

# Intermicellar Correlation in Light Scattering from Dilute Micellar Solutions of Dimethyloleylamine Oxide

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Angular dependence of light scattering from micellar solutions of dimethyloleylamine oxide has been measured in water and  $10^{-4}$  M NaCl at different micelle concentrations from the critical micelle concentration to  $0.15 \times 10^{-2}$  g cm<sup>-3</sup>. The angular dissymmetry is lower than unity and decreases with increasing micelle concentration. The observed angular dependence indicates stronger effect of external interference at higher micelle concentrations. The Zernike-Prins equation has been applied to derive the structure factor of micelles by separating the effect of external interference from that of internal interference and by choosing appropriate and consistent values of molecular weight and radius of gyration of micelles. The micelle size becomes larger by the addition of NaCl, and by an increase in micelle concentration. The micelle is rod-like but sufficiently flexible that it may be regarded as spherically symmetric. The radial distribution is obtained for the center of mass of a micelle, and, furthermore, the pair potential is derived by means of the Percus-Yevick equation or the Hypernetted Chain equation for the theory of simple liquids. The micelle molecular weight ranges from 370,000 to 1,030,000, depending on the condition, and, correspondingly, the radius of gyration changes from 213 to 300 Å. The intermicellar interaction distance is located around 1300–1600 Å.

## INTRODUCTION

The importance of the effect of external interference on scattering experiments has been observed and discussed for aqueous solutions with zero or low salt concentrations of globular proteins (1–4), polyelectrolytes (5, 6), and surfactant micelles (7), and even for nonaqueous solutions of synthetic polymer (8), since Oster and Riley (1–3) first gave it a theoretical interpretation based on the Zernike-Prins equation (9). Intra- and interparticle structural effects were also studied in colloidal dispersions of latex particles by means of optical scattering experiments (10–17). The structure factors derived from such experiments for latex dispersions were further analyzed by the method developed for simple fluids (13–17), and the forces of interaction between these colloidal particles were discussed in detail (10–12).

In this paper we report the results on light scattering from micellar solutions of dimethyloleylamine oxide,  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8\text{N}(\text{CH}_3)_2\text{O}$ , in water and  $10^{-4}$  M NaCl. The intensity of light scattered from the micellar solutions increases with an increase in scattering angle, in contrast to the usual behavior. This is caused by the effect of external interference stronger than that of internal interference (6, 8). Hence, in order to obtain any micellar properties from such light scattering data, we have to rely on a complicated analysis, according to the equation derived by Zernike and Prins (9), which takes into account the interference between scattering centers in different particles. Then, besides the micellar parameters such as molecular weight and radius of gyration, we can obtain the structure factor which arises from the intermicellar structural effect. The radial distribution function between centers of mass of micelles can be given by the inverse Fourier transform of the structure factor. Moreover, the intermicellar pair potential may be evaluated on the basis of theories of simple liquids (18).

## EXPERIMENTAL

**Materials.** An aqueous solution containing  $(9.00 \pm 0.01)$  weight % dimethyloleylamine oxide was kindly gifted by Dr. F. Hoshino of the Kao Soap Company, Inc., Wakayama. The dimethyloleylamine oxide was prepared from dimethyloleylamine by the reaction with  $H_2O_2$ . The concentration of the stock solution was determined by evaporating up an aliquot of the solutions and measuring its dry weight. Water was redistilled from alkaline  $KMnO_4$ . Special grade NaCl was ignited for 2 hr and stored in a desiccator until use. Solutions were prepared by diluting the stock solution with an adequate solvent, and kept overnight at room temperature  $(25 \pm 2^\circ C)$ .

**Methods.** The measurement of light scattering was carried out by a Shimadzu Light Scattering Photometer PG-21 with the unpolarized light of a mercury lamp at 436 nm. The intensities of light scattered in the directions or at the scattering angles,  $\theta$ , from  $30$  to  $150^\circ$  were measured in a cylindrical cell, which was put in a cell housing circulating water and kept at  $25^\circ C$ . The reduced intensity of scattered light at the scattering angle,  $\theta$ , was calculated by

$$R_\theta = \phi_{90} \frac{I_\theta}{I_0} \frac{\sin \theta}{1 + \cos^2 \theta} \quad [1]$$

where  $I_0$  and  $I_\theta$  are the intensities of incident and scattered light, respectively, measured by the deflection of galvanometer and calibrated for the attenuation by neutral filters. The calibration constant,  $\phi_{90}$ , for solutions was determined by

$$\phi_{90} = \frac{\tilde{n}_0^2}{\tilde{n}_b^2} \phi_b \quad [2]$$

by using purified benzene, for which  $\phi_b$  was measured from the known value of  $R_{90}$ ,  $48.5 \times 10^{-6} \text{ cm}^{-1}$ . Here  $\tilde{n}_0$  and  $\tilde{n}_b$  are the refractive indices of solvent and benzene, respectively.

