_s) - 2.845, \quad 0 \leqslant C_s \leqslant 4.00 \text{ M} \qquad (1)$$

as shown in Fig. 3. Values of the coefficient of $\log (C_0 + C_s)$ are 0.573 for aqueous NaBr solutions of DPB[4] and 0.703 for aqueous NaI solutions of 1-

Table 1. Critical Micelle Concentration and Specific Refractive Index Increment of Aqueous NaCl Solutions of DPC

C_s	$\tilde{n}_0$	c_0	C_0	$(\partial\tilde{n}/\partial c)_{C_s}$	K
M		10^{-2} g cm^{-3}	10^{-2} M	cm^3 g^{-1}	10^{-7} cm^2 g^{-2}
0	1.3367	0.465	16.38	0.170	5.884
0.01	1.3368	0.390	13.74	0.170	5.879
0.05	1.3372	0.216	7.61	0.169	5.858
0.10	1.3377	0.148	5.21	0.168	5.832
0.50	1.3418	0.063	2.22	0.164	5.626
1.00	1.3467	0.040	1.41	0.159	5.370
2.00	1.3561	0.025	0.88	0.152	4.867
3.00	1.3652	0.024	0.85	0.143	4.380
4.00	1.3740	0.017	0.60	0.135	3.909

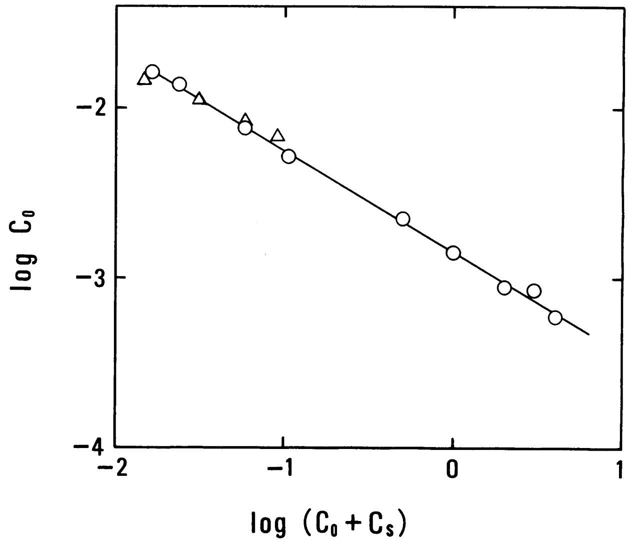

Fig. 3. The Corrin-Harkins plot for DPC micelles in aqueous NaCl solutions. ○, present. In aqueous KCl solutions: △, Ford et al.[6]

dodecylpyridinium iodide (DPI).[8]

The critical micelle concentration of DPC in water is 1.5 times larger than that of DPB in water,[4] and it is about 3 times larger than that of DPI in water.[8] The large value of the critical micelle concentration of DPC suggests a low aggregation number of its micelles.

Deviation of the critical micelle concentration at 0 and 0.01 M NaCl from the Corrin-Harkins equation might suggest that the low aggregation number of micelles does not permit their unique specification or determination owing to the polydispersity.

Table 1 gives values of the specific refractive index increment of solutions, together with those of refractive index of solutions. The specific refractive index increment is represented by

$$(\partial\tilde{n}/\partial c)_{C_s} = 0.1688 - 0.0087\, C_s \qquad 0 \leqslant C_s \leqslant 4.00\ \mathrm{M} \tag{2}$$

if values at 0 and 0.01 M NaCl and 4.00 M NaCl are omitted. This is shown in Fig. 4. The dependence is much smaller for DPC than for DPB. The values of the specific refractive index increment in water are 0.175 for DPB and 0.173 for DPI, and such an irregular order of the increment dependent on counterion species was also observed at 547 nm by Ford et al.[6]

Figure 5 shows Debye plots for micellar solutions of DPC at different NaCl concentrations. They give straight lines with positive slopes. The intercept lowers rather drastically and the slope also decreases, with increasing NaCl concentration. The Debye plot can be expressed by the equation

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

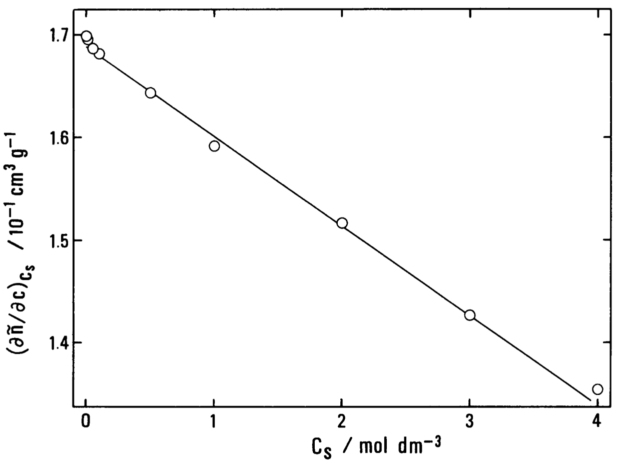

Fig. 4. Relationship between specific refractive index increment and NaCl concentration.

