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The Determination of the CMC of Surfactants in Some Organic Solvents

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Extra absorption spectra appeared when 7,7,8,8-tetracyanoquinodimethane (TCNQ) was solubilized into surfactant organic solvent solutions above the critical micelle concentration (CMC). It was found also that extra absorption spectra appeared when iodine was solubilized into surfactant organic solvent solutions above the CMC. In the former case, the extra absorption spectra are attributed to TCNQ anion radical salts formed between TCNQ and the surfactants. In the latter, the extra absorption spectra are due to charge-transfer interactions of iodine with the surfactants. The intensity of the absorption bands increased with the concentrations of the surfactant. The values of the CMC of the surfactants were determined from this spectral change. The CMC values obtained by the TCNQ solubilization method were larger than those obtained by the iodine solubilization technique. The difference in the CMC between the two methods was interpreted in terms of the difference in solubility and charge-transfer power to the organic solvent between iodine and TCNQ, and the difference in type of electron transition, that is, $n(D)\rightarrow\sigma(A)$ or $n(D)\rightarrow\pi(A)$.

The critical micelle concentrations (CMC's) of oil-soluble surfactants in organic solvents have frequently been determined in the past by three different methods, by the light-scattering method, by the vapour-pressure depression, and by the solubilization technique. As these methods are not easy, a more convenient and simple method is desirable.

In our previous paper,[1] we reported that when TCNQ, a well-known strong electron aceeptor, was solubilized into surfactant aqueous solutions above the CMC, a characteristic color appeared. This phenomenon was applied to the determination of the CMC of various surfactants in aqueous solutions.

Recently, we found that this solubilization is also useful for determining the CMC of oil-soluble surfactants in various organic solvents, for the TCNQ solubilized in surfactant organic solutions above the CMC has characteristic absorption spectra, probably because of the TCNQ anion radical formed by the charge transfer from the surfactant to the TCNQ.

The CMC's of surfactants have also been determined by an iodine-solubilization technique[2] in organic solvents.

In this paper, we will report on the characteristics of the charge-transfer solubilization of TCNQ into surfactant micelle in organic solvents and will compare our results with those of other methods.

Experimental

The surfactants used in this experiment were dodecyl pyridinium iodide and Aerosol OT.

Dodecyl pyridinium iodide (DPI) was synthesized by the usual method[3] in our laborotory; its purity was confirmed by the surface-tension and electroconductance methods.

Aerosol OT (sodium dioctyl sulfosuccinate) was supplied from the Nikko Chemical Co., and this sample was purified as follows. It was dissolved in methanol, and the undissolved material was excluded by means of a fine glass filter and subsequent drying.

TCNQ was synthesized according to a procedure described previously.[4] It was purified by five recrystallizations in acetonitrile. The crystals thus obtained had a rust-colored, flasky form; their purity was confirmed by elementary analysis and by studying the melting point.

Iodine of a G.R. garde was purified by sublimation.

Benzene, cyclohexane, *n*-heptane, and carbon tetrachloride were purified according to the procedure of Kitahara and Kon-no.[5] Chloroform, methyl alcohol, and acetonitrile were purified in the usual way.[6]

For ultraviolet, visible and near-infrared spectra studies, the TCNQ solutions were prepared as follows: a known quantity of the TCNQ was dissolved in a measured volume of various organic solvents (the TCNQ concentartion was about 10^{-4} mol/l), and then this solution was used as the stock solution of the TCNQ (A). The stock solution of the surfactant (B) contained a known concentration of the surfactant well above its CMC. By diluting the B solution with the A solution, a series of concentrations of the surfactant could be obtained, each with the same concentration of TCNQ. This series had to include concentrations above and below the CMC to be determined. All the solutions were prepared at room temperature.

Iodine-surfactant solutions were also prepared in the same manner as the TCNQ-surfactant solutions. In this case, the iodine concentration was kept at 5×10^{-4} mol/l for all the solutions.

The absorption spectra were measured by using a Hitachi Spectrophotometer (Model EPS-2).

Results and Discussion

Interaction between DPI and TCNQ. The absorption spectra of TCNQ solubilized in a chloroform solu-

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[1] a) S. Muto, K. Deguchi, K. Kobayashi, E. Kaneko, and K. Meguro, *J. Colloid Interface Sci.*, **33**, 475 (1970). b) S. Muto, K. Deguchi, Y. Aono, Y. Shimazaki, and K. Meguro, *ibid.*, **37**, 109 (1971). c) S. Muto, K. Deguchi, Y. Aono, Y. Shimazaki, and K. Meguro, This Bulletin, **44**, 2087 (1971).