The solvents and solutions were directly filtered into the cylindrical cell under pressure through a Millipore filter GSWP, having a pore size of  $0.22 \mu\text{m}$ . The Millipore filter had to be pretreated by redistilled water thoroughly

to wash out soluble contaminants. Otherwise, some ultraviolet-absorbing contaminants were eluted from the filter by the surfactant solution. The filtration was repeated at least five times, when the solvent or the solution was made dust-free and had a constant optical dissymmetry. The concentration of solutions after filtration was determined from the optical density at the maximum wavelength of an absorption band around  $190\text{--}220 \text{ nm}$ , by referring to the calibration curve of optical density.

The specific refractive index increment at  $25^\circ C$  was measured on a Shimadzu Differential Refractometer DR-3 at the wavelength of  $436 \text{ nm}$  of a mercury lamp. The calibration of the apparatus was performed by aqueous solutions of NaCl. The specific refractive index increment was constant over the range of surfactant concentrations up to  $0.3 \times 10^{-2} \text{ g cm}^{-3}$ . Its value was  $0.163 \text{ cm}^3 \text{ g}^{-1}$  in water and  $10^{-4} M$  NaCl solution.

## RESULTS

The dependence on surfactant concentration of reduced scattering intensity in the  $90^\circ$  direction,  $R_{90}$ , is shown in Fig. 1 for solutions of dimethyloleylamine oxide in water and  $10^{-4} M$

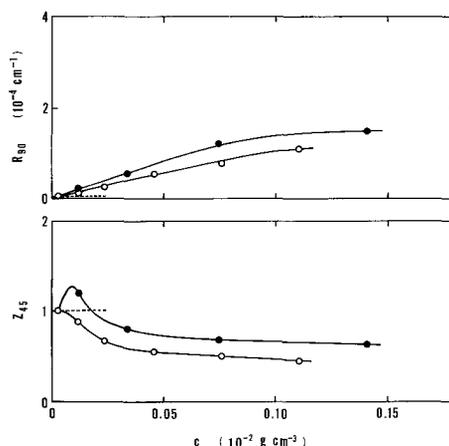


FIG. 1. The reduced intensity in the  $90^\circ$  direction,  $R_{90}$  (upper), and the angular dissymmetry at  $45^\circ$ ,  $z_{45}$  (lower), of scattered light as a function of surfactant concentration. (O) In water; (●), in  $10^{-4} M$  NaCl.

$M$  NaCl. Above the critical micelle concentration of  $0.004 \times 10^{-2} \text{ g cm}^{-3}$ , the reduced intensity gradually increases with increasing micelle concentration. The increase in intensity is higher in  $10^{-4} M$  NaCl than in water. As illustrated in Fig. 1, the angular dissymmetry,  $z_{45}$ , of light scattering is generally lower than unity as the surfactant concentration is higher than the critical micelle concentration; its value is lower in water than in  $10^{-4} M$  NaCl.

Unless the light scattering is subject to the external interference, its intensity in the scattering angle  $\theta$  from a dilute micellar solution irradiated by unpolarized light can be represented by the Debye equation

$$\frac{K(c - c_0)}{R_\theta - R_\theta^0} = \frac{1}{M_w P(\theta)} + 2B(c - c_0) \quad [3]$$

with the optical constant

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

where  $R_\theta$  and  $R_\theta^0$  are the reduced intensities of solutions at a surfactant concentration,  $c$  ( $\text{g cm}^{-3}$ ) and at the critical micelle concentration,  $c_0$ , respectively,  $M_w$  the weight-average molecular weight of micelles,  $B$  the second virial coefficient,  $(\partial \tilde{n} / \partial c)_c$ , the specific refractive index increment of solutions at a constant salt concentration,  $C_s(M)$ ,  $\lambda$  the wavelength of light *in vacuo*, and  $N_A$  is the Avogadro number. The particle scattering factor,  $P(\theta)$  is given by

$$\frac{1}{P(\theta)} = 1 + \frac{1}{3} \mu^2 (\overline{R_G^2})_s + \dots \quad [5]$$

with

$$\mu = \frac{4\pi \tilde{n}_0}{\lambda} \sin \frac{\theta}{2} \quad [6]$$

where  $(\overline{R_G^2})_s$  is the light-scattering-average-mean-square radius of gyration of micelles (19, 20).

