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INTERACTION OF RODLIKE MICELLES OF DIMETHYLOLEYLAMINE OXIDE IN AQUEOUS SOLUTIONS

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Light scattering measurements have been carried out on aqueous solutions of dimethyloleylamine oxide in water, 10^{-4} or 10^{-3} N HCl, in the absence or presence of NaCl to different concentrations up to 5×10^{-2} M. Large rodlike micelles are formed in all solutions.

In the presence of NaCl less than 10^{-3} M, light scattering is subject to strong external interference, giving anomalous angular dependence. Separation of the external effect from the internal interference yields radial distribution function of micelles, showing that rodlike micelles exist in solution nonrandomly or in clustering states.

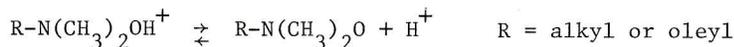
In the presence of more concentrated NaCl, angular dependence of light scattering is normal, indicating no external interference, and shows formation of large, flexible rodlike micelles. The electrostatic effect of protonation in 10^{-3} N HCl is not necessarily manifest, as the micelle size is compared with that in water. With increasing NaCl concentration, larger micelles are formed. In 10^{-3} N HCl in the presence of 10^{-2} M NaCl, the micelle formed has molecular weight of 18 million, and radius of gyration of 2,100 Å.

It is concluded that hydration of amine oxide prevents a rodlike micelle from further associating together, but the addition of NaCl dehydrates the amine oxide and increases the micelle size. Dehydration of amine oxide also induces hydrogen bonding between amine oxide and N-hydroxyammonium ion in a micelle.

INTRODUCTION

Dimethyloleylamine oxide, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8\text{N}(\text{CH}_2)_2\text{O}$, is highly soluble in water and aqueous salt solutions, in spite of its having a long hydrocarbon chain and a nonionic head group. We may expect from the micelle size observed for lower alkyl homologs^{1,2} that it can form large rodlike micelles above the low critical micelle concentration.^{3,4}

Amine oxide is a weak base, and it can be protonated at low pH to form N-hydroxyammonium ion:



Dimethyloleylamine oxide has a pK value of 3.7 to 4.3 in the micellar form, depending on the NaCl concentration. Accordingly, it forms non-ionic micelles in water or at alkaline pH; while it forms cationic micelles in aqueous HCl solutions at pH lower than 2. At intermediate pH, it is present as the cationic-nonionic micelles.

In this work we present our results of light scattering measurements on aqueous solution of dimethyloleylamine oxide in water, and 10^{-4} N or 10^{-3} N HCl, in the absence or presence of NaCl up to 5×10^{-2} M. In 10^{-3} N HCl dimethyloleylamine oxide is half-protonated, thus forming a micelle consisting of an equal composition of amine oxide molecules and N-hydroxyammonium ions. At lower pH our light scattering cells could not be used because of the low stability of their bottom corners against acids where some adhesive material was present.

Since we have encountered complicated situations concerning angular dependence of light scattering, we first give a brief account of light scattering behavior of the dilute micellar solutions. It will make the interpretation of our results more comprehensible. Then we will derive the micelle size and shape as well as the intermicellar interaction. It can be shown that large rodlike micelles are formed and their size and mutual interaction are strongly dependent on the hydration state of the amine oxide group.

LIGHT SCATTERING IN DILUTE SOLUTIONS

In light scattering from a dilute solution having surfactant concentration, c ($g\ cm^{-3}$), the reduced intensity of scattered light is given by

$$R_\theta = R_\theta^0 + K M_w (c - c_0) P(\theta) S(\theta) \quad (1)$$

where M_w is the weight-average molecular weight of micelles, and $P(\theta)$ and $S(\theta)$ are the particle scattering factor and the structure factor, respectively, which represent the effects of internal and external interference, respectively. The optical constant is expressed by

$$K = 2 \pi^2 \bar{n}_0^2 \left(\frac{dn}{dc} \right)_{C_A, C_S}^2 / N_A \lambda^4 \quad (2)$$

where N_A is Avogadro's number, \bar{n} is the refractive index of the solution for the light of wavelength, λ , and C_A and C_S are the molar concentrations of HCl and NaCl. The subscript A or superscript, o, refers to the solution of the critical micelle concentration, c_0 . The critical micelle concentration is very low for dimethyloleylamine oxide and dodecyl-dimethyl-N-hydroxyammonium chloride.^{3,4}