[2] S. Ross and J. P. Oliver, *J. Phys. Chem.*, **63**, 1671 (1959).

[3] K. Meguro and T. Kondo, *Nippon Kagaku Zasshi*, **80**, 818 (1959).

[4] D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

[5] K. Kon-no and A. Kitahara, *J. Colloid Interface Sci.*, **33**, 124 (1970).

[6] J. A. Riddick and E. E. Toops, "Organic Solvent," 2nd ed. (Technique of Organic Chemistry Vol. 7), Interscience (1955), pp. 410, 333, 435.

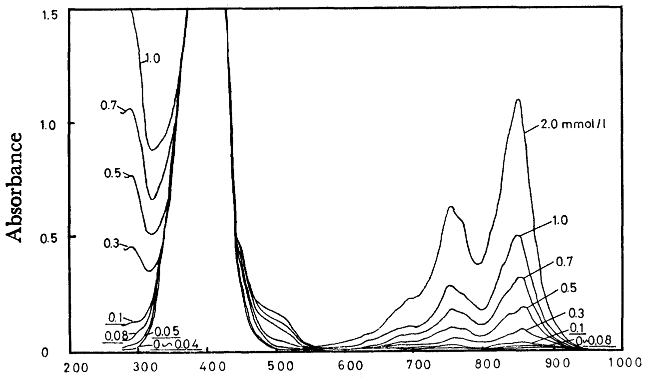

Fig. 1. Visible absorption spectra of TCNQ in DPI chloroform solutions.
TCNQ Concentration: 0.5 mmol/l

tion of DPI are shown in Fig. 1. As is shown in Fig. 1, the spectra at low surfactant concentrations have no appreciable absorption of the TCNQ anion radical (the underlined numbers show the concentration of the surfactant below the CMC). When the concentration reaches a certain value, the spectra change their form rapidly; new bands appear at 480, 680, 750, and 850 mμ, and the optical densities of these absorption bands increase with the concentration of the surfactant. The absorptions at 680, 750, and 850 mμ have already been confirmed as those of the TCNQ anion radical by many authors,[7] but the absorption at 480 mμ does not belong to the anion radical; this absorption band seems to be caused by charge-transfer interaction between the surfactant and the TCNQ. The rapid increase in optical densities at 680, 750, and 850 mμ above some surfactant concentration suggests a rapid increase in the amounts of TCNQ anion radicals in these systems. The reason for the rapid increase in the TCNQ anion radicals is considered to be as follows: it is known that the surfactants make inverted micelles at the CMC in organic solvents. Therefore, at concentrations above the CMC, the surfactant molecules concentrated in the micelle interact with the TCNQ and produce a kind of ionic charge-transfer complex; then the resulting TCNQ anion radicals which have ionic properties are solubilized in the hydrophilic inside of the inverted micelles. From this fact, it was recognized that the surfactant concentration at which the rapid increase in the absorption of the TCNQ anion radical occurred would correspond to the CMC value in organic solvents.

In Fig. 2, the optical density of the spectra of the TCNQ anion solubilized in DPI chloroform solutions is plotted against the surfactant concentrations. The CMC are given by an intercept of the resulting two lines. The CMC's of different surfactants in various organic solvents obtained by this method are summarized in Table 1.

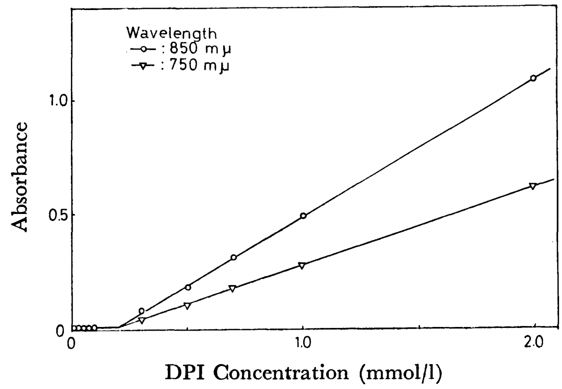

Fig. 2. Relationship between the absorbance and concentration of DPI chloroform solutions.

