

## THE ABSORPTION SPECTRA AND THE MICELLE SPECIES OF DIMETHYLOLEYLAMINE OXIDE IN AQUEOUS SOLUTIONS

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### ABSTRACT

Ultraviolet absorption spectra of dimethyloleylamine oxide have been recorded in aqueous solutions, either neutral or acidified by HCl. There are five characteristic bands between 200 and 189 nm, three of which are associated with monomeric species of the surfactant and two of which are assigned to spherical and rodlike micelles formed by the surfactant. The absorption bands of monomeric species and spherical micelles become stronger with increasing surfactant concentrations and reach a constant optical density, and the band of rodlike micelles shifts towards red and increases its optical density as the surfactant concentration increases.

The critical micelle concentrations (CMC) obtained from absorption spectra are compared with those from light scattering and surface tension measurements. It can be concluded that the CMC of spherical micelles may deviate from that of rodlike micelles.

### INTRODUCTION

If a surfactant has a chromophoric group in its molecule, its absorption spectra in solution should be subject to a change accompanying the formation of micelles [1–5]. Above the critical micelle concentration (CMC), either the molar extinction coefficient of an absorption band deviates from Lambert–Beer's law, or new absorption bands appear.

Dimethyloleylamine oxide,  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8\text{N}(\text{CH}_3)_2\text{O}$ , is a weak base: in water it is protonated to form oleyldimethyl *N*-hydroxyammonium ion on addition of HCl. Its CMC, measured by light scattering, is as low as 0.13–0.14 mM, depending on the degree of protonation [6, 7]. At the CMC, spherical micelles are formed and, in more concentrated solutions, they are in equilibrium with rodlike micelles.

We have observed that the CMC values derived from surface tension measurements [8] are much lower than those derived from light scattering measurements [6, 7] and have some complicated situation.

We have also noticed a pronounced effect of HCl on the surface tension [8] and light scattering [6, 7], which reflects the fact that the adsorption and micellar behavior are strongly dependent on the ionization of the amine oxide.

Aqueous solutions of dimethyloleylamine oxide show absorption bands around 200 nm, which can be assigned to a  $\pi \rightarrow \pi^*$  transition of the *cis*-alkene group. In this work, we record absorption spectra of dimethyloleylamine oxide in aqueous solutions at different HCl concentrations: 0, 0.001 and 0.01 M, and correlate their changes with the formation of micelles.

## EXPERIMENTAL

The sample of dimethyloleylamine oxide was the same as that used previously [6–8]. The purity of the surfactant was examined by the surface tension method: its aqueous solution did not show any minimum at the CMC on the surface tension curve. Water was redistilled from alkaline  $\text{KMnO}_4$  solution in a glass still. The stock solution of dimethyloleylamine oxide was diluted with water or HCl solution and each solution was kept overnight at room temperature before measurement.

The absorption spectra were recorded on a Shimadzu UV-200S spectrophotometer using a 1-cm cell, with water at  $25 \pm 0.01^\circ\text{C}$  circulating through the cell jacket. Water, or 0.001 or 0.01 M HCl was used as reference solution. Hydrogen chloride in water gave absorption bands with  $\epsilon_{193} = 121 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{191} = 87 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , but subtraction of these contributions could clearly separate an absorption band of the surfactant above 197 nm, even in 0.01 M HCl.

## RESULTS

### Water

The absorption spectra of dimethyloleylamine oxide in water are shown in Fig. 1(a). They have peaks at 191.5 and 193.0 nm and a shoulder around