The particle scattering factor, $P(\theta)$, is given by

$$P(\theta) = \sum_i \sum_j \frac{\sin \mu r_{ij}}{\mu r_{ij}} \quad (3)$$

where i and j stand for two scattering points by distance r_{ij} apart within a micelle, and μ is the magnitude of wave vector of scattered light:

$$\mu = (4\pi \bar{n}_0 / \lambda) \sin (\theta/2) \quad (4)$$

The summation extends over all pairs of scattering points within a micelle.

The structure factor, $S(\theta)$, is given by

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$$S(\theta) = 1 + 4\pi \frac{N_A (c - c_0)}{M_w} \int_0^\infty \{g(r) - 1\} \frac{\sin \mu r}{\mu r} r^2 dr \quad (5)$$

where r is the distance between centers of gravity of two micelles, and $g(r)$ is the radial distribution function of micelles.

Light scattering results are generally expressed in the form of reciprocal envelope, in order to represent angular and concentration dependences, so that $K(c - c_0)/(R_\theta - R_\theta^0)$ is plotted against $\sin^2(\theta/2) + a(c - c_0)$, where a is an arbitrary constant for adjustment of the envelope shape. This is because the reciprocal particle scattering factor can always be related to the radius of gyration, R_G , of the solute particle through

$$P^{-1}(\theta) = 1 + \frac{1}{3} \mu^2 R_G^2 \quad (6)$$

if μ or θ is small, and also because the reciprocal structure factor at zero angle, or the reciprocal increment of reduced intensity at zero angle, can be written in the form of virial expansion, which can be cast into

$$S(0) = 1 - 2 B M_w (c - c_0) \quad (7)$$

if $c - c_0$ is small, where B is the second virial coefficient.

Equation (3) indicates that $P^{-1}(\theta)$ increases with increasing μ or θ , and equation (5) shows that $S^{-1}(\theta)$ decreases with increasing θ or μ and depends on the micelle concentration, $c - c_0$. Then there are two limiting cases of angular dependence of the reciprocal envelope at a given concentration, as shown in Figure 1.

- (a) If the external interference is weak and $S(\theta) = S(0)$, then $K(c - c_0)/(R_\theta - R_\theta^0)$ increases at higher angles. This behavior has been observed for dilute micellar solutions of most surfactants, both spherical and rodlike.
- (b) If the internal interference is weak as compared with the external interference, or if only the external interference is strong, that is, if $P(\theta) = 1$, then $K(c - c_0)/(R_\theta - R_\theta^0)$ decreases at higher angles, dependent on the micelle concentration, $c - c_0$.

Usually, instead of the case (b), the two effects of interference are combined, the Zimm plot should appear as given in Figure 2, depending on whether the external interference is comparable with or much stronger than the internal interference.

RODLIKE MICELLES AT HIGHER IONIC STRENGTHS

Since the (rodlike) micelles of dimethyloleylamine oxide are large and comparable with the wavelength of light, internal interference always occurs. The micelle molecular weight ranges from 1 million to 18 million, as will be seen below.

In the presence of NaCl more than 10^{-3} M, the light scattering behavior is normal, and the reciprocal envelope rises with increasing scattering angle. Figure 3 shows the Zimm plot of light scattering from the micellar solutions in the presence of 0.05 M NaCl with different HCl concentrations. The plot increases linearly at low angles, when the micelle concentration is low, but it increases convex upward at high angles,

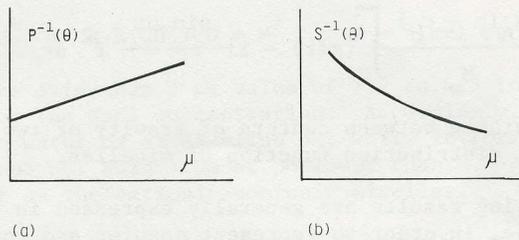


Figure 1. Angular dependence of reciprocal envelope of light scattering. (a) $P^{-1}(\theta)$, (b) $S^{-1}(\theta)$.