Table 1. CMC values of surfactants in various organic solvents (TCNQ method, at 20°C)

Surfactant	Solvent	CMC (mmol/l)	Wavelength (mμ)
DPI	Chloroform	0.2	850
	Benzene	0.07	850
	Methanol	—	
Aerosol OT	Chloroform	0.4	850
	Benzene	2.0	850
	Carbontetrachloride	0.6	277
	Methanol	—	

Ralston *et al.*[8] have found that dodecyl ammonium chloride in pure water makes a micelle and exhibits a clear break point in conductance-concentration curve at the CMC, but this break point does not become clear in suitable methyl-alcohol mixtures or in pure methyl alcohol. In these alcohol solutions, the dodecyl ammonium chloride behaves like a normal electrolyte over the entire range of concentration. They explain this fact by assuming a breakdown of the micelle.

This evidence was also confirmed by the spectra change between TCNQ and DPI in methyl alcohol solutions, in which the surfactant can not exist in the micelle form. Figure 3 shows the spectra of TCNQ in a methyl alcohol solution of DPI. The most characteristic feature of the spectra lies in the fact that the optical densities of the absorption peaks at 680, 750,

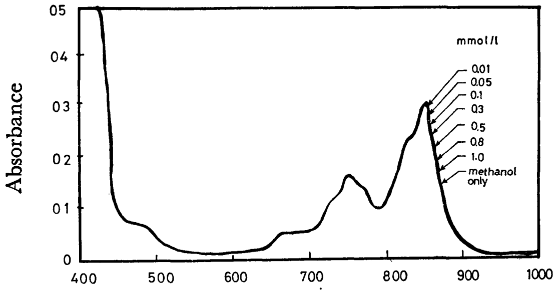

Fig. 3. Absorption spectra of TCNQ in DPI methanol solutions.

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[7] a) S. R. Melby, R. J. Harder, W. R. Heltler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962). b) A. Rembaum, A. M. Hermann, F. E. Stewart, and F. Gutmann, *J. Phys. Chem.*, **73**, 513 (1969). c) Y. Iida, This Bulletin, **42**, 71 (1969). d) Y. Iida, *ibid.*, **42**, 637 (1969).

[8] a) A. W. Ralston and D. N. Eggenberger, *J. Phys. Chem.*, **52**, 1494 (1948). b) A. W. Ralson and C. W. Hoerr, *J. Amer. Chem. Soc.*, **68**, 851 (1946).

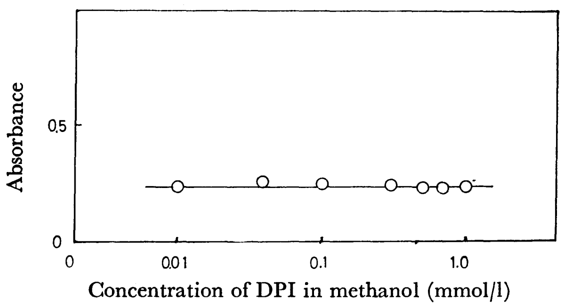

Fig. 4. Relationship between the absorption and concentration of DPI methanol solutions.

and 850 mμ, which are caused by the interaction between the TCNQ and the oxygen atom of methyl alcohol, are not influenced at all by the amounts of DPI. The optical density of TCNQ in DPI methyl alcohol solutions, plotted against the concentrations of DPI, are shown in Fig. 4, which shows more clearly that the optical densities do not change, but keep a constant value with the concentration of DPI. This can be explained by the breakdown of the micelle in the methyl alcohol solution.

Recently, Mukerjee *et al.*[9] found that a new band appeared at 290 mμ in a DPI micellar aqueous solution and a DPI chloroform solution. They reported that this band was due to the formation of a charge-transfer complex between the surfactant micelle and iodine, and also reported that this band could not be observed below the CMC.

We also confirmed that the appearance of the 290 mμ band can be used to as a means of recognizing the micelle formation of DPI in an organic solvent. When DPI was dissolved in chloroform, benzene, and water, a charge-transfer band was observed at 290 mμ. In the DPI methyl alcohol solution, however, the band was not found. This fact confirms that micelle formation does not occur in methyl alcohol solutions.

Interactions between Aerosol OT and TCNQ or Iodine. The absorption spectra of TCNQ solubilized in a chloroform solution of Aerosol OT are shown in Fig. 5. The shape of this absorption spectra is almost the same as that obtained in Fig. 1. This fact is particularly interesting. In this case, no remarkable absorption could be found in the spectra below the CMC, but new bands were observed at 480, 680, 750, and 850 mμ, above the CMC, and the intensities of these bands increased rapidly above the CMC of the surfactant. The surfactant concentration at which the rapid increase in optical densities of the TCNQ anion radical occurred would correspond to the CMC values in organic solvents. Indeed, the CMC value of Aerosol OT in benzene obtained by this method agrees with the data measured by Kon-no and Kitahara[10] (see Table 2). The CMC values of Aerosol OT in different organic solvents are summarized in Table 1.