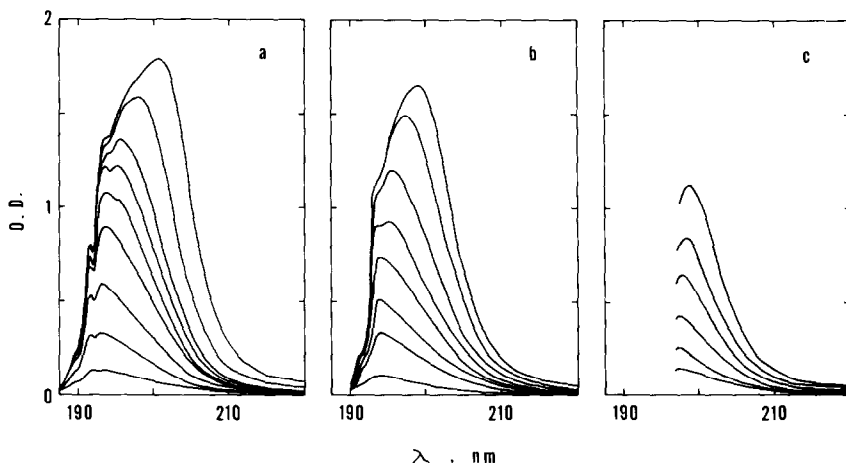


Fig. 1. Absorption spectra of dimethyloleylamine oxide in aqueous solutions. Surfactant concentration (mM) (down to up): (a), in water; 0.0218, 0.0544, 0.0979, 0.163, 0.230, 0.272, 0.354, 0.544, 1.15; (b), in 0.001 M HCl; 0.0210, 0.0629, 0.0978, 0.154, 0.210, 0.307, 0.489, 0.698; (c), in 0.01 M HCl; 0.0405, 0.0709, 0.130, 0.202, 0.283, 0.405.

189.5 nm over the surfactant concentration range up to 0.2 mM. The optical density of these bands increases with increasing surfactant concentration and reaches a constant value at high surfactant concentrations. At a surfactant concentration of 0.23 mM a band appears at 195.2 nm, which shifts towards red and becomes stronger with increasing surfactant concentration. However, this band is replaced by a new band at 197.4 nm, which becomes distinguishable at a concentration of 0.4 mM. The new band at the longest wavelength increases its optical density with a further increase in surfactant concentration, accompanying its red shift.

Figure 2 shows the dependence of peak position, optical density and molar extinction coefficient of these five bands on the surfactant concentration. Three bands at shorter wavelengths, observed in dilute solution, have constant optical densities at high surfactant concentrations. Their molar extinction coefficients are constant in dilute solutions up to a critical

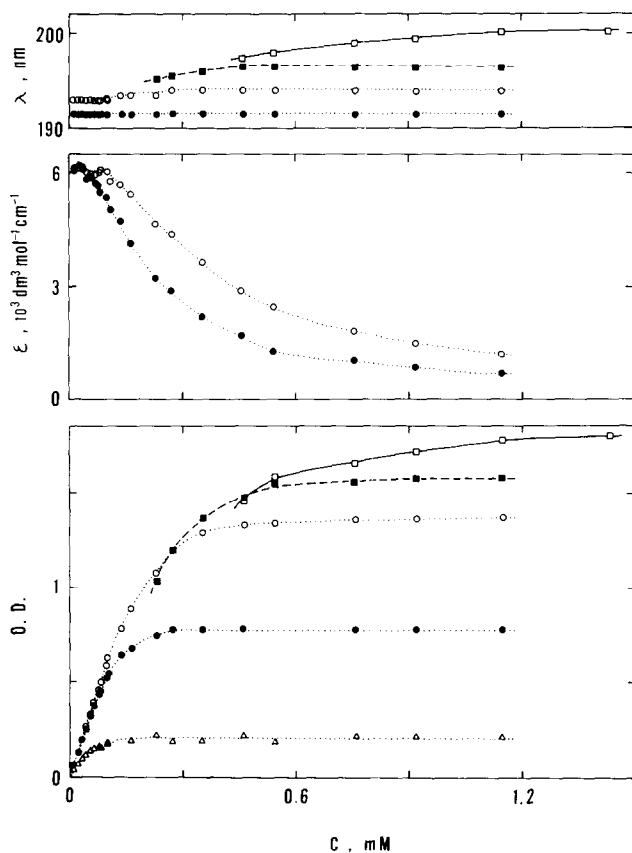


Fig. 2. Dependence of absorption bands on the concentration for dimethyloleylamine oxide in water. (top), peak position; (middle), molar extinction coefficient; (bottom), optical density. ( $\Delta$ ), 189.5 nm; ( $\bullet$ ), 191.5 nm; ( $\circ$ ), 193 nm; ( $\blacksquare$ ), 195 nm; ( $\square$ ), 197 nm.

concentration, but decrease with a further increase of surfactant concentration.

The critical concentration of 0.044 mM in water can be obtained from the molar extinction coefficient of the band at 191.5 nm, but the critical concentration from the molar extinction coefficient and the peak position of the 193.0 nm band is rather higher. This arises from the fact that the overlapping of absorption bands at longer wavelengths affects the 193.0 nm band more than the 191.5 nm band. The overlapping induces an apparent increase of its optical density beyond the critical concentration.

The band at 195.2 nm is isolated at surfactant concentrations  $> 0.23$  mM and its optical density saturates at high concentrations. Furthermore, a band at 197.4 nm appears at 0.4 mM and its optical density increases with increasing surfactant concentration. The peak position of the last band also shifts toward red at high surfactant concentrations, in spite of the constant wavelengths of the other bands.

