Determination of Critical Micelle Concentration of Detergent in Non-polar Solvent by Ultraviolet Absorption Spectra[*]

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Micelle formation of detergents in nonpolar solvents has been recently ascertained by many authors[1-4]. However, the existence of a concentration for micelle formation (CMC) in non-polar solvents is now questionable. Singleterry et al. have suggested the existence of the CMC of alkyl aryl carboxylate and sulfonate in benzene[3,5]. The present author has pointed out the existence of the apparent CMC in benzene solution of higher alkyl ammonium carboxylate by solubilization of water[6]. Pink et al. have not recognized the CMC in the case of a non-polar solution of a metal soap[4]. It seems, therefore, that the existence of the CMC in a nonpolar solvent is worth investigating by other methods and materials[**].

In order to make a further study on the existence of the CMC in a non-polar solvent, the concentration dependence of the ultraviolet absorption spectrum in cyclohexane solution of detergent was studied in the present investigation. The result is compared with that of solubilization of water, and the existence of the CMC is discussed. The determination of the CMC by the change of the ultraviolet spectra was originally made by Harkins et al. with aqueous solution[7]. But the behavior of the change of the spectra are different from that of this paper.

Experimental

Material: Dodecyl ammonium benzoate and octadecyl ammonium benzoate were used as detergents. They were prepared by heating the mixture of higher amine with an equivalent amount of benzoic acid at about 70°C. Boiling points of dodecylamine and octadecylamine used here were 131-133°C/15 mm and 188-190°C/4 mm, respectively. Benzoic acid showed the melting point of 120-121°C. Dodecyl ammonium benzoate was used without further purification, because it was soluble in any solvent. Octadecyl ammonium benzoate was recrystallized from petroleum ether. Both were dried *in vacuo* over anhydrous calcium chloride. The melting point of the former was 40-42°C and that of the latter was 64.0-65.5°C. Cyclohexane was purified until it showed no absorption in the range longer than 230 mμ and then dried and redistilled.

Method: Ultraviolet absorption spectra were measured with Shimazu photoelectric spectrophotometer. In order to gain the absorbance of higher accuracy in the concentration range used here, all measurements were carried out with use of a quartz cell of a light path of 1.0 mm, which was obtained by means of the insertion of a quartz block of 9.0 mm thick into a 10.0 mm quartz cell. The absorption spectra of cyclohexane solutions of dodecyl ammonium benzoate and of octadecyl ammonium benzoate were observed in the range from 230 mμ to 300 mμ with varying concentration of detergent from 1×10^{-3} to 4×10^{-2} mole/l. The point-by-point absorbance measurements were carried out at intervals of 0.5 mμ at the neighborhood of the peak. Each solution was made by dilution of a prepared stock solution. Absorption measurement was carried out immediately after every dilution.

The limiting amount of water solubilized into cyclohexane solutions of dodecyl ammonium benzoate and of octadecyl ammonium benzoate was determined at various concentrations of detergent. The method of the measurement was similar to that of the previous paper[6]. The temperature was kept at 20±2 and 30±2°C in both measurements of spectrum and solubilization.

Results and Discussion

Existence of CMC: Absorption peaks appeared at 263, 270 and 276.5-277 mμ on the ultraviolet spectra of dodecyl ammonium benzoate and of octadecyl ammonium benzoate in cyclohexane. These absorption peaks are corresponding to the C-band of benzoic acid in cyclohexane, which has

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[*] This paper was read at the Symposium on Colloid and Surface Chemistry held on November 18, 1956 at Tokyo University under the auspices of the Chemical Society of Japan.

[1] L. Arkin and C. R. Singleterry, *J. Am. Chem. Soc.*, **70**, 3965 (1948).

[2] M. van der Waarden, *J. Colloid Sci.*, **5**, 448 (1950).

[3] S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **7**, 453 (1952).

[4] S. M. Nelson and R. C. Pink, *J. Chem. Soc.*, **1952**, 1744.

[5] S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **10**, 139 (1955).

[6] A. Kitahara, This Bulletin, **28**, 234 (1955); **29**, 15 (1956).

[**] C. C. Addison and C. G. L. Furmidge have recently reported a CMC of alkylpyridinium iodides in xylene (*J. Chem. Soc.*, **1956**, 3229).

[7] W. D. Harkins, H. Krizek and M. L. Corrin, *J. Colloid Sci.*, **6**, 576 (1951).