The Zimm plots of light scattering are shown in Fig. 2. The reciprocal angular envelope at a micelle concentration of  $0.008 \times 10^{-2} \text{ g cm}^{-3}$  in  $10^{-4} M$  NaCl increases linearly with  $\sin^2(\theta/2)$  or  $\mu^2$ , as is usual. The

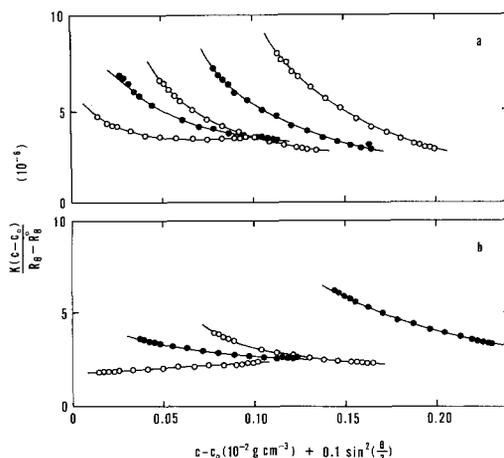


FIG. 2. The Zimm plots of light scattering for micellar solutions. (a) In water; (b) in  $10^{-4} M$  NaCl. Each curve represents the angular dependence for a solution.

value of  $M_w$ , 560,000, is obtained from the extrapolation to zero scattering angle, since the contribution of the term of second virial coefficient is proved to be negligibly small, and the value of  $(\overline{R_G^2})_s^{1/2}$  is evaluated as 255 Å from the initial slope, according to Eqs. [3] and [5].

The reciprocal angular envelope of light scattering for the other solutions either in water or in  $10^{-4} M$  NaCl decreases with increasing scattering angle. The tendency of the negative slope is manifest at high micelle concentrations and decreases in the presence of  $10^{-4} M$  NaCl. As a result of this negative slope, the angular dissymmetry is lower than unity. This can be interpreted as the effect of external interference due to the long-range interaction acting between micelles, which should have a larger effect at lower scattering angles (6, 8).

## ANALYSIS OF THE RESULTS

### Optical Interference Effects

If a solute particle consists of many scattering centers arranged in a spherically symmetric way, the reduced intensity of light scattered from a solution of such solute particles is generally given by (6, 8, 10–17)

$$R_\theta - R_\theta^0 = K(c - c_0) M_w P(\theta) S(\theta) \quad [7]$$

where  $S(\theta) \equiv S(\mu)$  is the structure factor arising

from the nonrandom arrangement of solute particles and is related by

$$S(\theta) = 1 + 4\pi\rho \int_0^\infty h(r) \frac{\sin \mu r}{\mu r} r^2 dr \quad [8]$$

Here

$$\rho = \frac{N_A(c - c_0)}{M_w} \quad [9]$$

is the number concentration of the particle and  $r$  is the distance between centers of mass of particles.

The total correlation function,  $h(r)$ , can be obtained by the inverse Fourier transform of Eq. [8] as

$$h(r) = \frac{1}{2\pi^2\rho} \int_0^\infty [S(\theta) - 1] \frac{\sin \mu r}{\mu r} \mu^2 d\mu \quad [10]$$

The radial distribution function,  $g(r)$ , denotes the probability of finding a center of mass of another particle at the distance,  $r$ , from the center of mass of a specified particle, and is related to the total correlation function,  $h(r)$ , by

$$g(r) = h(r) + 1 \quad [11]$$

There is the requirement that  $g(r) = 0$  at small  $r$  values. Hence, from Eqs. [10] and [11], it follows that

$$\int_0^\infty [S(\theta) - 1] \mu^2 d\mu = -2\pi^2\rho \quad [12]$$

For the micellar solutions in concern, we may suppose that the micelles are far apart from each other, so that the effect of external interference can be separated from that of internal interference. To this approximation, we may apply all the above equations to derive various parameters of the micellar solutions. For the present solutions the values of  $(\overline{R_G^2})_{ls}^{1/2}$  are small and around 255 Å, as will also be shown later. Then the particle scattering factor can be approximated as

$$P(\theta) = 1 - \frac{1}{3} \mu^2 (\overline{R_G^2})_{ls} \quad [13]$$

The numerical values of the molecular weight,  $M_w$ , and the radius of gyration,

