Biophysical Chemistry 11 (1980) 417–423
© North-Holland Publishing Company

SIZE AND SHAPE OF CHARGED MICELLES OF IONIC SURFACTANTS IN AQUEOUS SALT SOLUTIONS

Shoichi IKEDA, Sumio OZEKI and Shoji HAYASHI
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya, Japan

Light-scattering has been measured on aqueous NaCl solutions of dodecyldimethylammonium chloride and sodium dodecyl sulfate. From molecular weight determination it is confirmed that spherical micelles are formed at low NaCl concentrations, but at high NaCl concentrations the small micelles formed at the critical micelle concentration further associate to form large rod-like micelles with increasing micelle concentration. The reduction of repulsion between charged groups induces the sphere-rod transition of micelle shape. The dependence of molecular weight on ionic strength can be expressed by double logarithmic relations, which are dependent on the micelle shape. While dodecyldimethylammonium chloride dissolves even in 4.00 M NaCl, sodium dodecyl sulfate solutions exhibit some anomaly in angular dissymmetry at NaCl concentrations higher than 0.50 M at low temperatures.

1. Introduction

It is well known that surfactant molecules or ions are subject to reversible association to form micelles in aqueous solutions when their concentration exceeds some critical value called the critical micelle concentration (abbreviated as cmc). There are several methods for determining micelle size and shape, but conventional light-scattering has been most frequently and effectively employed so far. Various models for surfactant micelles have been proposed on the basis of either experimental or geometrical considerations, and among them either spherical or rod-like micelles have been found to exist in dilute surfactant solutions. However, the condition for formation of either of these micelles has never been clearly elucidated.

Anionic micelles of sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) have been investigated in most detail [1–3], and it is found that its micelles in aqueous NaCl solutions have a molecular weight of around $(1–4) \times 10^4$. Then the micelle shape must be spherical, although its size slightly increases with increasing NaCl concentration. Cationic micelles of dodecylammonium chloride ($C_{12}H_{25}NH_3Cl$) also have molecular weight of the same order in 0–0.05 M NaCl [4,5]. On the other hand, it was shown that cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$) in 0.178 M and 0.233 M KBr forms rod-like micelles having molecular weight as high as 10^6 [6]. It was also found that the dimethyldodecyl N-hydroxy-ammonium bromide ($C_{12}H_{25}(CH_3)_2NOHBr$) micelle is rod-like in 0.20 M NaBr and has a molecular weight higher than 10^5 [7]. Nevertheless, strong objections have been raised against the formation of such large rod-like micelles.

In this article we will investigate the effect of ionic strength on size and shape of charged micelles by means of conventional light-scattering and demonstrate the formation of rod-like micelles in concentrated salt solutions. The ionic surfactants are dodecyldimethylammonium chloride ($C_{12}H_{25}(CH_3)_2NHCl$) (abbreviated as DDAC) and sodium dodecyl sulfate (abbreviated as SDS), and the added salt is NaCl. The Krafft point is about −4°C for DDAC [8], while it is 16°C for SDS [9]. More details of the experimental results have been published in two current papers [10,11].

2. Experimental

DDAC and SDS were prepared or purified as previously described [10–12].

Light-scattering was measured on a Shimadzu Light Scattering Photometer PG-21 using a mercury lamp at 436 nm. Preparation and clarification of SDS solutions were performed under temperature control, and measurements of light-scattering for SDS solutions were carried out at constant temperatures within ±0.01°C, which was reached by lowering the temperature of solution from higher. For DDAC solutions no such special precaution for temperature regulation was applied partly because of the low Krafft point of DDAC.