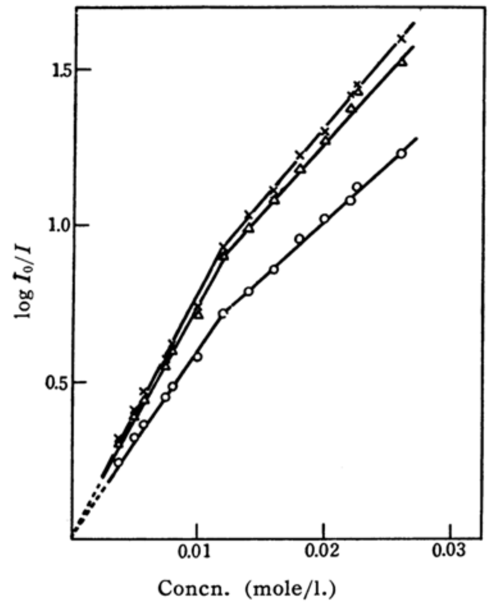

Fig. 1. Plot of absorbance (log I_0/I) *vs.* concentration in cyclohexane solution of dodecyl ammonium benzoate at 30±2°C. —△—, for 263 mμ; —×—, 270 mμ; —○—, for 276.5 mμ.

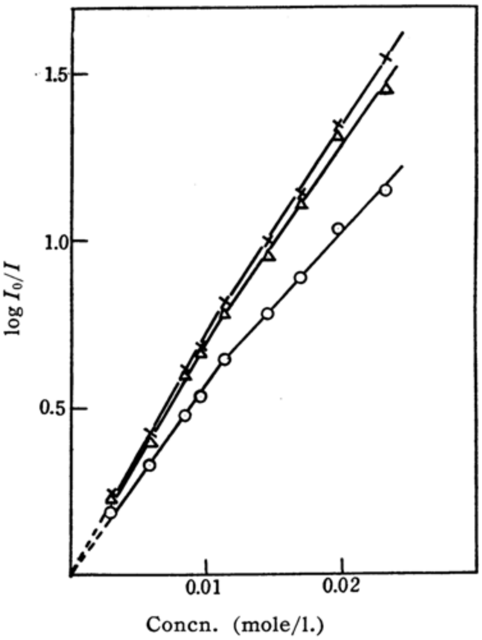

Fig. 3. Plot of absorbance (log I_0/I) *vs.* concentration in cyclohexane solution of dodecyl ammonium benzoate at 20±2°C. —△—, for 263 mμ; —×—, 270 mμ; —○—, for 277 mμ.

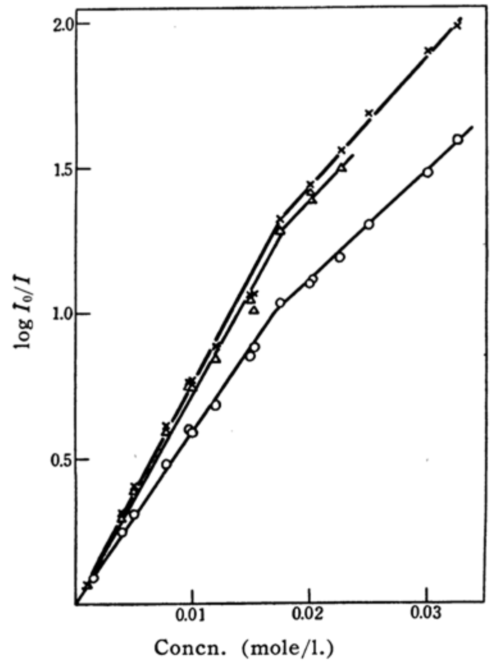

Fig. 2. Plot of absorbance (log I_0/I) *vs.* concentration in cyclohexane solution of octadecyl ammonium benzoate at 30±2°C. —△—, for 263 mμ; —×—, 270 mμ; —○—, for 276.5 mμ.

the peaks of 276 and 284 mμ[8]. No shifts were recognized in each absorption peak with varying concentration. The concentration dependence of the absorbance (log I_0/I) of each peak at 30 and 20°C was depicted in Figs. 1, 2 and 3. The concentration was described in terms of the molecular weight of a monomer of alkyl ammonium benzoate. It is readily recognized from the figures that the plots of the absorbance against the concentration consist of two linear parts within the concentration range studied in this experiment. This behavior was not very clear for the peaks of 263 and of 270 mμ of the solution of dodecyl ammonium benzoate at 20°C. The extrapolation of the linear parts of the lower concentration range passes the origin of the coordinates. That is, Beer's law is valid in this concentration range. It is, therefore, thought that the solute exists as monomeric molecule within this range. The break in this linear line at a certain concentration shows us that the state of the solute might be changed above this concentration. In the case of the cyclohexane solution of benzoic acid, no breaks appeared in the

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[8] H. E. Ungnade and R. W. Lamb, *J. Am. Chem. Soc.*, **74**, 3789 (1952).

TABLE I

CMC OBTAINED FROM SOLUBILIZATION (A) AND CONCENTRATION OF BREAK IN ABSORBANCE LINE (B)

		A (mole/l.)	B (mole/l.)
Dodecyl ammonium benzoate	30°C	0.012±0.002	0.012±0.001
〃 〃 〃	20°C	0.015±0.002	0.012±0.001
Octadecyl ammonium benzoate	30°C	0.014±0.002	0.018±0.001

TABLE II

THE VALUES OF ε_s, ε_m AND C_s (mole/l.)