$(\overline{R_G^2})_{ls}^{1/2}$ , and the structure factor,  $S(\theta)$ , of micelles can, in principle, be evaluated from Eqs. [7], [12], and [13]. Our procedure for this is as follows. First, the observed values of  $(R_\theta - R_\theta^0)/K(c - c_0)$  are plotted against  $\mu$ , whose value extends from about 1 to 4, and the obtained curve is smoothly extended down to  $\mu \rightarrow 0$  and also up to a value of  $\mu$  slightly higher than 4; the extrapolation toward high  $\mu$  values can be safely truncated at a  $\mu$  value around 4 or slightly higher, where it proves that  $S(\theta) \rightarrow 1$ , because small values of  $S(\theta) - 1$  and high values of  $\mu$  are found to contribute negligibly to the integral of Eq. [10] or to the evaluation of  $h(r)$ . Then the values of  $(R_\theta - R_\theta^0)/K(c - c_0)$  are read over the region of  $\mu$  values at every 0.1 interval.

Next, appropriate values of  $M_w$  and  $(\overline{R_G^2})_{ls}^{1/2}$  are assumed, and the values of  $P(\theta)$  are calculated over all the  $\mu$  values by using Eq. [13]. Dividing the "observed" or extrapolated and interpolated values of  $(R_\theta - R_\theta^0)/K(c - c_0)$  by the assumed  $M_w$  value and the calculated  $P(\theta)$  values, Eq. [7] yields the values of  $S(\theta)$  over the region of  $\mu$  values. To examine the resulting  $S(\theta)$  values for consistency, the integration of the left-hand side of Eq. [12], or actually, its summation by 0.1 intervals, is performed over the region of  $\mu$  from 0 to the assigned value for  $S(\theta) = 1$ , and the resulting value is compared with the right-hand side of Eq. [12], which is derived from the micelle concentration. If the values of both hand-sides do not coincide with each other, the revised values of  $M_w$  and  $(\overline{R_G^2})_{ls}^{1/2}$  are chosen, and the above procedure is repeated again. Until the agreement is reached, the same procedure is pursued.

The optimum values of  $M_w$  and  $(\overline{R_G^2})_{ls}^{1/2}$  obtained in this way for solutions of different micelle concentrations are listed in Table I. The corresponding values of weight-average aggregation number,  $m_w = M_w/311.6$ , are also included in Table I. It is seen that the micelle size increases with increasing micelle concentration and is larger in the presence of  $10^{-4}$  M NaCl than in its absence.

Figure 3 shows the structure factor,  $S(\theta)$ , as

TABLE I

Calculated Micelle Parameters of Dimethyloleylamine Oxide in Water and  $10^{-4} M$  NaCl

	$c - c_0$ ( $10^{-2} \text{ g cm}^{-3}$ )	$M_w$	$m_w$	$(R_g^2)_0^{1/2}$ ( $\text{\AA}$ )
Water	0.008	370,000	1200	213
	0.020	410,000	1300	215
	0.042	580,000	1900	220
	0.072	730,000	2300	235
	0.107	890,000	2900	250
NaCl ( $10^{-4} M$ )	0.008	560,000 <sup>a</sup>	1800	255 <sup>a</sup>
	0.030	670,000	2200	280
	0.071	940,000	3000	295
	0.137	1,030,000	3300	300

<sup>a</sup> The values represent the directly observed ones.

a function of  $\mu$  derived in this way. From this structure factor the total correlation function,  $h(r)$ , can be obtained by means of Eq. [10], and then the radial distribution function,  $g(r)$ , is readily found by Eq. [11]. Figure 4 illustrates the behavior of  $g(r)$  as a function of intermicellar distance,  $r$ . There is a small maximum on the  $g(r)$  curve at an intermicellar distance around 1300–1600  $\text{\AA}$ . It shifts to shorter distances and enhances slightly with an increase

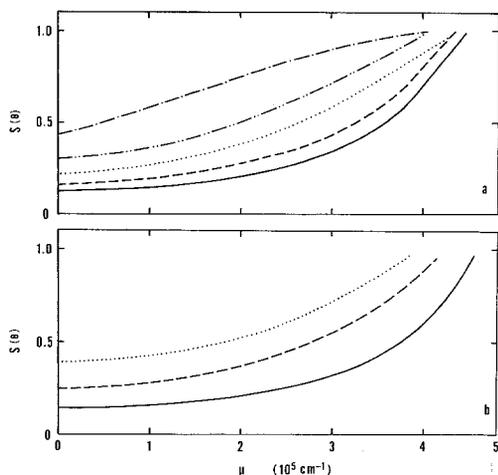


FIG. 3. The structure factor,  $S(\theta)$ , as a function of  $\mu$ .  $c$  ( $10^{-2} \text{ g cm}^{-3}$ ): (a) in water; (---), 0.008; (-·-·-·), 0.020; (···), 0.042; (---), 0.072; (—), 0.107. (b) In  $10^{-4} M$  NaCl; (···), 0.030; (---), 0.071; (—), 0.137.

