Light Scattering Investigation for Growth and Interaction of Nonionic Micelles in Aqueous Solutions

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Static and dynamic light scattering has been measured for aqueous solutions of heptaoxyethylene alkyl ethers (C_nE_7) and analyzed by one concentration method. While the micelle aggregation number, the radius of the sphere, and the second virial coefficient are independent of micelle concentration for $C_{10}E_7$ in water and in 1 *M* NaCl and $C_{12}E_7$ in water, these change with micelle concentration for $C_{10}E_7$ in 2 *M* NaCl, $C_{12}E_7$ in 1 *M* NaCl, and $C_{14}E_7$ in water. The third virial coefficient, the friction coefficient, and the hydrodynamic virial coefficient are independent of micelle concentration for all systems. With variation of micelle aggregation numbers from 60 to 220, the second virial coefficient decreases from 2.4 to 0.7 $\times 10^{-4}$ mole cm^3 g^{-2}, and the third virial coefficient, the friction coefficient, and the hydrodynamic virial coefficient are (0.4–1.1) $\times 10^{-3}$ mole cm^6 g^{-3}, (11–19) cm^3 g^{-1}, and (0.7–1.3) cm^3 g^{-1}, respectively.

INTRODUCTION

With the development of light scattering instruments equipped with laser light sources, micelle formation and the size and shape of micelles have been investigated by many workers. Moreover, by concurrent static and dynamic measurements, plausible information concerning intermicellar interaction was obtained.

Corti and Degiorgio (1–5) measured laser light scattering for aqueous salt solutions of sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (C_{16}TAB). They found that molecules of ionic surfactants form small ellipsoidal micelles in a solution of low salt concentration (1, 2), whereas large aggregates form in 0.6 *M* NaCl solutions of SDS (3). In 0.1 *M* NaCl, SDS micelles did not change their size with micelle concentration (2), but in 0.6 *M* NaCl micelles exhibited dependence of size on micelle concentration (2, 3). Corti and Degiorgio also evaluated intermicellar interaction coefficients (1, 4, 5). For aqueous NaCl solutions of SDS, positive interaction coefficients decreased with an increase in NaCl concentration and changed to negative at larger values of NaCl concentration (4, 5). The observed coefficients were compared with the theoretical values.

Candau *et al.* (6–9) investigated the properties of small micelles by measurement of light scattering. They obtained interaction coefficients for small micelles of dodecyltrimethylammonium bromide (C_{12}TAB) and tetradecyltrimethylammonium bromide (C_{14}TAB), under the assumption that variation of diffusion coefficient and scattering intensity with micelle concentration reflects intermicellar interaction.

Cheng and Gulari (10) performed measurements of integrated intensity and diffusion coefficient for aqueous solutions of sodium dodecyl benzene sulfonate (SDBS) and deduced that the size and shape of SDBS micelles and the intermicellar interaction are a function of surfactant and NaCl concentrations and temperature. The length of spherocylindrical micelles increased with NaCl concentration and decreased with temperature. The intermicellar interaction coefficients decreased with an increase in NaCl concentration from 0.05

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to 0.3 *M*, consistent with the theoretical estimation.

Evans *et al.* (11) investigated the aggregation of surfactant in ethylammonium nitrate by static and dynamic light scattering and obtained the size of spherical micelles and the second virial coefficient.

Drifford *et al.* (12) carried out light scattering experiments for spherical micelles of ionic surfactants. Dependence of the scattered intensity and mutual diffusion coefficient on surfactant concentration was analyzed on the basis of a theoretical approach, and the role of counterions was discussed.

Chatenay *et al.* (13) performed light scattering and self-diffusion experiments for micellar solutions of $C_{12}TAB$ with three different salinities and characterized the interactions between micelles. They concluded that, if 0.5 *M* KBr was added to the micellar solution, micelles behaved like hard spheres in consequence of the balance of the electrostatic repulsion by the van der Waals attraction.

Investigators who were concerned with micelle properties in solutions obtained the micelle size at infinite dilution and the intermicellar interaction at finite micelle concentrations, or, otherwise, they evaluated the micelle size at finite concentrations without considering the intermicellar interaction. Such an analysis at finite concentrations is sometimes perilous, since micelle growth and intermicellar interaction often occur simultaneously.