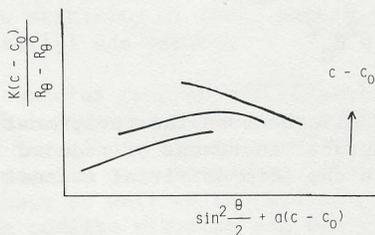


Figure 2. Behavior of Zimm plots with different combinations of internal and external interference.

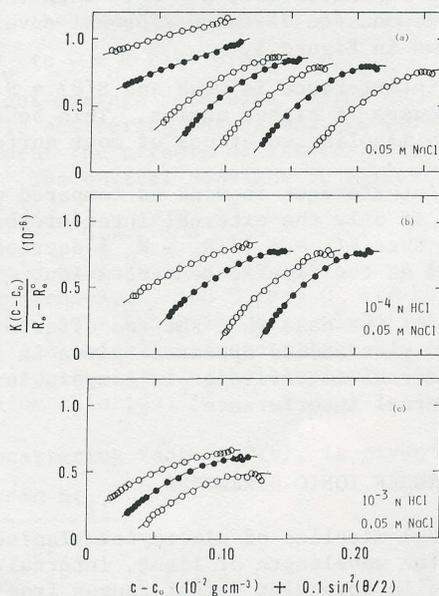


Figure 3. Zimm plots of light scattering from the micellar solutions of dimethyloleylamine oxide in the presence of 0.05 M NaCl. The curves from left to right correspond to the micelle concentrations, $c - c_0$ (10^{-2} g cm^{-3}): (a) 0.05 M NaCl; 0.008, 0.018, 0.047, 0.063, 0.092, 0.121, 0.163. (b) 10^{-4} N HCl + 0.05 M NaCl; 0.026, 0.053, 0.098, 0.129. (c) 10^{-3} N HCl + 0.05 M NaCl; 0.015, 0.027, 0.038.

when the micelle is subject to the inter- holds true.¹⁵

Equation (1), the extrapolation of apparent micelle m that its initials extrapolation give radius of gyration in Figure 4 (b).

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when the micelle concentration is high. This behavior is interpreted as subject to the internal interference alone, so that the case (a) above holds true.¹⁵

Equation (1), together with equations (6) and (7), indicates that the extrapolation of the Zimm plot to zero angle gives the reciprocal of apparent micelle molecular weight at a given micelle concentration, and that its initial slope yields the radius of gyration of micelle. The extrapolation gives the Debye plot, as shown in Figure 4 (a), and the radius of gyration is also given as a function of micelle concentration in Figure 4 (b).

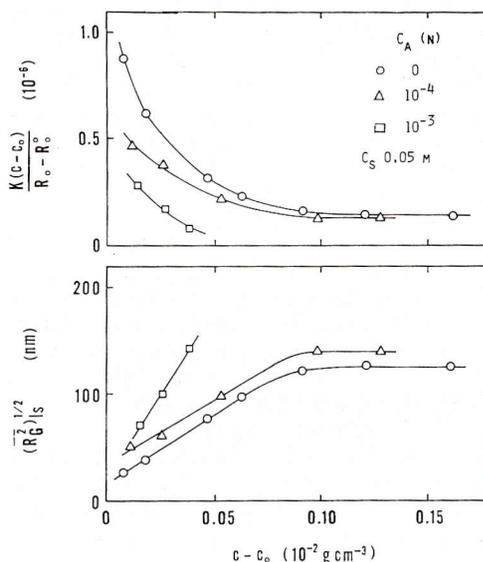


Figure 4. Debye plots of light scattering and the radius of gyration of rodlike micelles in 0.05 M NaCl.