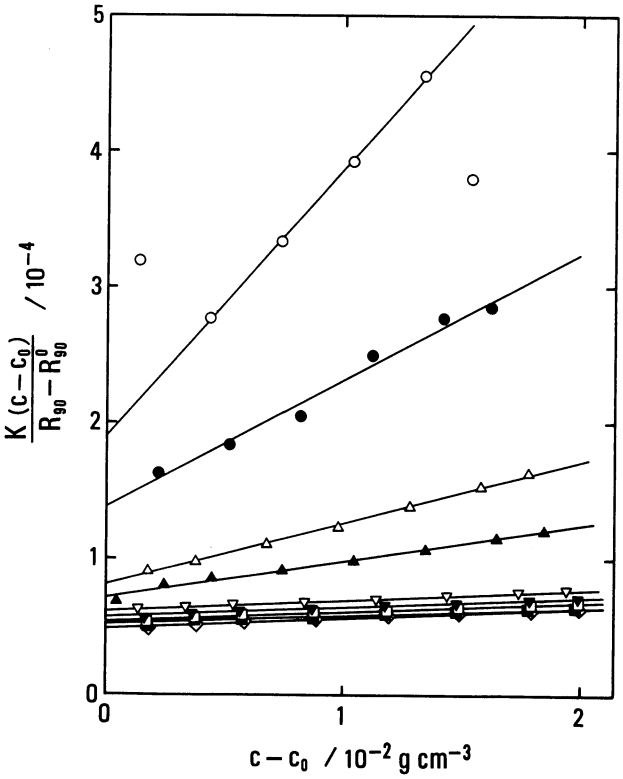

Fig. 5. Debye plots for light scattering from aqueous NaCl solutions of DPC. C_S (M): ○, 0; ●, 0.01; △, 0.05; ▲, 0.10; ▽, 0.50; ▼, 1.00; □, 2.00; ■, 3.00; ◇, 4.00.

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

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

Table 2. Molecular Weight, Aggregation Number, and Second Virial Coefficient of DPC Micelles in Aqueous NaCl Solutions

C_s M	M	m	B 10^{-3} cm^3 g^{-1}
0	5280	18.6	9.88
0.01	7260	25.6	4.68
0.05	12350	43.5	2.28
0.10	13990	49.3	1.34
0.50	16310	57.5	0.40
1.00	17450	61.5	0.35
2.00	18420	64.9	0.34
3.00	19120	67.4	0.30
4.00	20410	71.9	0.37

where N_A is Avogadro's number and λ is the wavelength (488 nm).

Values of the micelle molecular weight and the second virial coefficient are given in Table 2, together with those of the micelle aggregation number, $m=M/283.8$. The micelle aggregation number of DPC in water, 18.6, is very small, as compared with that for the other dodecyl derivatives in water.[1,9,10] It is in agreement with the value, 20, reported by Ford et al.[6] This micelle can not have such a compact structure as the spherical micelle consisting of more than 40 surfactant ions. It would have a porous structure except for its compact core.[11]

The micelle aggregation number increases with increasing NaCl concentration, sharply up to 0.05 M and then gradually up to 4.00 M. In 0.05 M NaCl the micelle aggregation number of DPC is 43.5, which is of the same order of magnitude as that of DPB in water. The spherical micelle of DPC in 0.05 M NaCl would have a structure similar to that of dodecyltrimethylammonium chloride in water[2] or DPB in water.[4] The spherical micelles having aggregation number about 40 would be compact following the geometrical or molecular requirement, when the surfactant is a dodecyl derivative.[12-15] Further increase in aggregation number would make the micelle structure more compact and larger, and it would finally cause the micelle shape to deviate from the sphere to oblate ellipsoids. Even in 4.00 M NaCl, the micelle aggregation number is 71.9, which is still small compared to the maximum aggregation number of spherical micelles formed by DPI.

Discussion

Spherical micelles of DPC in water are considerably small when compared to those of other surfactants with dodecyl group. The aggregation number, 18.6, is not sufficient to form spherical micelles with a fully occupied structure. In 0.01 M NaCl the same is true. Formation of such small micelles occurs less cooperatively and obscures the critical micelle concentration. This can be seen in the surface tension curve in Fig. 1. Figure 6 shows the double logarithmic plot of micelle molecular weight and ionic strength for DPC. The linear relation is approximated by

$$\log M = 0.655 \log (C_0 + C_s) + 0.093 \qquad 0 \leqslant C_s \leqslant 0.05 \text{ M} \tag{5}$$

Only above 0.05 M NaCl, the aggregation number of DPC is in the range of that of spherical micelles formed by the other surfactants such as dodecyltrimethylammonium chloride[2] and DPB,[4] that can not form rodlike micelles. The micelles of DPC may behave as spherical micelles in aqueous solutions of 0.05—4.00 M NaCl. At ionic strengths larger than 0.05 M, the linear relation.

$$\log M = 0.093_3 \log (C_0 + C_s) + 4.239 \qquad 0.05 \leqslant C_s \leqslant 4.00 \text{ M} \tag{6}$$

holds for spherical micelles, as shown in Fig. 6.

In view of the presence of the size limit of spherical micelles of DPB, spherical micelles of DPC might also have such a threshold NaCl concentration. However, it is not definite for PDC whether the maximum and constant size of spherical micelle exists or not in aqueous NaCl solutions.

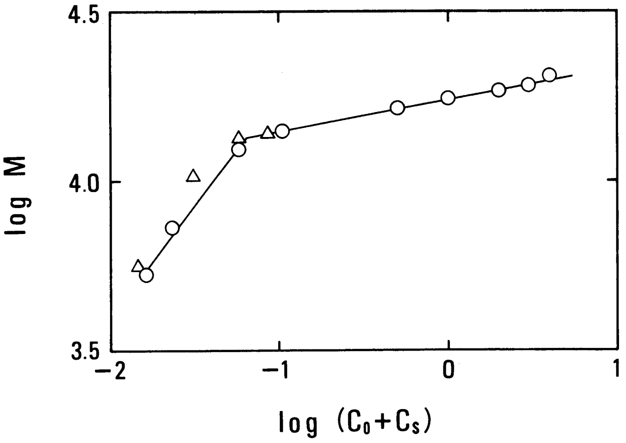

Fig. 6. The double logarithmic relationship between micelle molecular weight and ionic strength. ○, present. In aqueous KCl solutions: △, Ford et al.[6]

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