3. Results

3.1. *Condition for measurements of refractive index increment*

In order to obtain the micelle molecular weight, M_m, from the light-scattering measurements, we should measure the refractive index increment for a series of surfactant solutions of a given chemical potential, μ_s, of added salt, NaCl [13–16]. In this case it is assumed that the chemical potential of surfactant monomer remains constant. If the weight concentration of surfactant is c and the cmc is c_0, the Debye equation is then represented by

$$\frac{K'(\partial\tilde{n}/\partial c)^2_{T,P,\mu_s}(c-c_0)}{R_{90}-R^0_{90}} = \frac{1}{M_\mu} + 2B_\mu(c-c_0)\,, \qquad (1)$$

where R_{90} is the reduced intensity in the 90° direction and R^0_{90} is that at cmc, $\tilde{n}$ the refractive index, K' the optical constant and B_μ is the second virial coefficient. Here it is postulated that no internal interference occurs.

In the present work light-scattering and refractive index increment were measured on a series of surfactant solutions of a given molar concentration of added salt, NaCl, C_s. In this case we have

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

where M is the apparent micelle molecular weight and B is the corresponding second virial coefficient. The optical constant is given by $K = K'(\partial\tilde{n}/\partial c)^2_{T,P,C_s}$. It was demonstrated [13,15] that the relation

$$M = M_\mu[1+\phi'(\partial c_s/\partial c)_{T,P,\mu_s}]^2\,, \qquad (3)$$

holds between M and M_μ, where

$$\phi' = (\partial\tilde{n}/\partial c_s)_{T,P,c}/(\partial\tilde{n}/\partial c)_{T,P,c_s}\,, \qquad (4)$$

and c_s is the weight concentration of NaCl.

Instead of making measurements of the refractive index increment at constant chemical potential of added salt, the Prins–Hermans–Princen–Mysels theory [17,18] gives an equivalent method to derive the micelle molecular weight, M_m, from the measurements at constant concentration of added salt. It leads to the result

$$M = M_m/q\,, \qquad (5)$$

where

$$1/q = 1 - E(p/m) + E^2((p^2+p)/4m^2)\,, \qquad (6)$$

$$E = (C_0 + fC_s)/(C_0 + C_s)\,, \qquad (7)$$

$$f = (\partial\tilde{n}/\partial C_s)_{T,P,C}/(\partial\tilde{n}/\partial C)_{T,P,C_s}\,. \qquad (8)$$

Here it is assumed that the micelle behaves ideally and the second virial coefficient, B, arises from the effective micelle charge, p. In the above m is the micelle aggregation number and C is the molar concentration of surfactant.

It will be seen below that at high ionic strengths the micelles become large and the internal interference becomes manifest. Then the Debye equation is modified into

$$\frac{K(c-c_0)}{R_\theta - R^0_\theta} = \frac{1}{MP(\theta)} + 2B(c-c_0)\,, \qquad (9)$$

where

$$1/P(\theta) = 1 + (16\pi^2\tilde{n}_0^2/3\lambda^2)R_G^2\sin^2(\theta/2) + \ldots\,, \qquad (10)$$

λ being the wavelength of light, $\tilde{n}_0$ the refractive index of solvent, and θ the scattering angle. The radius of gyration of the micelle is represented by R_G, and for a rigid rod-like micelle the length, L, is equal to $\sqrt{12}R_G$.

3.2. *Spherical micelles formed at low ionic strengths*

For solutions of both surfactants the reduced intensity increases with increasing concentration above the cmc. Reduced intensities of DDAC micelles in 0–0.50 M NaCl and SDS micelles in 0.01 and 0.10 M NaCl gave curves convex upward above the cmc, as shown in fig. 1 for DDAC. Fig. 2 illustrates the Debye plots for SDS in 0.01 and 0.10 M NaCl, together with that in 0.50 M NaCl. The reciprocal intercept of the Debye plot gives the apparent micelle molecular weight, M, and then the apparent micelle aggregation number, m'. Table 1 summarizes these values, M and m', for DDAC and SDS at low ionic strengths, as well as those of the cmc, C_0. The values of micelle molecular weight,

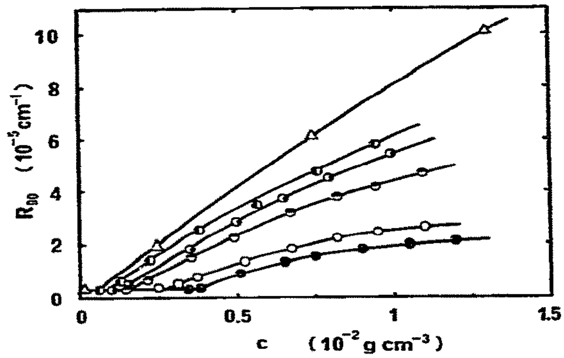

Fig. 1. The relation of R_{90} with c for DDAC in aqueous solutions at 25°C. NaCl concentration (M): ●, 0; ○, 0.01; ◓, 0.05; ◑, 0.10; ◐, 0.20; △, 0.50.