Figure 4 shows that both the apparent molecular weight and radius of gyration of micelles increase with increasing micelle concentration and reach constant values above $0.10 \times 10^{-2} \text{ g cm}^{-3}$. This suggests that the second virial coefficient, B , of the solution is small and negligible, and that the apparent micelle molecular weight is approximately equal to the weight-average molecular weight of micelles. In 10^{-3} N HCl these micelle parameters did not attain constant values before phase separation into two liquid phases occurred at high micelle concentrations.

Table I lists the constant values of molecular weight and radius of gyration of micelles, together with the aggregation number, $m = M/311.6$. These values can be assigned to the large rodlike micelles formed above the critical micelle concentration. It was not necessarily possible to obtain the corresponding values at the critical micelle concentration by extrapolation. Table I also includes the values of $(dn/dc)_{C_A, C_S}$ and c_0 .

Figure 4 then shows that small spherical micelles are formed at the critical micelle concentration and, with increasing micelle concentration, large rodlike micelles are also formed. Thus a concentration-dependent equilibrium would exist between spherical and rodlike micelles, and it shifts from the side of spherical micelle to that of rodlike micelle at higher micelle concentrations.¹⁶

Similar angular and concentration dependences of light scattering were observed for the micellar solutions in the presence of 0.01 M NaCl with different HCl concentrations, and the micelle molecular weight and radius of gyration were derived from them.

Table I. Micellar Properties of Dimethyloleylamine Oxide in 0.05 M NaCl

C_A (M)	$(dn/dc)_{C_A, C_S}$ ($\text{cm}^3 \text{g}^{-1}$)	c_o (10^{-2}g cm^{-3})	M_w (10^6)	m	R_G (A)
0	0.161	0.003	6.90	22,100	1,270
10^{-4}	0.161	0.004	7.58	24,300	1,410
10^{-3}	0.167	0.004	(> 15.0)	phase separation	

MICELLAR SOLUTIONS AT LOWER IONIC STRENGTHS

In the absence of NaCl or its presence at a low concentration, the situation of light scattering is more complicated, and the reciprocal envelope varies with the scattering angle differently, depending on the micelle concentration as well as on the HCl concentration.

Figure 5 shows Zimm plots of light scattering from the micellar solutions in the absence of NaCl with different HCl concentrations.^{17,18} In water and 10^{-4} N HCl, the plots decrease with increasing scattering angle, when the micelle concentration is high; but in 10^{-4} N HCl the plot increases and levels off or passes a maximum with increasing angle, if the micelle concentration is low.

This behavior can all be adequately interpreted by assuming the strong effect of external interference, such as illustrated in Figure 2. Thus we have to distinguish the effect of external interference from the effect of internal interference, in order to derive the micelle parameters and the intermicellar interaction.^{19,20}

In 10^{-3} N HCl the angular dependence of light scattering appears not to be very anomalous but to follow the normal behavior resulting from the internal interference alone. Nevertheless, its concentration dependence is very large, as can be seen from the wide range of observed values of reciprocal envelope. This behavior can also be explained by assuming that the effect of external interference is so strong that one-contact approximation does not hold well. Thus we have to rely on equation (1), instead of (7), for the analysis of the Zimm plots.

In order to separate the structure factor from the particle scattering factor, we have to postulate values of molecular weight and radius of gyration of micelle in equation (1). Then the value of $P(\theta)$ can be calculated by means of equation (6) from the value of R_G , and from the assumed values of M_w , together with the calculated $P(\theta)$ value, the value of $S(\theta)$ can be derived by means of equation (1) from the observed value of $R_\theta - R_\theta^o$ at a given micelle concentration, $c - c_o$.

It can be shown that the structure factor, $S(\theta)$, must satisfy the condition

Figure 5. Zimm plots of light scattering from the micellar solutions of dimethyloleylamine oxide in water and 10^{-4} N HCl. The plots decrease with increasing scattering angle, when the micelle concentration is high; but in 10^{-4} N HCl the plot increases and levels off or passes a maximum with increasing angle, if the micelle concentration is low.

$$\int_0^\infty [S(\theta) - 1] \mu^2 d\mu$$

From the Fourier transform

$$g(r) = 1 + \frac{1}{2\pi}$$

under the requirement

$$g(r) = 0$$

Thus we have to derive the values of M_w and R_G from the experimental data. We have to revise the procedure.