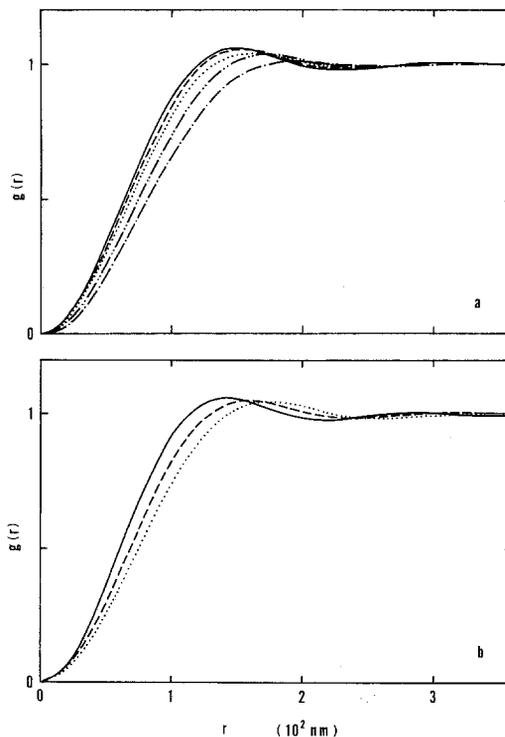


FIG. 4. The radial distribution function,  $g(r)$ , as a function of intermicellar distance,  $r$ .  $c$  ( $10^{-2} \text{ g cm}^{-3}$ ): (a) in water; (---), 0.008; (-·-·-·), 0.020; (···), 0.042; (---), 0.072; (—), 0.107. (b) In  $10^{-4} M$  NaCl; (···), 0.030; (---), 0.071; (—), 0.137.

in micelle concentration. The perturbation of the  $g(r)$  function in water is the same as or slightly larger than that in  $10^{-4} M$  NaCl.

For dilute micellar solutions Eq. [7] reduces to (6, 21)

$$\frac{K(c - c_0)}{R_\theta - R_\theta^0} = \frac{1}{M_w P(\theta)} + 2BQ(\theta)(c - c_0) \quad [14]$$

where

$$2B = -\frac{N_A}{M_w^2} \int_0^\infty [g(r) - 1] 4\pi r^2 dr \quad [15]$$

and

$$Q(\theta) = \frac{1}{P(\theta)} \frac{\int_0^\infty [g(r) - 1] \frac{\sin \mu r}{\mu r} 4\pi r^2 dr}{\int_0^\infty [g(r) - 1] 4\pi r^2 dr} \quad [16]$$

Both  $P(\theta)$  and  $Q(\theta)$  approach unity at small  $\theta$  values, and then Eq. [14] becomes identical with Eq. [3].

Moreover, the combination of Eq. [8] for small  $\theta$  values with Eq. [15] leads to

$$2B = \frac{1 - S(0)}{M_w(c - c_0)} \quad [17]$$

Then the extrapolation to zero scattering angle of the  $S(\theta)$  curve permits us to calculate the value of second virial coefficient. Calculated values of second virial coefficient for micellar solutions in water and  $10^{-4}$  M NaCl are  $2B = (9.2 \text{ and } 6.1) \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$ , respectively, at the highest concentrations of micelles examined.

#### Intermicellar Interaction Potential

The mutual arrangement of the particles in solution represented by  $g(r)$  is generally associated with the interacting forces between the individual particles. The relation of the pair potential between particles with the radial distribution function is given by the theory of simple liquids (18). The analytical expression of such a relation depends on the nature of the approximation used. The Percus-Yevick (PY) equation or the Hypernetted Chain (HNC) equation has been most widely used to calculate the interparticle pair potential,  $v(r)$ .