#### *0.001 M HCl Solution*

The dilute solutions of dimethyloleylamine oxide in 0.001 M HCl exhibit a band peak at 193.5 nm with a shoulder around 191.5 nm, as seen in the absorption spectra in Fig. 1(b). These bands have a constant optical density at high surfactant concentrations, as illustrated in Fig. 3. The molar extinction coefficient of the 193.5 nm band is constant up to the critical concentration of 0.1 mM, while the peak position shifts to red at concentrations  $> 0.075$  mM.

The bands at 195.5 and 197.0 nm appear at 0.210 and 0.405 mM, respectively. They also shift to red and increase their optical densities as the surfactant concentration is increased. However, the band at 195.5 nm ceases to shift and stays at constant wavelength and constant optical density at high surfactant concentrations.

#### *0.01 M HCl Solution*

Since a strong absorption band associated with added HCl disturbs the measurement of absorption spectra of dimethyloleylamine oxide, only spectra at wavelengths  $> 197$  nm are observable. The absorption spectra are shown in Fig. 1(c), where it can be seen that there is a band in this region. The concentration dependence of this band is shown in Fig. 4. The molar extinction coefficient deviates from a constant value at surfactant concentrations  $> 0.15$  mM. Above this concentration, the wavelength of peak position shifts to red up to 100 nm, and the optical density keeps increasing.

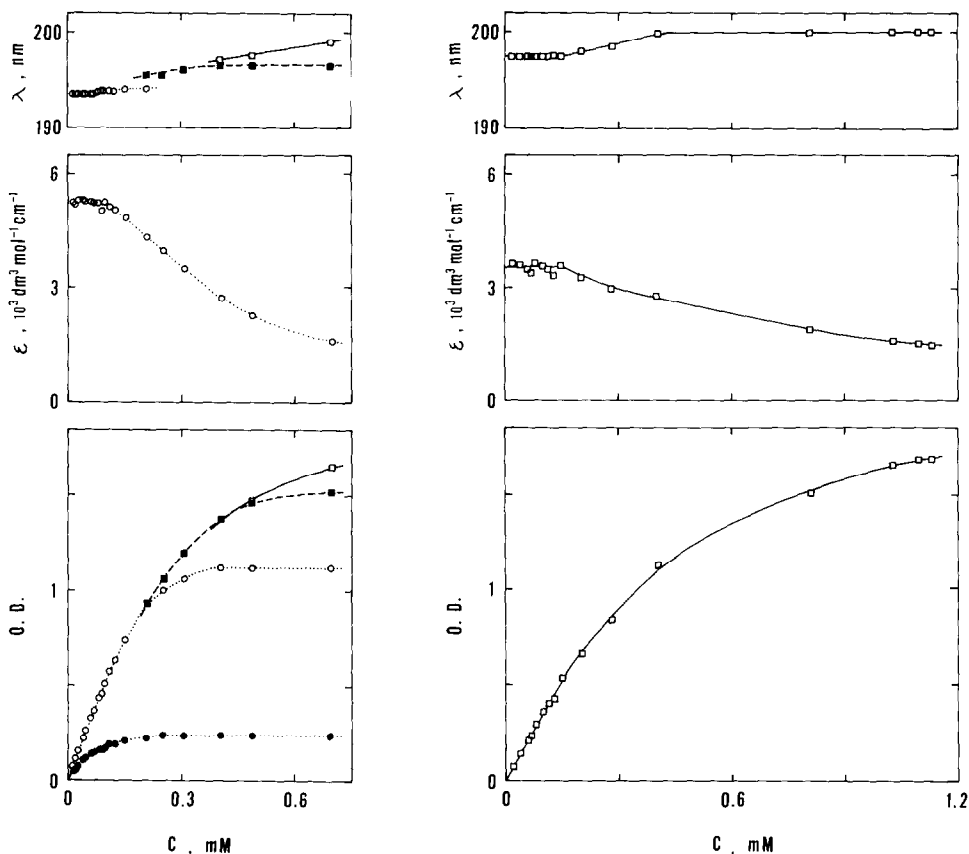


Fig. 3. Dependence of absorption bands on the concentration for dimethyloleylamine oxide in 0.001 *M* HCl solution. Symbols are the same as in Fig. 2.

Fig. 4. Dependence of absorption bands on the concentration for dimethyloleylamine oxide in 0.01 *M* HCl solution. Symbols are the same as in Fig. 2.

## DISCUSSION

There are five characteristic bands in the absorption spectra of aqueous solutions of dimethyloleylamine oxide. Their peak positions are listed in Table 1. They are independent of the presence or absence of HCl, in spite of the surfactant being fully protonated in 0.01 *M* HCl and nonionic in water. This is reasonable since the chromophore for these bands is the *cis*-alkene, which is located far from the directly protonated amine oxide group. However, the addition of HCl slightly influences the molar extinction coefficient of absorption bands because of the possible change in the environment of the chromophoric group. The pH values are given in Table 2.