In this paper, light scattering measurements for aqueous NaCl solutions of C_nE_7 (n = 10, 12, 14) are reported. Micelle size and intermicellar interaction at each micelle concentration will be evaluated at the same time, by combining the results of the static and dynamic experiments. The dependence of micelle size and interaction coefficients on micelle concentration is discussed, and the intermicellar interaction of nonionic micelles is compared with that of ionic micelles.

EXPERIMENTAL

Samples of $C_{10}E_7$, $C_{12}E_7$, and $C_{14}E_7$ were purchased from Nikko Chemicals Co., Ltd. (Tokyo), and used without purification. NaCl was ignited for 1 h and water was redistilled from alkaline $KMnO_4$.

Measurement of specific refractive index increments was carried out at 25°C on an Otsuka Denshi Differential Refractometer RM-102 by using a light of 488-nm wavelength. The apparatus was calibrated by aqueous solutions of sucrose.

Static and dynamic light scattering was measured on an Otsuka Denshi Dynamic Light Scattering Spectrophotometer DLS-700. A light of 488-nm wavelength from an argon ion laser was used, and the scattering angle was changed from 20 to 150°. The cell housing was filled with di-*n*-butyl phthalate and kept at 25°C. Solvents and solutions were filtered five times through a Millipore membrane filter. Details of the static light scattering measurement have been described elsewhere (14).

Measurement of dynamic light scattering was performed in the homodyne mode: the second-order photoelectron-count autocorrelation function of the scattered electric field was measured by a correlator, and the first-order normalized correlation function was computer calculated. The normalized correlation function was analyzed by the cumulant method to obtain the average decay rate of the field correlation function, $\bar{\Gamma}$. The effective diffusion coefficient, D, was evaluated by $D = \bar{\Gamma}/\mu^2$, where μ is a magnitude of the scattering vector.

Significant angular dependence of light scattering was not observed for solutions examined here; computer-extrapolated values of the Debye plot to zero scattering angle and numerical-averaged values of the effective diffusion coefficient at each scattering angle were obtained for static and dynamic light scattering, respectively.

RESULTS AND ANALYSIS

Figure 1 shows static and dynamic light scattering for aqueous solutions of C_nE_7 as a function of micelle concentration. As the micelle concentration increases, the Debye plots