According to the theory, PY or HNC, the pair potential can be derived by

$$\frac{v_{\text{PY}}(r)}{kT} = \ln \left[ 1 - \frac{c(r)}{1 + h(r)} \right] \quad [18]$$

or

$$\frac{v_{\text{HNC}}(r)}{kT} = h(r) - c(r) - \ln [1 + h(r)] \quad [19]$$

respectively, where  $k$  is the Boltzmann constant and  $T$  is the temperature. The direct correlation function,  $c(r)$ , can be calculated by the Ornstein-Zernike equation together with Eq. [8] (18), and then it is given by

$$c(r) = \frac{1}{2\pi^2\rho} \int_0^\infty \frac{[S(\theta) - 1]}{S(\theta)} \frac{\sin \mu r}{\mu r} \mu^2 d\mu \quad [20]$$

For the micellar solutions in concern, we apply these equations by assuming that all the interactions between micelles arise from their centers of mass, irrespective of their shape or structure. Then the distance between centers of mass of two micelles is supposed to be  $r$ . Figures 5 and 6 show the intermicellar pair potential for micellar solutions in water and  $10^{-4}$  M NaCl, which has been calculated from  $S(\theta)$  values together with Eqs. [10] and [20], based on the PY and HNC equations, [18] and [19], respectively.

The curves obtained from the two equations slightly deviate from each other at short intermicellar distances. Otherwise, all of the curves reveal nearly the same features; at the intermicellar distance around 1800 Å, there is a very shallow minimum of pair potential, which becomes slightly deeper with an increase in micelle concentration. The intermicellar repulsive potential seems to increase with increasing micelle concentration and to be slightly larger in water than in  $10^{-4}$  M NaCl, as can be seen from the marked increase of the potential at intermicellar distances less than 1000 Å.

It might be relevant to comment about the mean force potential,  $U(r)$ , acting on a micelle, which can be directly derived by  $-kT \ln g(r)$ . It is found that, as compared with the pair potential, the mean potential is much shifted toward smaller intermicellar distances, and the minimum is around 1300–1600 Å. It is evident that the mean force potential cannot be substituted by the pair potential.

## DISCUSSION

### Angular Dissymmetry

Light scattering from the micellar solutions of dimethyloleylamine oxide in water and  $10^{-4}$  M NaCl is characterized by the angular dissymmetry less than unity, as was previously observed for bovine serum albumin molecules (4) and also for surfactant micelles (7) in water. This suggests that micelles of dimethyloleylamine oxide exhibit the external interference

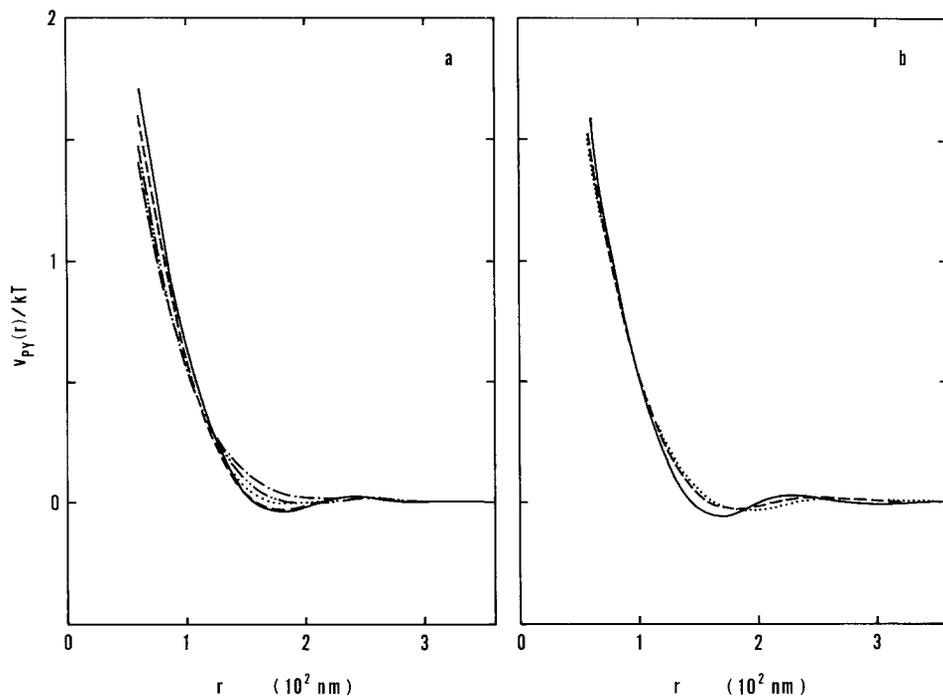


FIG. 5. The intermicellar pair potential calculated by the PY approximation as a function of intermicellar distance,  $r$ . (a) In water; (b) in  $10^{-4} M$  NaCl. Curves shown are for the same concentrations as in Figs. 3 and 4.

effect superior to the internal interference effect.