In this way we can derive the values of M_w and R_G for the micellar solutions in water, and compare them with the corresponding data of $S(\theta)$.

Then we can derive the values of M_w and R_G for the micellar solutions in solution of different HCl concentrations. Each of them means that the mean values of M_w and R_G are different there. Since the mean values of M_w and R_G are different there, the mean values of M_w and R_G are different there.

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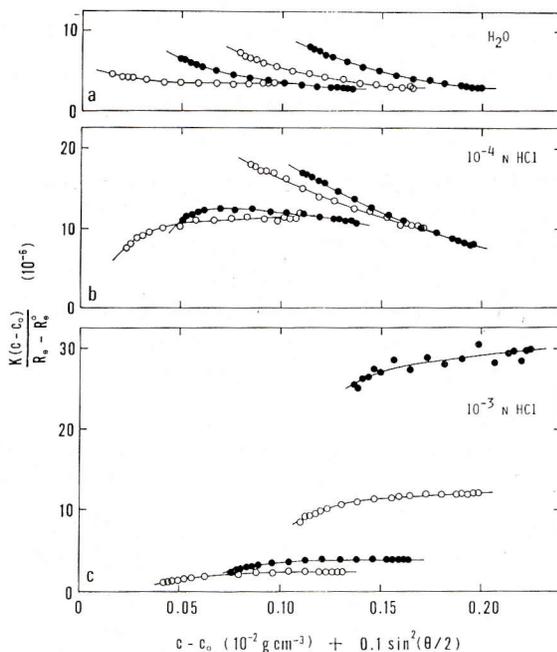


Figure 5. Zimm plots of light scattering from the micellar solutions of dimethyloleylamine oxide in water, 10^{-4} N and 10^{-3} N HCl without added NaCl. The curves from top to bottom correspond to the micelle concentrations, $c - c_0$ (10^{-2} g cm^{-3}): (a) H_2O ; 0.107, 0.072, 0.042, 0.008. (b) 10^{-4} N HCl; 0.103, 0.077, 0.044, 0.016. (c) 10^{-3} N HCl; 0.132, 0.106, 0.072, 0.038.

$$\int_0^{\infty} [S(\theta) - 1] \mu^2 d\mu = -2 \pi^2 \frac{N_A (c - c_0)}{M_w} \quad (8)$$

From the Fourier transform of equation (5), we have

$$g(r) = 1 + \frac{M_w}{2 \pi^2 N_A (c - c_0)} \int_0^{\infty} [S(\theta) - 1] \frac{\sin \mu r}{\mu r} \mu^2 d\mu \quad (9)$$

under the requirement

$$g(r) = 0 \quad (10)$$

Thus we have to examine whether the derived values of $S(\theta)$ for assumed values of M_w and R_G satisfy equation (8) or not. If they do not, we have to revise the set of values for M_w and R_G and to repeat the above procedure.

In this way we can find reasonable values of M_w and R_G for micellar solutions in water, 10^{-4} N and 10^{-3} N HCl, as given in Table II. Corresponding data of $S(\theta)$ for the micelles in water are plotted in Figure 6.

Then we can derive the radial distribution function of rodlike micelles in solution by means of equation (9). Figure 7 illustrates some of them. Each of them has a small hump around 1,400 - 1,650 A. This means that the mean potential acting on a rodlike micelle has a minimum there. Since the mean potential is given by

Table II. Micellar Parameters of Dimethyloleylamine Oxide in the Absence of NaCl.