M_m, and aggregation number, m, calculated by the Prins–Hermans–Princen–Mysels theory, are also listed in table 1. We see that the value of q amounts, at most, to 1.17 in the absence of added salt, and decreases with increasing NaCl concentration. We may then anticipate that q will be unity at high ionic strengths, as far as the situation remains the same.

3.3. *Rod-like micelles formed at high ionic strengths*

DDAC dissolves readily in more concentrated NaCl solutions, but these solutions show light-scattering having angular dissymmetry when the surfactant concentration is higher than the cmc. The curvature of reduced intensity becomes convex downward against surfactant concentration, as shown in fig. 3. Then the Debye plot gives a curve decreasing with increasing micelle concentration, as shown in fig. 4. This suggests that the micelles formed at the cmc further associate with one another to form larger micelles. The larger micelles of DDAC grow up to molecular weight as large as 10^6 in 4.00 M NaCl.

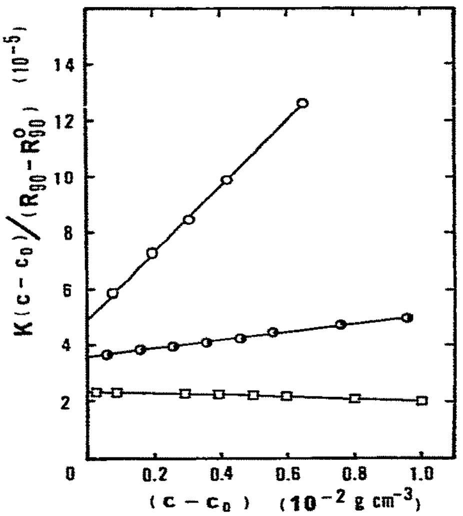

Fig. 2. The Debye plots for SDS in aqueous solutions at 25°C. NaCl concentration (M): ○, 0.01; ◑, 0.10, □, 0.50.

By measuring the angular dependence of reduced intensity at each micelle concentration, the Debye plots free from internal interference can be drawn by extrapolation to 0° direction. The angular dependence of the Debye equation is illustrated in fig. 5.

Since the NaCl concentration is sufficiently high, the interaction between charged micelles would be small other than the excluded volume effect. Then we postulate that the reciprocal of the micelle molecular weight at each surfactant concentration can be directly

Table 1
Spherical micelles formed at low ionic strengths (25°C)

	C_s (M)	C_0 (10^{-3} M)	M	m'	M_m	m	q
DDAC	0	14.9	13 900	55.6	16 200	65	1.17
	0.01	11.6	15 200	60.8	16 700	67	1.10
	0.05	6.8	17 600	70.4	18 500	74	1.05
	0.10	5.0	19 400	77.6	20 200	81	1.04
	0.20	3.5	21 500	86.0	22 700	91	1.06
	0.50	2.5	25 200	101	26 400	106	1.05
SDS	0.01	5.2	20 200	70.1	22 100	77	1.10
	0.10	1.5	27 800	96.5	29 100	101	1.05