We can interpret the concentration dependence of the dissymmetry qualitatively, according to the Zernike-Prins equation. Equation [8] can be rewritten as (4, 5, 8)

$$S(\theta) = 1 - 2BM_w\Phi(\mu\bar{R}^2)(c - c_0) \quad [21]$$

where  $\bar{R}^2$  is the mean square radius of a micelle, as was previously defined by other workers. The function,  $\Phi(\mu\bar{R}^2)$ , is a continuously decreasing function. Then, with an increase in micelle concentration, the value of dissymmetry,  $z_{45} = P(45)S(45)/P(135)S(135)$ , should monotonically decrease from that of the intrinsic dissymmetry,  $[z_{45}] = P(45)/P(135)$ , at zero micelle concentration. Specifically, when the internal interference is not so large that the particle scattering factor is close to unity, values of the dissymmetry should be less than unity.

### Micelle Parameters

The effect of external interference yields a negative slope for the angular dependence of reciprocal envelope in light scattering. This was already observed for synthetic polymers in water (6) and in organic solvents (8). According to the equation derived by Zernike and Prins (9), which considers the external interference, we have obtained the numerical values of micelle parameters,  $M_w$  and  $(\bar{R}_G^2)_{ls}^{1/2}$ , for dimethyloleylamine oxide. The values of micelle aggregation number in water and  $10^{-4} M$  NaCl are so large that the shape of micelles at finite micelle concentrations may not be spherical but would be rod-like.

It has been suggested by many workers that the micelles with large aggregation number of nonionic surfactants at finite concentrations in aqueous solution assume the rod-like structure, if the hydrophobicity is much stronger than the hydrophilicity (7, 22-28). Evidently

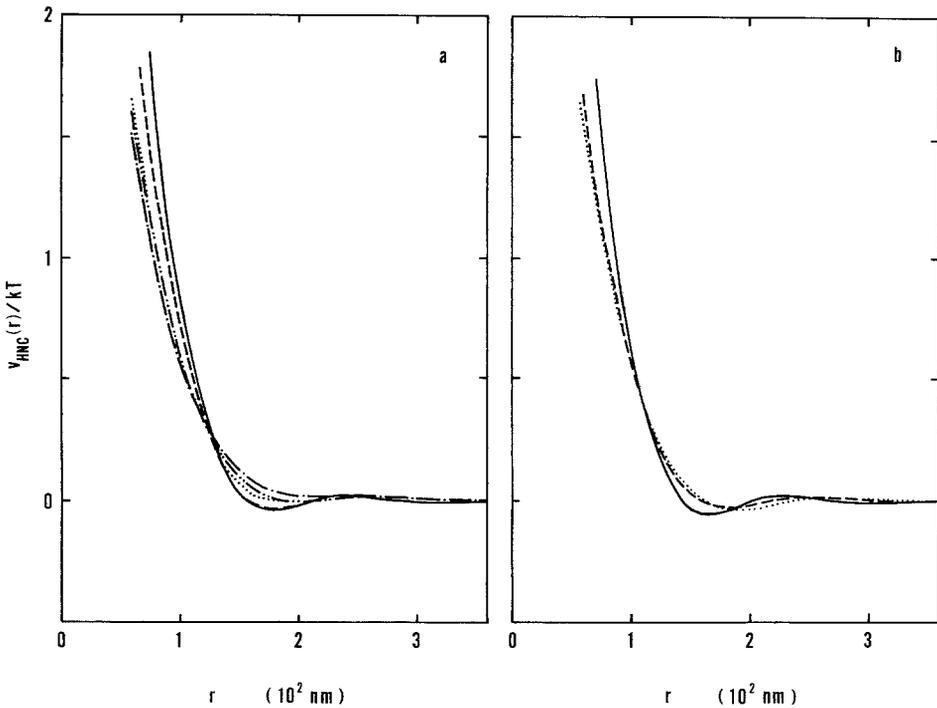


FIG. 6. The intermicellar pair potential calculated by the HNC approximation as a function of intermicellar distance,  $r$ . (a) In water; (b) in  $10^{-4} M$  NaCl. Curves shown are for the same concentrations as in Figs. 3 and 4.

the formation of rod-like micelles by dimethyloleylamine oxide must be attributed to the strong cohesion of long hydrocarbon chains in solution, since spherical micelles are more stable for dimethyldodecylamine oxide in aqueous solutions (29).