C_A (N)	$(dn/dc)_{C_A, C_S}$ ($\text{cm}^3 \text{g}^{-1}$)	c_o (10^{-2}g cm^{-3})	M_w (10^6)	m	R_G (A)
0	0.163	0.004	0.89	2,900	250
10^{-4}	0.162	0.004	0.83	2,700	390
10^{-3}	0.167	0.004 ₅	0.89	3,100	440

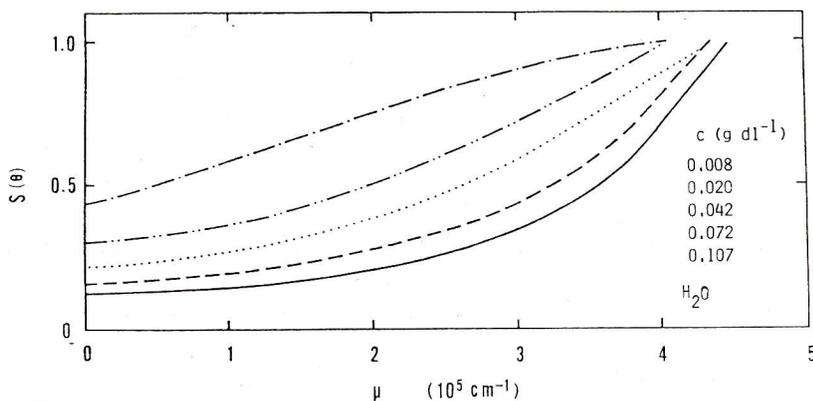


Figure 6. Structure factor, $S(\theta)$, vs. μ for the micellar solutions of dimethyloleylamine oxide in water. Surfactant concentrations are as indicated from top to bottom.

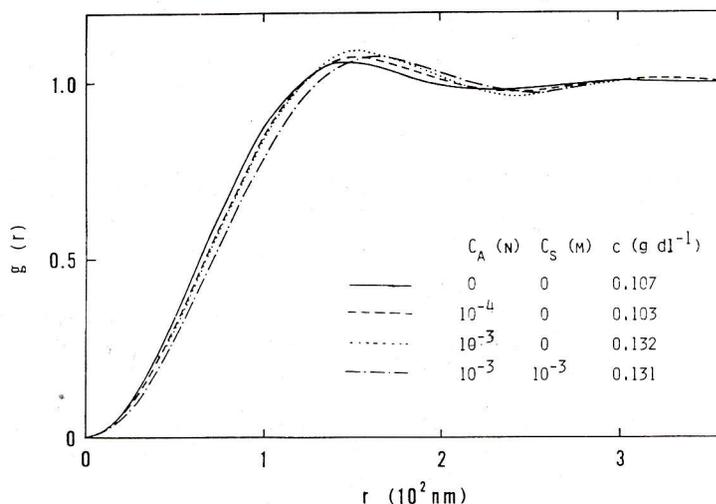


Figure 7. The radial distribution function of the rodlike micelles of dimethyloleylamine oxide under different conditions.

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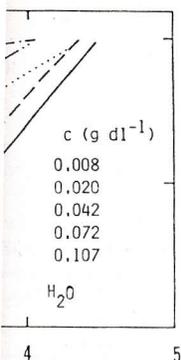
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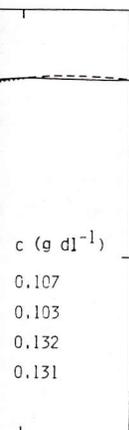
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$$u(r) = -kT \ln g(r) \quad (11)$$

the hump at r_m corresponds to the minimum of the potential well, where k is Boltzmann's constant and T is the temperature. The values of $u(r_m)$ is $-0.01 kT$ at 1,400 Å in water and $-0.06 kT$ at 1,650 Å in 10^{-3} N HCl.

MOLECULAR WEIGHT OF MICELLES AND THEIR MUTUAL INTERACTION

Table III summarizes values of the molecular weight, aggregation number, radius of gyration of rodlike micelles, together with values of the minimum of mean potential of the intermicellar interaction. It also includes the values of the second virial coefficient, either derived from the Debye plot or from the structure factor at zero scattering angle. The former is a direct method usually made, and the latter has to rely on equation (7).