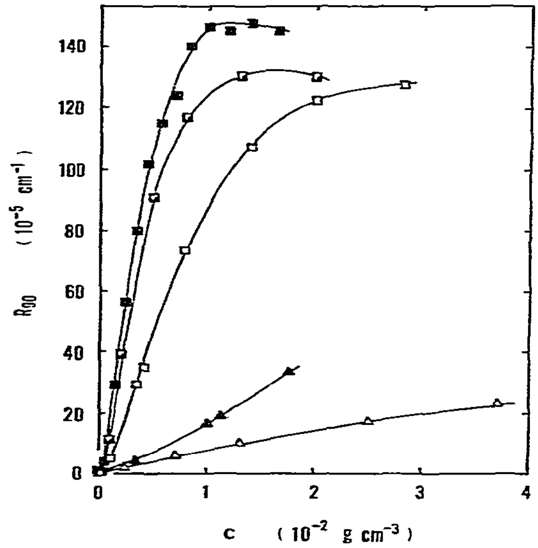

Fig. 3. The relation of R_{90} with c for DDAC in concentrated NaCl solutions at 25°C. NaCl concentration (M): △, 0.50; ▲, 1.00; □, 2.00; ◪, 3.00; ■, 4.00.

obtained from the ordinate of the Debye plot. The micelle molecular weight increases sharply with increasing micelle concentration and reaches some value characteristic of the NaCl concentration. This is apparent from fig. 4. To a first approximation, the largest molecular weight attained can be assigned to the large micelle, although small amounts of small micelles formed at the cmc would coexist. In the simplest way we may treat the micellar solution as subject to the association equilibrium of small micelles with large micelles, each having a size defined by the NaCl concentration. Then the surfactant solution should contain three kinds of surfactant species, i.e., monomer, small micelle, and large micelle. The small micelle would be considerably monodisperse and the amount of the large micelle increases with increasing concentration.

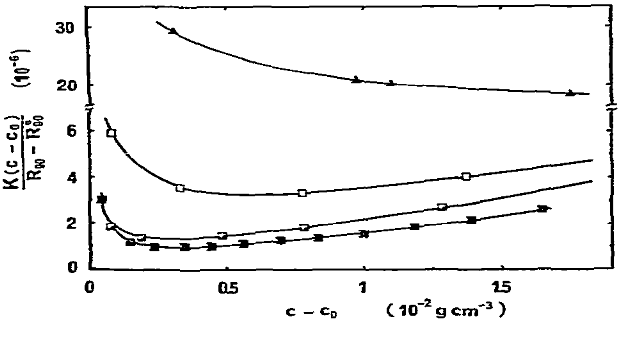

Fig. 4. The Debye plots for DDAC in concentrated NaCl solutions at 25°C. The light scattered in the 90° direction. NaCl concentration (M): ▲, 1.00; □, 2.00; ◪, 3.00; ■, 4.00.

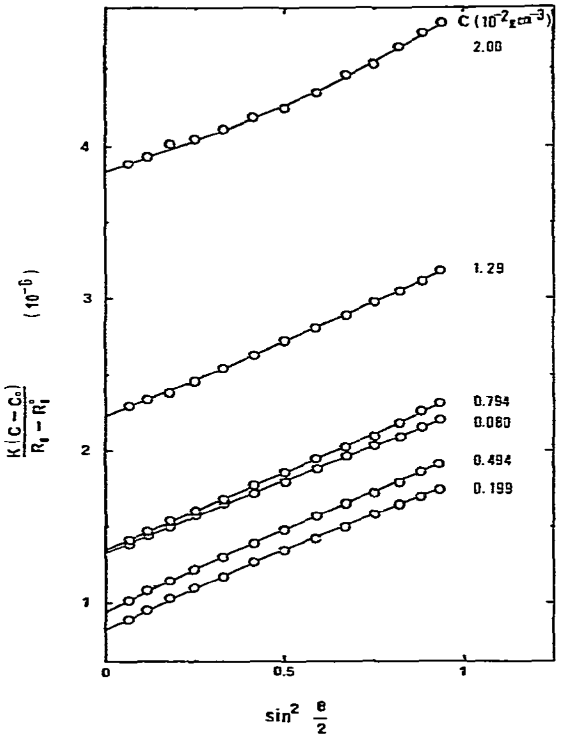

Fig. 5. Angular dependence of Debye plot for DDAC in 3.00 M NaCl solution at 25°C.