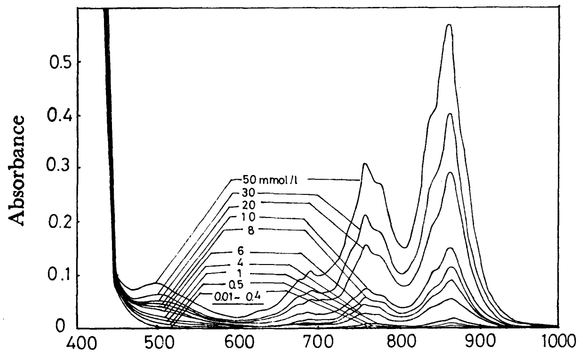

Fig. 5. Visible absorption spectra of TCNQ in Aerosol-OT chloroform solutions.
TCNQ concentration: 0.5 mmol/l

Table 2. Comparison of the CMC of Aerosol OT benzene solution (mmol/l)

Method	Light scattering[a]	Depression of[a] vapour pressure	TCNQ method
CMC	2.8	2.3	2.0

a) K. Kon-no, and A. Kitahara, *Kogyo Kagaku Zasshi*, **68**, 2058 (1965).

The data in Table 1 suggest that the micelle formation is influenced by the nature of the solvent; that is, the CMC values increase with the polarity of the solvent (see Table 3). The values in Table 3 agree with the results given by Kitahara and Kon-no.[10]

Table 3. The relationship between the CMC of surfactants and dielectric constant of organic solvents (Aerosol OT)

TCNQ method Solvent	Dielectric constant	CMC (mmol/l)
Benzene	2.27	2.0
Carbontetrachloride	2.24	0.6

Iodine method Solvent	Dielectric constant	CMC (mmol/l)
Benzene	2.27	0.9
Carbontetrachloride	2.24	0.3
Cyclohexane	2.01	0.2

Ross *et al.*[2] have described that iodine dissolved in benzene has a band at 490 mμ in its spectrum, but this band decreases upon the addition of a surfactant to this system and a new band appears at 360 mμ, the optical density of which increases with the concentration of the surfactant. They determined the CMC's of many surfactants in nonaqueous media by using the optical density of the iodine spectrum at 360 mμ.

When Aerosol OT was dissolved in various iodine solutions, such as benzene, cyclohexane, chloroform, and carbon tetrachloride, a new iodine band appeared; this band had a slight dependency on the character of the organic solvent. The ordinary band of iodine in an organic solvent, and the new band appearing after the addition of the surfactant, are listed in Table 4. A typical change in the spectrum of iodine in a cyclo-

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[9] a) A. Ray and P. Mukerjee, *J. Phys. Chem.*, **70**, 2138 (1966). b) P. Mukerjee and A. Ray, *ibid.*, **70**, 2144 (1966).

[10] K. Kon-no and A. Kitahara, *Kogyo Kagaku Zasshi*, **68**, 2058 (1965).

Table 4. CMC values of Aerosol OT in organic solvents (iodine method at 20 °C)

Surfactant	Solvent	CMC (mmol/l)	New band (wavelength) mμ	Original band (wavelength) mμ
Aerosol OT	Cyclohexane	0.2	386	522
	Chloroform	0.24	272	510
	Benzene	0.9	390	490
	Carbontetrachloride	0.3	280	520

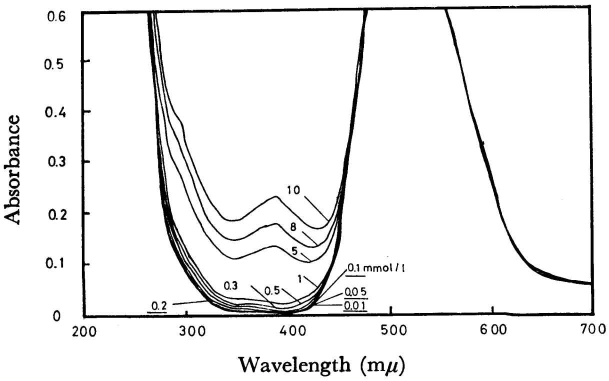

Fig. 6. Visible absorption spectra of I_2 in Aerosol OT cyclohexane solutions.
I_2 concentration: 1 mmol/l