From Table III it can be seen that the micelles are all rodlike at the finite micelle concentrations. The micelle molecular weight increases moderately with increasing NaCl concentration, owing to the salting-out effect in water and 10^{-4} N HCl, and to the effect of electrostatic shielding in 10^{-3} N HCl.

It is clear that the size-limiting factor of the rodlike micelles is hydration of amine oxide group, and, possibly, also of N-hydroxyammonium group, as well as the exchangeability of constituent molecules or ions in them.¹⁶ The salting-out effect of NaCl is to reduce the hydration that acts as the intermicellar repulsion.

In 10^{-4} N and 10^{-3} N HCl, the protonation of amine oxide group does occur⁵ to form N-hydroxyammonium group, as is manifest in the pH titration. The protonation of micelles could reduce the micelle size owing to the electrostatic repulsion, but the coexistence of both amine oxide and N-hydroxyammonium also has some effect of increasing the micelle size due to the intramicellar hydrogen bonding.

In 10^{-3} N HCl the effect of hydrogen bonding between amine oxide molecules and N-hydroxyammonium ions in a micelle is strong, especially in the presence of NaCl, because an equal number of moles of the two species is present and is most favorable for the hydrogen bonding. The effect of added NaCl on micelle growth is appreciable. It cannot be attributed to the electrostatic shielding alone but must be caused by the salting-out effect. The dehydration of amine oxide and N-hydroxyammonium promotes their hydrogen bonding within a micelle, thus stabilizing large micelles. In the presence of 0.01 M NaCl this effect is quite large. Further addition of NaCl forms too large micelles which cannot be stable in solution but induce separation of solution into two liquid phases.^{5,21} The molecular weight of micelles would not exceed 20 million in solution. The two liquid phases are both isotropic, so that rodlike micelles are semiflexible.

The second virial coefficient of micellar solution stands for the intermicellar repulsion, and its decrease with an increase in NaCl concentration must be attributed mainly to the dehydration of amine oxide group, and, probably, also of N-hydroxyammonium group.

Thus the intermicellar interaction potential in aqueous solutions of dimethyloleylamine oxide in the absence and presence of HCl and NaCl at low concentrations arises mainly from the repulsive hydration and the van der Waals attraction of semiflexible rodlike micelles. The radial distribution function of micelles represents nonrandom arrangements of micelles clustering at the potential minima.

Table III. Molecular Weight, Aggregation Number, Radius of Gyration of Rodlike Micelles, and Depth of Their Mean Potential in Solution and Second Virial Coefficient of Micellar Solution.

C_S (M)	C_A (N)	0	10^{-4}	10^{-3}
	α	~ 0		
	pH	~ 7		~ 5
0	M_w (10^6)	0.89	0.83	0.98
	m_w	2,900	2,700	3,400
	R_G (A)	250	390	440
	$u(r)$	- 0.01 kT	- 0.04 kT	- 0.06 kT
	$2B$ (10^{-3})	0.92	1.05	0.72
10^{-4}	M_w (10^6)	1.03		
	m_w	3,300		
	R_G (A)	300		
	$u(r)$	- 0.01 kT		
	$2B$ (10^{-3})	0.61		
5×10^{-4}	M_w (10^6)	1.47		
	m_w	4,720		
	R_G (A)	560		
10^{-3}	M_w (10^6)	2.70		1.49
	m_w	8,670		4,780
	R_G (A)	850		420
	$u(r)$			- 0.04 kT
	$2B$ (10^{-3})	0.214		0.40
10^{-2}	M_w (10^6)	4.76	5.00	18.00
	m_w	15,300	16,000	58,000
	R_G (A)	1,120	1,120	2,100
	$2B$ (10^{-3})	0	0.07	0.258
5×10^{-2}	M_w (10^6)	6.90	7.58	liquid-liquid phase separation
	m_w	22,100	24,000	
	R_G	1,270	1,410	
	$2B$ (10^{-3})	0	0	

SUMMARY

Dimethyloleylamine oxide forms large rodlike micelles in aqueous solutions, and their molecular weight and mutual interaction are strongly influenced by the addition of HCl up to 10^{-3} N and also by the addition of NaCl up to 0.05 M. In water nonionic micelles are present, while in 10^{-3} N HCl half-protonated micelles are formed.