From the angular dependence of the Debye equation the radius of gyration of the large micelle can be derived. Comparing the micelle molecular weight with the radius of gyration, the large micelle is found to be rod-like. Values of molecular weight, M, aggregation number, m', and length, L, of the large rod-like micelle observed at a given surfactant concentration, c, are listed in table 2.

On the other hand, SDS is unstable in solutions of NaCl more concentrated than 0.50 M. The temperature of solubility limit or the critical micelle temperature is

Table 2
Rod-like micelles of DDAC formed at high ionic strengths (25°C)

C_S (M)	c (10^{-2} g cm^{-3})	M	m'	L (Å)
1.00	2.50	56 000	224	
2.00	0.78	333000	1 330	600
3.00	0.20	1200000	4 800	1780
4.00	0.24	2940000	11 800	3060

recorded, for example, to be 24.7 °C in 0.50 M NaCl and 25.4 °C in 0.60 M NaCl [19]. The critical micelle temperature in the absence of added salt is coincident with the Krafft point. Thus the SDS solutions were prepared and filtered at 36 °C and then brought to the temperature for light-scattering measurement. We could have clear SDS solutions even in the presence of 0.80 M NaCl at 25 °C which must be metastable.

The reduced intensity in the 90° direction gave curves concave downward against surfactant concentration, as illustrated in fig. 6. This indicates that the micelles formed at the cmc further grow with increasing micelle concentration, as shown in fig. 2. More marked growth of micelles can be observed in more concentrated NaCl solutions.

However, some anomaly was generally noticed in angular dissymmetry for solutions of SDS concentrations slightly higher than the cmc, when the temperature was low. The anomaly is such that the dissymmetry value varies (increases) with time but reaches a high steady value. Nevertheless, the anomaly reduces with increasing micelle concentration, as can be seen in fig. 6. The angular dependence of light-scattering showed that the high dissymmetry value came from the strong scattering at low angles and it could be attributed to the presence of trace amounts of microgels, possibly formed by small micelles [11]. In 0.80 M NaCl at 35°C however, light-scattering exhibited angular dissymetry, which was not caused by anomaly but because of the formation of large micelles.

The reduced intensity in the 90° direction is free from the anomaly, and the Debye plot in the 90° direction can be regarded as representing the micelle characteristics. The Debye plot gave curves lowering with increasing micelle concentration: the small micelles formed at the cmc associate together to form large micelles at higher concentrations. Table 3 gives values of the apparent micelle molecular weight, M, and apparent aggregation number, m', at the cmc, and their maximum values reached at a finite micelle concentration, c.

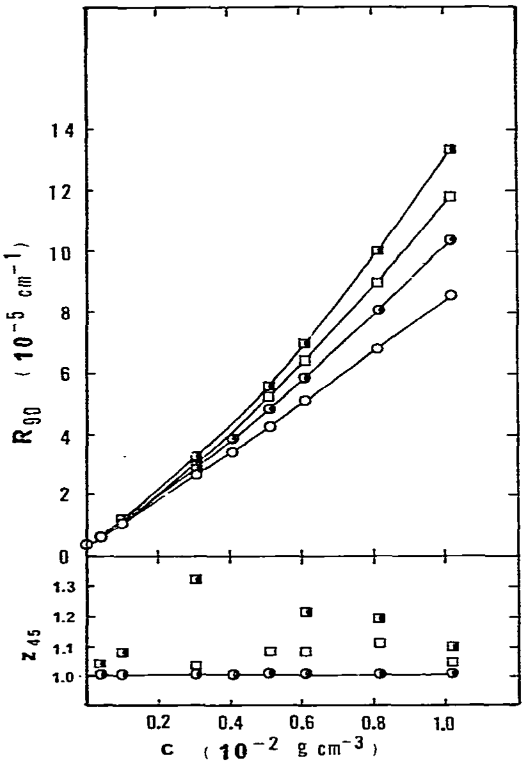

Fig. 6. The relations of R_{90} and z_{45} with c for SDS in 0.50 M NaCl solution at different temperatures. Temperature (°C): ○, 30; ◑, 25; □, 23; ◨, 21.