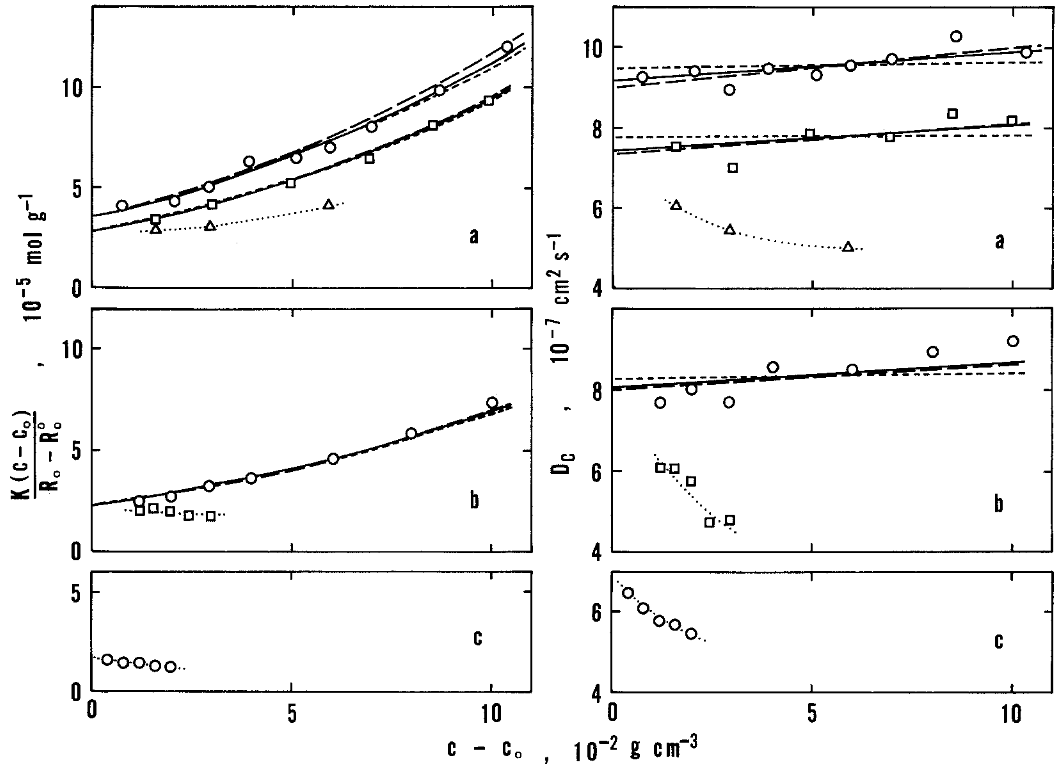

FIG. 1. Debye plots and diffusion coefficients at zero scattering angle for aqueous NaCl solutions of C_nE_7 at 25°C. Left, Debye plot; right, diffusion coefficient. (a) $C_{10}E_7$; (b) $C_{12}E_7$; (c) $C_{14}E_7$. NaCl concentration (M): ○, 0; □, 1; △, 2. ——, with $k_{f0} = 6.55$; – – –, with $k_{f0} = 6.44$; ---, with $k_{f0} = 6.88$; · · ·, based on observed data.

and the diffusion coefficients for $C_{10}E_7$ and $C_{12}E_7$ in water increase with a positive slope. The slope diminishes with an increase in NaCl concentration and becomes negative for the Debye plot of $C_{12}E_7$ in 1 M NaCl and the diffusion coefficient of $C_{10}E_7$ in 2 M NaCl and $C_{12}E_7$ in 1 M NaCl. The Debye plot and the diffusion coefficient for $C_{14}E_7$ in water decrease gradually with increasing micelle concentration. These dependences of light scattering on micelle concentration, NaCl concentration, and alkyl chain length may be attributed to intermicellar interaction and micellar growth.

The static light scattering for dilute micellar solutions is described by

$$K(c-c_0)/(R_0-R_0^\circ) = 1/M_{\text{app}} = 1/M + 2B_2(c-c_0) + 3B_3(c-c_0)^2, \quad [1]$$

where K is the optical constant; R_0 and R_0° are the reduced scattering intensities at zero scattering angle for solutions of the surfactant concentration, c, and the critical micelle concentration, c_0, respectively; and M is the molecular weight of a micelle. The subscript app means that the values are apparent. B_2 and B_3 are the second and third virial coefficients, respectively, for static light scattering.

Suppose that a hard-sphere model can be applied to spherical micelles; then,

$$B_2 = 4N_A[(4/3)\pi R_s^3]/M^2 \quad [2]$$

and

$$B_3 = (5/8)B_2^2 M, \quad [3]$$

where N_A is Avogadro's number and R_s is the radius of a sphere (15).

The dynamic light scattering for dilute micellar solutions can be written as

$$D_c = k_B T / 6\pi\eta_0 R_{s,\mathrm{app}}$$

$$= D_0[1 + k_D(c - c_0)] \quad [4]$$

and

$$D_0 = k_B T / 6\pi\eta_0 R_s, \quad [5]$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity of the solvent. D_c and D_0 are the diffusion coefficient at zero scattering angle and the translational diffusion coefficient, respectively.

The virial coefficient for dynamic light scattering, k_D, can be given by (15)

$$k_D = 2B_2M - k_f - \bar{v}. \quad [6]$$

The partial specific volume, $\bar{v}$, and the frictional coefficient, k_f, for a spherical micelle are described by

$$\bar{v} = N_A[(4/3)\pi R_s^3]/M \quad [7]$$

and

$$k_f = k_{f0}N_A[(4/3)\pi R_s^3]/M, \quad [8]$$

respectively. Burgers (16), Batchelor (17), and Felderhof (18) predicted the values of k_{f0} = 6.88, 6.55, and 6.44, respectively, for a hard sphere.

It is assumed in Eqs. [2] to [8] that the hydrodynamic radius is equivalent to the radius of a hard-sphere micelle. This is reasonable if hydrated water is included in the domain of ethylene oxide in a micelle.