Three bands at lower wavelengths for solutions in water and two bands in 0.001 *M* HCl can be assigned to the monomeric form of the surfactant,

TABLE 1

The peak position (nm) of absorption bands for aqueous solutions of dimethyloleylamine oxide in water and in the presence of HCl

Assignment	HCl (M)		
	0	0.001	0.01
Monomer	189.5		
	191.5	191.5	
	193.0–194.0	193.5–194.0	
Spherical micelles	195.2–196.5	195.5–196.5	
Rodlike micelles	197.4–200.3	197.0–199.0	197.5–200.1

TABLE 2

Critical micelle concentration (CMC, mM) of dimethyloleylamine oxide in water and in aqueous HCl solutions<sup>a</sup>

		HCl (M)		
		0	0.001	0.01
Absorption spectra	191.5 nm	0.044 (0.0014)		
	193 nm	0.095 (0.0030)	0.10 (0.0031)	
	197.5 nm			0.15 (0.0047)
Light scattering <sup>b</sup>		0.13 (0.004)	0.14 (0.0045)	
Surface tension <sup>c</sup>		0.0403 (0.00126)	0.0891 (0.00278)	0.0675 (0.00210)
pH <sup>d</sup>		6–6.5	3–3.5	2–2.5

<sup>a</sup>Numbers in parentheses give the CMC values in the unit of  $10^{-2}$  g cm<sup>-3</sup>.

<sup>b</sup>Refs [6, 7].

<sup>c</sup>Ref. [8].

<sup>d</sup>Values represent the pH range for solutions used in this experiment.

since they already appear at surfactant concentrations lower than the critical concentration. The constant optical densities of these bands at high surfactant concentrations indicate that the concentration of surfactant in a monomeric form is maintained constant in these solutions.

A band at 195–196.5 nm can be observed at surfactant concentrations

above the critical concentration and may be assigned to the surfactant species in spherical micelles. Since a constant optical density is attained at high surfactant concentrations, the concentration of this species remains constant.

At high surfactant concentrations where the concentration of rodlike micelles increases [6, 7], the band at the longest wavelength increases its optical density, shifting toward red up to 200 nm. Therefore, the band should be associated with rodlike micelles. The concentration of rodlike micelles increases with an increase of surfactant concentration.

In the rodlike micelles the chromophoric groups are arranged in such a way that they form a long sequence, so that the absorption band for the rodlike micelles is more red-shifted than that for the spherical micelles.

The CMC is detectable by the deviation of the molar extinction coefficient from Lambert-Beer's law. The CMC values obtained from the absorption spectra are given in Table 2 and compared with those from light scattering [6, 7] and surface tension [8] measurements.

It should be noted that the absorption band at 197.5 nm observed at surfactant concentrations  $< 0.15$  mM could have resulted artificially from incomplete compensation for the effect of the strong band in 0.01 M HCl. If this was the case, the molar extinction coefficient at 197.5 nm could not be assigned to that of rodlike micelles. Nevertheless, the CMC value may be derived correctly from the molar extinction coefficient of this band, as shown in Fig. 4.

The CMC obtained from the band at 191.5 nm is close to that obtained from surface tension measurements. However, the CMC values from bands at 193 and 197.5 nm are rather high and similar to those from light scattering measurements. It is likely that the CMC for spherical micelles differs from that for rodlike micelles: the CMC determined from surface tension measurements is related to the formation of spherical micelles and that determined from light scattering reflects the formation of rodlike micelles.

Surface tension behavior can detect the formation of spherical micelles, which should take place at a rather lower concentration than the formation of rodlike micelles.

Since dimethyloleylamine oxide can further associate into rodlike micelles at a surfactant concentration only slightly higher than the CMC for spherical micelles, the reduced intensity of light scattering is insensitive to the existence of a small amount of spherical micelles. In fact, the amount of spherical micelle is 0.05–0.09 mM and that of monomer is 0.04–0.09 mM.

As an example which demonstrates the deviation of the CMC for rodlike micelles from that for spherical micelles, it is reported that dodecyltrimethylammonium bromide in 2 and 3 M NaBr solutions undergoes a concentration-dependent two-step micellization [9]. The first and second CMCs differ by a factor as large as 15–22. If the difference in two CMCs is small, as we are suggesting in the case for dimethyloleylamine oxide, it

could often be overlooked. However, the different absorption bands, attributed to spherical and rodlike micelles in this work, suggest the existence of both micelles.

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