In 0.80 M NaCl at 35 °C, for which no anomaly of angular dissymmetry was observed, the angular dependence of light-scattering leads to the micelle molecular weight, 284 000, and the radius of gyration, 172 Å, which fit a rod-like micelle of length, 587 Å. Formation of the rod-like micelles of SDS was recently demonstrated on 2.00 g dl^{-1} SDS solution in 0.60 M NaCl at temperatures lower than 40 °C, by using (quasi-elastic) light-scattering method [19,20].

4. Discussion

We have shown that both DDAC and SDS can form rod-like micelles well above the cmc when they are in

Table 3
Rod-like micelles of SDS formed at high ionic strengths

C_s(M)	T (°C)	c_0 (10^{-2} g cm^{-3})	M	m'	M	m'	c (10^{-2} g cm^{-3})
			at cmc		at max.		
0.50	25	0.013	42 600	148			
	30	0.014	39 300	136			
0.60	25[a]	0.012	50 000	174	152 000	528	2.0
	30	0.013	43 500	151	111 000	385	2.0
0.80[b]	25[a]	0.011			470 000	1630	1.1
	30[a]	0.012			352 000	1220	0.7
	35	0.013			262 000	910	0.5

[a] Anomalous dissymmetry.
[b] The values of M are actually for those of MP(90).

concentrated NaCl solutions, while their micelles are spherical at low NaCl concentrations. If the micelle molecular weight is approximated by M and the largest value is taken at high NaCl concentrations, it is found that the two linear relations hold between logarithms of micelle molecular weight and ionic strength, as shown in fig. 7. Here the ionic strength is represented by the sum of cmc, C_0, and NaCl concentration, C_s. The relations are expressed by

$$\log M = 0.105 \log (C_0 + C_s) + 4.44, \quad C_s \leqslant 0.80, \quad (11a)$$

$$\log M = 2.64 \log (C_0 + C_s) + 4.70, \quad C_s \geqslant 0.80, \quad (11b)$$

for DDAC, and

$$\log M = 0.118 \log (C_0 + C_s) + 4.54, \quad C_s \leqslant 0.45, \quad (12a)$$

$$\log M = 4.68 \log (C_0 + C_s) + 6.15, \quad C_s \geqslant 0.45, \quad (12b)$$

for SDS, both at 25°C. Eq. (11a) or (12a), in which M is the value at the cmc, fits to the spherical micelle, and eq. (11b) or (12b), in which M is the largest value at a finite concentration, can be assigned to the rod-like micelle. Similar relations are found to hold for two cationic surfactants, dodecylammonium chloride [5] and Hyamine 1622 [21], in aqueous NaCl solutions, and it is presumed that these two cationics are also subject to the sphere-rod transition induced by the NaCl concentration.

The simplest scheme of micelle formation of these surfactants in concentrated NaCl solutions can be represented by

$$m\mathrm{D} \rightleftarrows \mathrm{D}_m, \quad n\mathrm{D}_m \rightleftarrows \mathrm{D}_{mn},$$

where D is the monomer, D_m the spherical micelle and D_{mn} the rod-like micelle. It is known that the micelle formation is caused by the balance of the hydrophobic interaction and the repulsion between amphiphiles. The present results indicate that the decrease in repulsion between polar head groups induces the transition of micelle shape from sphere to rod. Then we should anticipate that nonionic surfactants can form rod-like micelles, if the hydrocarbon part is long enough. This is supported by the published data on heptaoxyethylene cetyl ether ($C_{16}H_{33}O(CH_2CH_2O)_7H$) [22].