When Eqs. [1] to [8] are combined and the observed numerical values from light scattering are used, the optimum values of M and R_s can be calculated at each micelle concentration and the numerical values of B_2, B_3, k_f, and K_D are evaluated at the corresponding micelle concentrations.

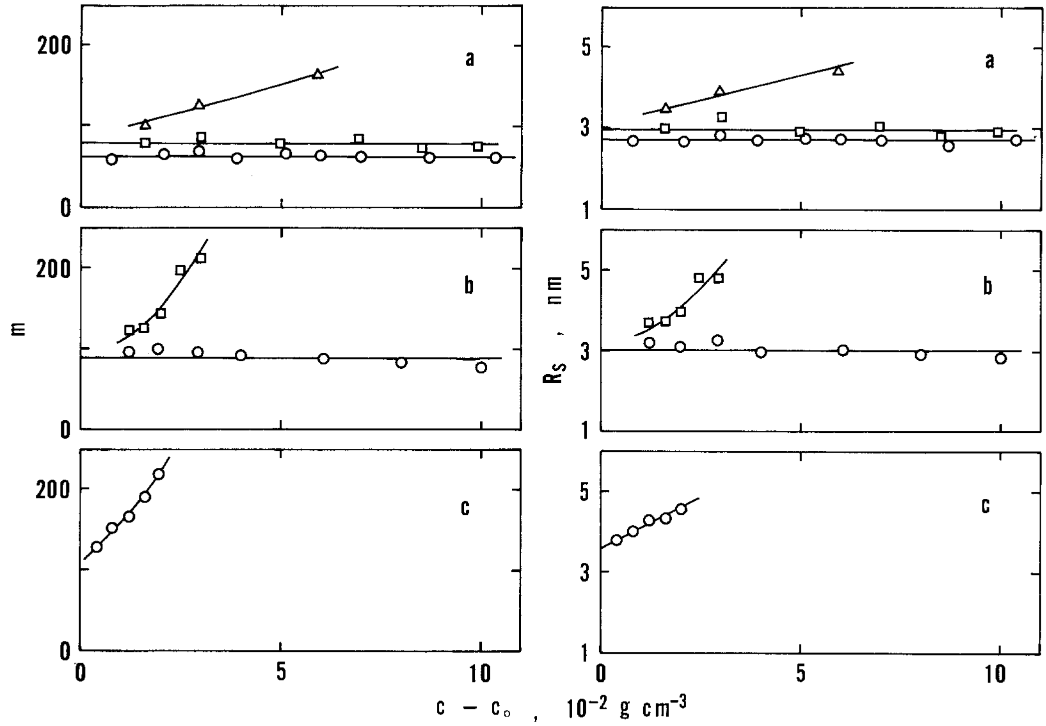

FIG. 2. Micelle aggregation number and radius of sphere as a function of micelle concentration (with a parameter of k_{f0} = 6.55). Left, micelle aggregation number; right, radius of sphere. The symbols have the same meanings as in Fig. 1.

For $k_{f0} = 6.55$, the values of the micelle aggregation number, $m = M/M_1$, that were obtained are plotted against micelle concentration in Fig. 2 together with the calculated values of R_s, where M_1 is a molecular weight of monomeric surfactant. Figures 3 and 4 show the micelle concentration dependence of B_2, B_3, k_f, and k_D. The aggregation number, the radius of sphere, and the second virial coefficient for $C_{10}E_7$ in water and in 1 *M* NaCl and $C_{12}E_7$ in water are independent of the micelle concentration, while those for $C_{10}E_7$ in 2 *M* NaCl, $C_{12}E_7$ in 1 *M* NaCl, and $C_{14}E_7$ in water change with an increase in micelle concentration. On the other hand, meaningful dependence on micelle concentration is not detectable for the second virial coefficient, the friction coefficient, and the hydrodynamic virial coefficient.