In the presence of NaCl less than 0.01 M or in its absence, the micelle has molecular weight of 1 to 2 million, and these micelles interact strongly and are arranged nonrandomly, thus exhibiting strong external interference in light scattering.

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REFERENCES

1. K. W. Herrm
2. S. Ikeda, M
(1979).
3. T. Imae, H.
4. T. Imae, H.
5. T. Imae, H.
6. F. Zernike
7. P. Doty and
8. A. Guinier
New York, 1
9. P. Debye, J
10. L. M. Kushn
11. P. Debye an
12. K. W. Herrm
13. S. Ikeda, i
Editors, Vo
14. T. Imae and
15. T. Imae and
16. S. Ikeda, J
17. T. Imae and
18. T. Imae and
19. E. A. Niuwe
(1979).
20. R. H. Ottew
(1982).
21. T. Imae and

r, Radius of
depth of Their
and Virial

10^{-3}
~ 0.5
~ 5

0.98
3,400
440
- 0.06 kT
0.72

1.49
4,780
420
- 0.04 kT
0.40

18.00
58,000
2,100
0.258

liquid-liquid
phase separation

elles in aqueous
raction are strongly
so by the addition
present, while in

ts absence, the
ese micelles in-
ibiting strong ex-

, the micelle mole-

cular weight exceeds 5 million. Nevertheless, the intermicellar interaction is generally weak, so that internal interference appears strongly in light scattering. By the addition of NaCl to 10^{-3} N HCl, the micelle becomes so large that finally the solution separates into two liquid phases.

The observed behavior of large rodlike micelles may be explained by the formation of intramicellar hydrogen bonding between amine oxide and N-hydroxyammonium and the dehydration of the head groups by the salting-out effect of NaCl.

REFERENCES

1. K. W. Herrmann, *J. Phys. Chem.*, **66**, 295 (1962).
2. S. Ikeda, M. Tsunoda and H. Maeda, *J. Colloid Interface Sci.*, **70**, 448 (1979).
3. T. Imae, H. Araki and S. Ikeda, *Colloids Surfaces*, **17**, 207 (1986).
4. T. Imae, H. Araki and S. Ikeda, *Colloids Surfaces*, **17**, 221 (1986).
5. T. Imae, H. Konishi and S. Ikeda, *J. Phys. Chem.*, **90**, 1417 (1986).
6. F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927).
7. P. Doty and R. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).
8. A. Guinier and G. Fournier, "Small Angle Scattering of X-Rays," Wiley, New York, 1955.
9. P. Debye, *J. Phys. Colloid. Chem.*, **53**, 1 (1949).
10. L. M. Kushner and W. D. Hubbard, *J. Colloid Sci.*, **10**, 428 (1955).
11. P. Debye and E. W. Anacker, *J. Phys. Colloid. Chem.*, **55**, 644 (1951).
12. K. W. Herrmann, *J. Phys. Chem.*, **68**, 1540 (1964).
13. S. Ikeda, in "Surfactants in Solution," K. L. Mittal and B. Lindman, Editors, Vol. 2, p. 825 Plenum Press, New York (1984).
14. T. Imae and S. Ikeda, these Proceedings, previous paper.
15. T. Imae and S. Ikeda, *Colloid Polymer Sci.*, **262**, 497 (1984).
16. S. Ikeda, *J. Phys. Chem.*, **88**, 2144 (1984).
17. T. Imae and S. Ikeda, *J. Colloid Interface Sci.*, **98**, 363 (1984).
18. T. Imae and S. Ikeda, *Colloid Polymer Sci.*, **263**, 756 (1984).
19. E. A. Niuwenhuis and A. Vrij, *J. Colloid Interface Sci.*, **72**, 321 (1979).
20. R. H. Ottewill and R. A. Richardson, *Colloid Polymer Sci.*, **260**, 708 (1982).
21. T. Imae and S. Ikeda, *J. Colloid Interface Sci.*, **113**, 449 (1986).