	Dodecyl ammonium benzoate						Octadecyl ammonium benzoate		
Temperature	30°			20°			30°		
Wave length (mμ)	ε_s	ε_m	C_s	ε_s	ε_m	C_s	ε_s	ε_m	C_s
263	73_5	440	0.013	670	610	0.014	730	440	0.018
270	77_5	460	0.013	700	630	0.013	770	440	0.017
276.5-277	580	370	0.013	560	450	0.012	56_5	370	0.018

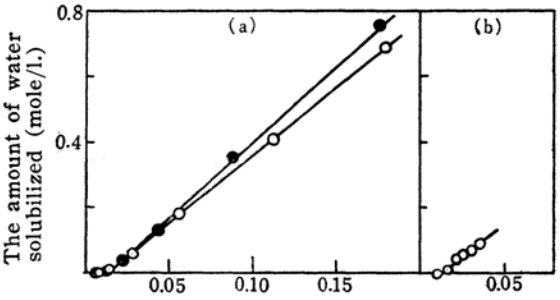

Fig. 4. The amount of water solubilized into the cyclohexane solution.

(a) —○—, for dodecyl ammonium benzoate at 30±2°C.
—●—, for dodecyl ammonium benzoate at 20±2°C.
(b) —○—, for octadecyl ammonium benzoate at 30±2°C.

absorbance lines for any peak of 276 and 284 mμ.

The relation between the limiting amount of water solubilized into detergent solutions and the concentration of detergent is shown in Fig. 4. It is seen in the figure that the relation is linear within the concentration range studied, though the linearity is somewhat ambiguous in the case of octadecyl ammonium benzoate because of its lower solubility. The concentration extrapolated to zero solubilization might be assumed to be the CMC6). The values of the CMC (A) obtained thus are listed in Table I. On the other hand, the concentrations corresponding to the break of absorbance lines (B), which are obtained from Figs. 1, 2 and 3 are also shown in the same table. The comparison of the values of B with the corresponding values of A shows us that both are in agreement with each other within the experimental error. Hence it will be reasonable to assume that the break in the absorbance line shows the initiation of micelle formation and that the concentration of the break is the CMC*. It will be, therefore, known that the measurement of the ultraviolet absorption spectrum has also ascertained the existence of the CMC.

Monomer Concentration: The equation $\log I_0/I=\varepsilon Cl$ may be used above the CMC. In this case, it is assumed that the overall extinction coefficient (ε) above the CMC can be expressed as follows:

$$\varepsilon=n_s\varepsilon_s+n_m\varepsilon_m, \tag{1}$$

where n is mole fraction and ε the extinction coefficient, subscripts s and m representing a monomeric molecule and a molecule participating in micelle formation. If the concentration of a monomeric molecule above the CMC is shown by C_s, $n_s=C_s/C$ and $n_m=(C-C_s)/C$, where C is the total concentration described in terms of the molecular weight of a monomer. Then formula (1) may be rewritten as follows:

$$\varepsilon C=\varepsilon_m C+C_s(\varepsilon_s-\varepsilon_m). \tag{2}$$

As seen in Figs. 1, 2 and 3 the linear relation is obtained between $\log I_0/I$ and C in the range above the CMC. Accordingly, ε_m can be estimated from the slope of the straight line above the CMC and $C_s(\varepsilon_s-\varepsilon_m)$ from the intercept on the ordinate by extrapolating it. ε_s is obtained from the slope of the linear part below the CMC. Hence C_s can be calculated. The values of ε_s, ε_m and C_s obtained for each absorption peak are tabulated in Table II.

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* It was presented at the same Symposium by H. Sasaki, H. Okuyama and S. Saito of Osaka University that the extinction coefficient of cetyl pyridinium chloride in the aqueous solution begins to diminish sharply at the CMC.

ε_m is independent of the concentration as the result of the linearity of the absorbance curve above the CMC. As Harkins et al. pointed⁷⁾, the result just mentioned may be taken to indicate that the micelle size is constant in this range or that the transition probability of a molecule participating in micelle formation is not influenced by the micelle size. As the matter of course, the values of C_s are independent of the concentration and equal to the CMC from the assumption of the formula (1). This constancy of C_s corresponds to the case of higher aggregation of the results calculated from the law of mass action by Singleterry et al.³⁾ It is seen in Table II that the values of C_s obtained for separate peaks are all equal within the experimental error. This suggests that the assumption of the formula (1) might be reasonable. The effect of temperature on the CMC was recognized with difficulty in the case of dodecyl ammonium benzoate.

Summary

The concentration dependence of the absorbance for the ultraviolet absorption spectra was measured for cyclohexane solutions of dodecyl ammonium benzoate and of octadecyl ammonium benzoate at 20±2 and 30±2°C. The break has been observed in the absorbance-concentration relationship. On the other hand, the relation between the amount of water solubilized into solutions and the concentration of the detergent showed us the values of the CMC. The concordance found between the value corresponding to the break of the absorbance and the assumed CMC obtained from solubilization makes the existence of the CMC more probable. The concentration of the monomeric molecule and the molar extinction coefficient of the molecule participating in micelle formation were calculated with use of a simple assumption.

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