The numerical values obtained at each micelle concentration are summarized in Table I with values of the specific refractive index increment, $(\partial\tilde{A}n/\partial c)_{C_s}$, at constant NaCl concentration, C_s, where $\tilde{n}$ is the refractive index of a solution. The values for $C_{10}E_7$ in water and in 1 *M* NaCl and $C_{12}E_7$ in water are averaged. Spherical micelles in aqueous salt solutions are not strictly spherical but somewhat spheroidal. When the micelles are assumed to be prolate ellipsoids, $(4/3)\pi R_s^3$ in Eqs. [2] to [8] should be replaced with $(4/3)\pi a^2 b$, where *a* and *b* are the lengths of the long and short axes, respectively, of a prolate ellipsoid. If the value of *a* is taken as the radius of a sphere formed by $C_{10}E_7$ and $C_{12}E_7$ in water and at zero micelle concentration by $C_{14}E_7$ in water, the numerical values of *b* can be calculated, as included in Table I.

With an increase in NaCl concentration, micelle concentration, and alkyl chain length, the aggregation number increases from 60 to 220, the long axis of an ellipsoid varies from

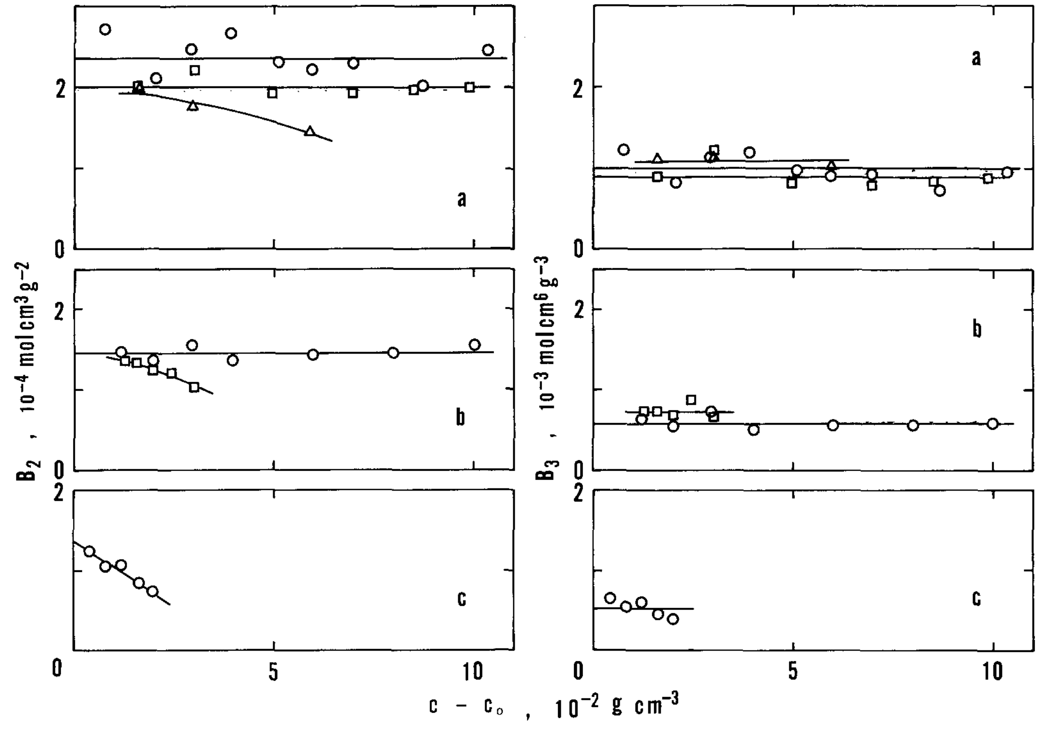

FIG. 3. Second and third virial coefficients as a function of micelle concentration (with a parameter of $k_{f0} = 6.55$). Left, second virial coefficient; right, third virial coefficient. The symbols have the same meanings as in Fig. 1.