The structure of rod-like micelles can be derived

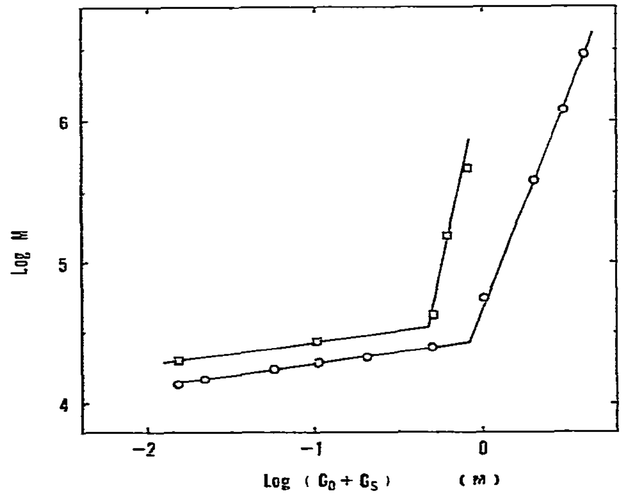

Fig. 7. The double logarithmic relation between micelle molecular weight and ionic strength at 25 °C. ○, DDAC; □, SDS.

from the relation of its length and aggregation number, if the cross-section of the molecule is assumed. The molecular pitch, L/m', of DDAC is found to be 0.45, 0.37 and 0.26 Å, with increasing m' value, indicating considerable flexibility of the rod. Assuming the molecular pitch of the rod to be 0.40 Å and the molecular cross section to have a diameter 6.0 Å, the rod-like micelle has a cross-section composed of 15 molecules or ions. From the published data on dodecylammonium chloride and dimethyldodecyl N-hydroxyammonium bromide we have similar values for the molecular pitch of their rod-like micelles. On the other hand, the molecular pitch for the rod-like micelle of SDS, 0.60 Å, is much longer than those for these cationics, irrespective of similar molecular size and cross-section.

References

[1] K.J. Mysels and L.H. Princen, J. Phys. Chem. 63 (1959) 1696.
[2] H.F. Huisman, Proc. Koninkl. Ned. Akad. Wetenschap. B57 (1964) 388.
[3] M.F. Emerson and A. Holtzer, J. Phys. Chem. 71 (1967) 1898.
[4] P. Debye, J. Phys. Colloid. Chem. 53 (1949) 1.
[5] L.M. Kushner, W.D. Hubbard and R.A. Parker, J. Res. Nat. Bur. Stand. 59 (1957) 113.
[6] P. Debye and E.W. Anacker, J. Phys. Colloid. Chem. 55 (1951) 644.
[7] K.W. Herrmann, J. Phys. Chem. 68 (1964) 1540.
[8] S. Ozeki and S. Ikeda, to be published.
[9] J.K. Weil, F.S. Smith, A.J. Stirfon and R.G. Bistline, J. Am. Oil Chem. Soc. 40 (1963) 538.
[10] S. Ikeda, S. Ozeki and M. Tsunoda, J. Colloid Interface Sci. 73 (1980) 27.
[11] S. Hayashi and S. Ikeda, J. Phys. Chem. 84 (1980) 744.
[12] S. Ozeki, M. Tsunoda and S. Ikeda, J. Colloid Interface Sci. 64 (1978) 28.
[13] W.H. Stockmayer, J. Chem. Phys. 18 (1950) 58.
[14] D. Stigter, J. Phys. Chem. 64 (1960) 842.
[15] A. Vrij and J.Th.G. Overbeek, J. Colloid Sci. 17 (1962) 570.
[16] H. Inoue and S.N. Timasheff, J. Am. Chem. Soc. 90 (1968) 1890.
[17] W. Prins and J.J. Hermans, Proc. Koninkl. Ned. Akad. Wetenschap. B59 (1956) 162.
[18] L.H. Princen and K.J. Mysels, J. Colloid Sci. 12 (1967) 594.
[19] N.A. Mazer, G.B. Benedek and M.C. Carey, J. Phys. Chem. 80 (1976) 1075.
[20] C.Y. Young, P.J. Missel, N.A. Mazer, G.B. Benedek and M.C. Carey, J. Phys. Chem. 82 (1978) 1375.
[21] I. Cohen and T. Vassiliades, J. Phys. Chem. 65 (1961) 1774.
[22] D. Attwood, J. Phys. Chem. 72 (1968) 339.