If all of micelles of dimethyloleylamine oxide were rigid rods, their length should be  $L = 12^{1/2}(\overline{R_G^2})_{ls}^{1/2}$ . The calculated values of  $L$  are 870 and 1040 Å for solutions in water and in  $10^{-4} M$  NaCl, respectively, at the highest concentration of micelles. As can be seen in Table I, however, the values of  $(\overline{R_G^2})_{ls}^{1/2}$  are not proportional to the aggregation number,  $m_w$ , but rather they are more closely related to  $m_w^{1/2}$ . This means that a rod-like micelle is very flexible and behaves like a random coil, in which scattering centers are distributed spherically symmetric.

The second virial coefficient is inversely pro-

portional to the square of molecular weight, as seen in Eq. [15]. Such a relation between  $B$  and  $M_w$  is proved to hold approximately for the present solutions. More strictly, the product,  $BM_w^2$ , is slightly lowered by the addition of NaCl, which implies that the effective excluded volume is decreased in the presence of NaCl, if the nature of  $B$  is solely composed of the excluded volume effect. It is likely that the suppression of intermicellar interaction by the addition of NaCl is also responsible for the decrease in the second virial coefficient.

The effect of added salt on the second virial coefficient may be generally smaller for non-ionic surfactants than for ionic surfactants. However, the decrease of the second virial coefficient by the addition of NaCl was reported for aqueous solutions of methoxypolyoxyethylene dodecyl ether (30) and polyoxyethylene nonylphenyl or octadecyl ether (31).

Its opposite dependence on NaCl concentration was observed on aqueous solutions of dimethyldodecylamine oxide (29).

#### *Mutual Arrangement of Micelles*

Recently it was reported for latex dispersions of moderate concentrations that an intensity maximum was exhibited in their light scattering (11, 14–17), which could be ascribed to the short-range ordering of the latex particles (10–12). Such intense ordering also leads to a strong maximum on the  $S(\theta)$  curve (10, 11, 13–17) and on the  $g(r)$  curve (10, 13–15), respectively. However, the feature of the Zimm plots and the  $g(r)$  curves observed for the present solutions suggests that the non-random arrangement of the surfactant micelles is not so intensive as that of those latices.

The situation of the mutual arrangement of the micelles in solution is represented by the maxima on the  $g(r)$  curves. The intermicellar interaction distances obtained are around 1300–1600 Å, which are more than five times larger than the average radii of gyration. Thus the application of the Zernike–Prins equation to the present solution would be justified.

#### *Intermicellar Forces*

The behavior of the colloidal particles is similar to that of molecules in simple liquids, and from their analogies the pair potential associated with the radial distribution function for the colloidal dispersion has been discussed in terms of some theories of simple liquids. Schaefer (13) evaluated the structure factors for a suspension of highly charged polystyrene latex spheres, using methods developed for simple fluids, and compared them with those obtained from measurements by optical techniques. He found that the HNC approximation is superior to the PY approximation. Through the theories of simple liquids, Nieuwenhuis and Vrij (15) calculated the pair potential curve from the structure factor measured by light scattering for polymethyl meth-

acrylate latex dispersions in a nonpolar solvent. The pair potential curves obtained from the HNC and PY approximations were nearly the same.

Owing to uncertainties produced through many steps during the calculation process, it would be better to claim that the pair potentials calculated by the two approximations are not distinguishable for the micelles of dimethylolelylamine oxide. In spite of their uncertainties, the pair potential shows a steep increase at intermicellar distances shorter than a certain distance, indicating a strong repulsive interaction between micelles.

The nature of the pair potential between the nonionic micelles, primarily, of repulsive, is difficult to be imagined. The van der Waals attraction will be effective for such large micelles, although it must be still weak. It is quite likely that an amine oxide, being a weak base, is slightly, or at most, 10%, protonated in neutral solutions; thus long-range electrostatic repulsion could occur. Actually, the pair potential undergoes suppression by the presence of NaCl, indicating the possible operation of electrostatic effect. The steric repulsion leading to the excluded volume effect must be dominant, especially, at short distances.

#### *Effect of Addition of Salt*

While the aggregation number or the size of micelles increases with an increase in NaCl concentration, the external interference effect on the light scattering from solutions of dimethylolelylamine oxide decreases. Micelles of dimethylolelylamine oxide in water interact with each other, mainly, through intermicellar repulsive forces, and are mutually arranged in a nonrandom manner. With increasing NaCl concentration in solution, the intermicellar repulsion may steeply decrease, partly because the intermicellar distance defined by the excluded volume effect increases with an increase in micelle size, and partly because the long-range electrostatic repulsion is suppressed by an increase in ionic strength. The

growth of the micelle size also induces the intense increase of the internal interference effect, which becomes, after all, superior to the external interference effect. Thus we can suggest that at high NaCl concentrations the external interference effect becomes negligible under the strong internal interference effect.

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