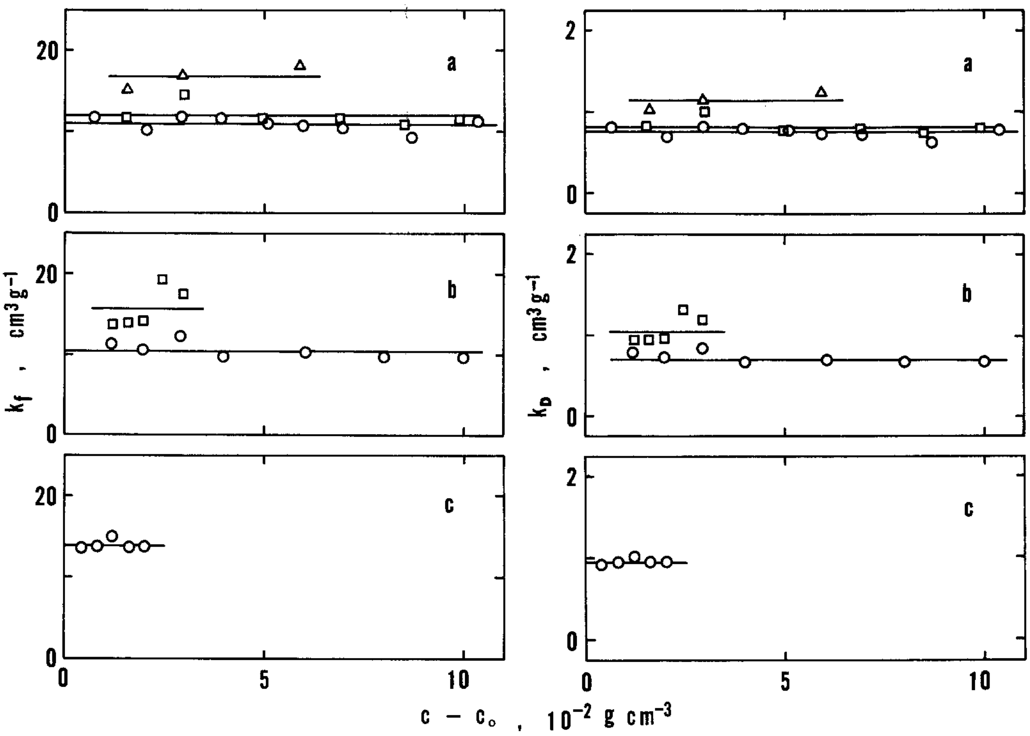

FIG. 4. Friction coefficient and hydrodynamic virial coefficient as a function of micelle concentration (with a parameter of k_{f0} = 6.55). Left, friction coefficient; right, hydrodynamic virial coefficient. The symbols have the same meanings as in Fig. 1.

2.7 to 12 nm, and the second virial coefficient decreases from 2.4 to 0.7 × 10^{-4} mole cm^3 g^{-2}. The dependence of the third virial coefficient on NaCl and micelle concentrations is rather small and the values of (0.9–1.1), (0.6–0.9), and (0.4–0.6) × 10^{-3} mole cm^6 g^{-3} are obtained for $C_{10}E_7$, $C_{12}E_7$, and $C_{14}E_7$, respectively. The values of the friction coefficient are (11–19) cm^3 g^{-1} and those of the hydrodynamic virial coefficient range between 0.7 and 1.3 cm^3 g^{-1}, independent of NaCl and surfactant concentrations and alkyl chain length.

The values of k_{f0} = 6.44 and 6.88 are used and the same procedure can be applied. The difference with numerical values calculated from k_{f0} = 6.55 is rather small, except for k_D values, as seen in Tables II and III. The values of k_D are (0.8–1.7) cm^3 g^{-1} for k_{f0} = 6.44 and (0.2–0.3) cm^3 g^{-1} for k_{f0} = 6.88.

The lines calculated from the numerical values given in Tables I to III are drawn in Fig. 1 for $C_{10}E_7$ in water and in 1 *M* NaCl and $C_{12}E_7$ in water. Although the curve fitting with observed data is good for three kinds of k_{f0}, it is recognized that the value of k_{f0} = 6.55 is most suitable.

DISCUSSION

When the alkyl chain length is less than 14 and little or no salt is added, the size of the micelles formed in aqueous solutions of C_nE_7 remains constant, even if micelle concentration increases. As alkyl chain length and salt concentration increase, micelles grow with micelle concentration. With an increase in micelle size, the second virial coefficient decreases, whereas the third virial coefficient, the friction coefficient, and the hydrodynamic virial coefficient do not indicate any obvious change.