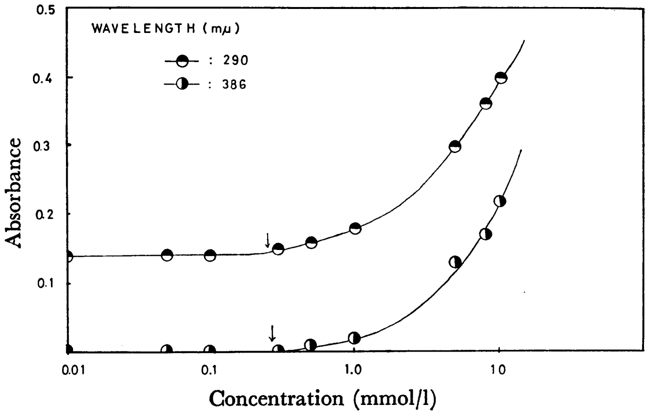

Fig. 7. Relationship between the absorbance and concentration of Aerosol OT cyclohexane solutions.

hexane solution upon the addition of a surfactant is shown in Fig. 6; the figure indicates that a new band appears at 386 mμ and increases in intensity with the concentration of the surfactant. In Fig. 7 the optical density of iodine in Aerosol OT cyclohexane solutions is plotted against the concentrations of Aerosol OT. In this figure, the value of the CMC is given by the change in the slope. The CMC's of several surfactants obtained by this iodine-solubilization technique are summarized in Table 4.

A comparison of the CMC values obtained by the TCNQ solubilization method with those obtained by the iodine method shows that the CMC values estimated by the iodine method are smaller than those obtained by the TCNQ method. At present, although we can not explain exactly why the difference occurs, it may be considered to be that the interaction between the TCNQ and the surfactant is a n(D)→π(A) transition, while the interaction between the iodine and the surfactant is a n(D)→σ(A) transition.

Strong *et al.*[11] have previously reported that the transition energy, ($h\nu_{ct}$), of the n(D)→σ(A) electron transition between a lower alcohol and iodine is about 5 eV.

The $h\nu_{ct}$ value found between Aerosol OT and iodine in cyclohexane and carbon tetrachloride is about 4.6 eV. This value agrees roughly with the value of 5 eV obtained by Strong *et al.* Accordingly, it may be concluded that the transition between Aerosol OT and iodine in cyclohexane and carbon tetrachloride is a n(D)→σ(A) transition.

On the other hand, the interaction between the TCNQ and the nitrogen atom or oxygen atom in the surfactant can be considered to be a n(D)→π(A) transition. From these results, the difference in the CMC between the two methods may originate from the difference in the type of transition between the TCNQ and iodine molecule, and from the difference in solubility to organic solvents.

The ionization potential of organic solvents can be

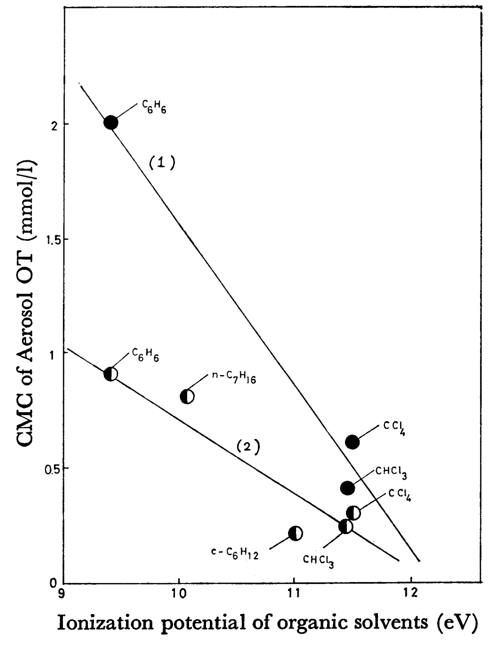

Fig. 8. Relationship between the CMC of Aerosol OT and ionization potential of organic solvents.
●: n–π type ◐: n–σ type

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[11] R. L. Strong, S. J. Rand, and J. A. Britt, *J. Amer. Chem. Soc.*, **82**, 5053 (1960).

considered to be a measure of the relative donor capacity of organic solvents. The plots of the CMC of Aerosol OT *vs.* the ionization potential of organic solvents are shown in Fig. 8, which suggests that the CMC values obtained by the n(D)→π(A) transition are larger than those obtained by the n(D)→σ(A) transition. In Fig. 8, Line (1) is the plot of CMC estimated by the TCNQ method against the ionization potential, while Line (2) is the plot of the CMC estimated by the iodine method against the ionization potential, as the TCNQ method depends on the n(D)→π(A) transition, and the idoine method, on the n(D)→σ(A) transition.

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