TABLE I

Characteristics of Spherical Micelles of Heptaoxyethylene Alkyl Ethers in Aqueous NaCl Solutions at 25°C (with a Parameter of k_f = 6.55)

	C_s (M)	$(\partial\tilde{n}/\partial c)_{C_s}$ (cm^3 g^{-1})	$c - c_0$ (10^{-2} g cm^{-3})	M (10^4 g mole^{-1})	m	R_s (nm)	b (nm)	B_2 (10^{-4} mole cm^3 g^{-2})	B_3 (10^{-3} mole cm^6 g^{-3})	k_f (cm^3 g^{-1})	k_D (cm^3 g^{-1})
$C_{10}E_7$	0	0.131	0–10	2.86	61	2.67	2.67	2.36	1.00	11.0	0.76
	1	0.121	0–10	3.67	79	2.99	3.75	2.00	0.92	12.0	0.83
	2	0.112	1.62	4.62	99	3.47	5.87	1.98	1.13	15.0	1.03
			2.95	5.86	126	3.92	8.47	1.77	1.14	17.0	1.17
			5.92	7.62	163	4.39	11.9	1.47	1.03	18.4	1.26
$C_{12}E_7$	0	0.133	0–10	4.41	89	3.03	3.03	1.45	0.58	10.5	0.72
	1	0.130	1.23	6.10	123	3.70	5.52	1.38	0.72	13.7	0.94
			1.58	6.21	126	3.73	5.65	1.36	0.72	13.8	0.95
			1.98	7.08	143	3.95	6.71	1.24	0.68	14.4	0.99
			2.45	9.74	197	4.83	12.3	1.20	0.88	19.2	1.32
			2.99	10.4	210	4.78	11.9	1.03	0.68	17.4	1.20
$C_{14}E_7$	0	0.136	0[a]	5.60	107	3.58	3.58				
			0.40	6.67	128	3.80	4.28	1.25	0.50	13.6	0.94
			0.80	7.93	152	4.04	5.14	1.06	0.56	13.8	0.95
			1.20	8.68	166	4.29	6.16	1.06	0.61	15.1	1.04
			1.61	9.94	190	4.35	6.42	0.85	0.44	13.8	0.95
			2.00	11.4	218	4.57	7.45	0.74	0.39	13.9	0.95

[a] Extrapolated values.

TABLE II

Characteristics of Spherical Micelles of Heptaoxyethylene Alkyl Ethers in Aqueous NaCl Solutions at 25°C (with a Parameter of k_f = 6.44)

	C_s (M)	$c - c_0$ (10^{-2} g cm^{-3})	M (10^4 g mole^{-1})	m	R_s (nm)	b (nm)	B_2 (10^{-4} mole cm^3 g^{-2})	B_3 (10^{-3} mole cm^6 g^{-3})	k_f (cm^3 g^{-1})	k_D (cm^3 g^{-1})
$C_{10}E_7$	0	0–10	2.88	62	2.72	2.72	2.47	1.11	11.4	1.09
	1	0–10	3.67	79	3.02	3.72	2.01	0.95	12.1	1.05
	2	1.62	4.63	99	3.48	5.70	2.00	1.15	14.9	1.29
		2.95	5.92	127	3.95	8.33	1.78	1.17	17.0	1.47
		5.92	7.84	168	4.47	12.1	1.47	1.06	18.6	1.62
$C_{12}E_7$	0	0–10	4.46	90	3.06	3.06	1.46	0.59	10.5	0.79
	1	1.23	6.11	124	3.71	5.45	1.38	0.73	13.6	1.18
		1.58	6.22	126	3.74	5.59	1.37	0.73	13.7	1.19
		1.98	7.11	144	3.97	6.68	1.25	0.69	14.3	1.24
		2.45	9.82	199	4.87	12.3	1.21	0.91	19.2	1.67
		2.99	10.5	212	4.82	12.0	1.03	0.70	17.4	1.52
$C_{14}E_7$	0	0[a]	5.60	107	3.58	3.58				
		0.40	6.67	128	3.80	4.28	1.25	0.65	13.4	1.17
		0.80	7.94	152	4.05	5.18	1.06	0.56	13.6	1.18
		1.20	8.69	166	4.30	6.20	1.07	0.62	14.9	1.30
		1.61	9.96	191	4.37	6.51	0.85	0.45	13.7	1.19
		2.00	11.5	220	4.59	7.55	0.75	0.40	13.8	1.20

[a] Extrapolated values.

TABLE III

Characteristics of Spherical Micelles of Heptaoxyethylene Alkyl Ethers in Aqueous NaCl Solutions at 25°C (with a Parameter of $k_f = 6.88$)

	C_s (M)	$c - c_0$ (10^{-2} g cm^{-3})	M (10^4 g mole^{-1})	m	R_s (nm)	b (nm)	B_2 (10^{-4} mole cm^3 g^{-2})	B_3 (10^{-3} mole cm^6 g^{-3})	k_f (cm^3 g^{-1})	k_D (cm^3 g^{-1})
$C_{10}E_7$	0	0–10	2.77	59	2.59	2.59	2.31	0.93	11.0	0.19
	1	0–10	3.52	75	2.89	3.60	1.97	0.86	11.9	0.21
	2	1.62	4.58	98	3.43	6.02	1.94	1.08	15.3	0.27
		2.95	5.71	122	3.82	8.31	1.73	1.06	17.0	0.30
		5.92	7.05	151	4.16	10.7	1.46	0.94	17.7	0.31
$C_{12}E_7$	0	0–10	4.30	87	2.96	2.96	1.42	0.55	10.5	0.18
	1	1.23	6.08	123	3.67	5.64	1.35	0.69	14.1	0.25
		1.58	6.17	125	3.69	5.73	1.33	0.68	14.1	0.25
		1.98	7.01	142	3.89	6.72	1.21	0.64	14.6	0.25
		2.45	9.50	192	4.72	12.0	1.18	0.82	19.3	0.34
		2.99	10.1	204	4.66	11.6	1.00	0.63	17.4	0.30
$C_{14}E_7$	0	0[a]	5.60	107	3.58	3.58				
		0.40	6.66	127	3.79	4.25	1.24	0.64	14.2	0.25
		0.80	7.92	151	4.02	5.07	1.05	0.54	14.2	0.25
		1.20	8.64	165	4.25	5.99	1.04	0.59	15.5	0.27
		1.61	9.88	189	4.31	6.24	0.83	0.42	14.1	0.25
		2.00	11.3	216	4.51	7.16	0.73	0.37	14.1	0.25

[a] Extrapolated values.

Several workers have obtained the numerical values of interaction coefficients for spherical micelles of ionic surfactants. The coefficients for the dependence of reciprocal scattering intensity and diffusion coefficient on micelle concentration, $k_I \equiv 2B_2M$ and k_D, respectively, were evaluated for spherical micelles of SDS and C_{16}TAB in aqueous solutions (1, 4, 5). The k_I and k_D values of 40.2 and 16.1 cm^3 g^{-1}, respectively, were obtained for SDS micelles of $M = 2.7 \times 10^4$ g mole^{-1} in 0.1 M NaCl and at 25°C, and these values decreased with an increase in salt concentration.

The dependence of k_I and k_D on salt concentration was investigated for aqueous NaCl solutions of SDBS (10) and for aqueous KBr solutions of C_{14}TAB (12), and a remarkable decrease of these coefficients was observed. The large numerical values of the interaction coefficients for ionic micelles are attributed to the strong electrostatic Coulomb repulsion interaction, and such an interaction is depressed by the electrostatic shielding effect on the presence of excess salt.

It has been reported (8) that the values of interaction coefficients, k_I and k_D, increase in order of C_{14}TAB < C_{12}TAB < SDS, that is, in the order of the degree of ionization of the micelles. This indicates that the electrostatic repulsion is a main factor in interaction between ionic micelles.

The second virial coefficient for micellar solutions of C_{12}TAB decreased to zero on addition of 0.5 M KBr (13), indicating that the electrostatic repulsion is balanced to the van der Waals attraction.

On the other hand, it was demonstrated (11) that the second virial coefficient calculated for a hard-sphere model was consistent with the observed values for micelles of tetradecylpyridinium and hexadecylpyridinium bromides in ethylammonium nitrate, because of high shielding of electrostatic interaction by ethylammonium nitrate.

Different with ionic micelles, the second virial coefficient for nonionic micelles such as C_nE_7 includes only the contribution from the steric repulsion interaction, but not the contribution from the electrostatic repulsion interaction. As a result, the interaction coefficients may be small and less dependent on the salt concentration. Actually, the interaction coefficients for nonionic C_nE_7 micelles in aqueous solutions of low salt concentrations were smaller than those for ionic micelles with similar molecular weights.

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