Determination of Critical Micelle Concentration of Surfactant by Ultraviolet Absorption Spectra

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Abstract

A method was investigated for determining the critical micelle concentration (CMC) by the shift of absorption maxima when an organic compound (I) with ultraviolet absorption was added to an aqueous solution of a surfactant. When I was added to the surfactant solution at higher concentrations (above the CMC), λ_{max} of I approached the value in *n*-octane, since I was solubilized in the hydrocarbon atmosphere of the inner part of the surfactant micelle. At lower concentrations (below the CMC), however, I was present in the water phase and λ_{max} approached the value in water. The curve of λ_{max} vs. surfactant concentration declined from the high concentration values as the CMC was approached and at the CMC, the curve broke upward sharply. Then, it rose for some time and approached the value in water. N,N′-diethylaniline was used because it exhibited larger shifts of λ_{max}. The standard amount used was 0.002 ml/3–10 ml of aqueous solution of the surfactant. The CMC values obtained agreed with those obtained by the electric conductivity method, dye adsorption method and light scattering method, for surfactants such as tetradecyldimethylbenzylammonium chloride, sodium dodecyl sulfate and polyoxyethylene cetyl ether.

Introduction

Many methods have been developed for determining critical micelle concentration (CMC) and more than 30 are known including the electric conductivity method, the dye adsorption method, the solubilization method, the surface tension method, etc. (1,2). The author has investigated surface active properties of aqueous solutions of binary systems consisting of a surfactant and a metal soap (3–6). In most cases the conventional methods did not give satisfactory results when applied to measure the CMCs of the mixed systems. The methods for measuring CMC can be classified into two basic types. The first are methods which detect abrupt changes in the monomolecular concentration, such as the surface tension and electric conductivity methods. The second type detects micelles and includes the dye adsorption method, the solubilization method, the light scattering method, etc. In mixed systems of surfactants, the monomolecular concentration changes continuously in the vicinity of the CMC (7), so that the first type of methods is not feasible; any of the second type are feasible in theory since they detect the appearance of mixed micelles. Although the dye adsorption method is simple, in practice color and fluorescence variations are often indistinct, especially in the case of a crude sample or a mixed system. In the light scattering and solubilization methods, problems arise concerning the measuring time, equipment required, etc. Therefore, the UV absorption spectrum method was investigated in comparison to the above mentioned methods.

Applications of the UV absorption spectrum to micellar phenomena have been reported. Harkins et al. (8) determined the CMC from variations in molar extinction coefficient and optical density at specified wave lengths for alkyl pyridinium iodide. Kitahara (9) synthesized alkyl ammonium benzoate and determined the CMC by utilizing the fact that the curve of optical density at specified wave lengths versus concentration breaks at the CMC values in a nonpolar solvent. Riegelman et al. (10) measured the UV absorption spectra of several compounds such as ethylbenzene and naphthalene solubilized in aqueous solutions of dodecylamine hydrochloride, potassium laurate, etc., also the spectra of the same solubilizates in several solvents such as water and *n*-octane. From a comparison between their fine structures, he inferred the positions in the micelles where solubilization occurred. Donbrow and Rhodes (11) and Mulley and Metcalf (12) have reported the solubilization conditions of benzoic acid, etc., and their interaction with polyoxyethylene chain, by measuring the ultraviolet absorption spectrum, in connection with a study of adverse effects of surfactants on the antibacterial action of disinfectants.

In this study, the UV absorption spectra were measured with various concentrations of an aqueous solution of surfactant containing an UV absorbent organic compound, such as benzene, N,N′-diethylaniline (DEA) and the shifts of λ_{max} (the wave length where the maximum absorption occurred) were examined. The λ_{max} of the solubilizate at higher surfactant concentrations in aqueous solution (above the CMC) were almost the same as λ_{max} of the same solubilizates in the hydrocarbon. At lower concentrations (below the CMC) they were almost the same as λ_{max} in water. On the curve of λ_{max} vs. concentration (logarithm), there was a very distinct break. The concentration at the break agreed well with the CMC value determined by the dye adsorption and other methods. This, therefore, can serve as a method for determining the CMC of many surfactants; the method is simple and accurate.

Experimental Procedures

Materials

Tetradecyldimethylbenzylammonium Chloride. High purity commercial tetradecyldimethylbenzylammonium chloride (TDMBAC) was recrystallized four times from a solution of methanol, acetone and petroleum ether at −20 C. In the third and fourth recrystallizations, water equivalent to about one molecule of the water of crystallization was added.

Analysis. Calculated for $C_{14}H_{29}(CH_3)_2C_6H_5CH_2\text{-}NCl \cdot H_2O$: C, 71.56; H, 11.49; N, 3.63; Cl, 9.18. Found: C, 72.02; H, 11.69; N, 3.61; Cl, 9.12.

Sodium Di-2-ethylhexylsulfosuccinate. High purity commercial sodium di-2-ethylhexylsulfosuccinate (SDEHSS) was dissolved in acetone. The yellow-colored impurity insoluble in acetone (0.6%, water soluble) was removed by centrifugation and a colorless transparent solution was obtained. This solution was evaporated to dryness, the residue dissolved in

TABLE I
The Shift of λ_{max} of Organic Compounds and Attendant Data for the UV Method

Compound	Solubility in H_2O[a]	λ_{max} $(m\mu)$[b]				Maximum shift $(m\mu)$		Position of solubilizate in micelle[d]
		H_2O	SDEHSS[c] 0.0001 (mol/liter)	SDEHSS[c] 0.01	*n*-Octane	λ_{max} *n*-octane $-\lambda_{max}H_2O$	$\lambda_{max}{}^c$ $-\lambda_{max}{}^c$	
Ethylbenzene	insol.	261.2	261.4	261.9	262.1	0.9	0.5	1
Benzene	0.07g/100g	254.0	254.2	255.0	255.5	1.5	0.8	1
N,N-Diethylaniline	1.42% (20 C)[e] 0.024 wt % (20 C)[f]	252.7	254.2	260.0	261.0	8.3	5.8	2
N,N-Dimethylaniline	insol.	244.1	245.2	245.7	251.8	7.7	0.5	3
Acetophenone	sl. sol.	244.8	246.0	245.6	239.3	−5.5	−0.4	3
Nitrobenzene	0.206g/100g	269.0	268.6	268.7	253.5	−15.5	0.1	3
m-Toluidine	sl. sol.	283.0	283.8	283.6	289.6	6.6	−0.2	3
m-Cresol	2.5%	272.9	272.9	273.2	273.6	0.7	0.3	3
Diethyl phthalate	0.10% (25 C)	276.6	277.1	276.7	276.0	−0.6	−0.4	4
Dimethyl phthalate	0.43g/100ml	276.5	276.9	276.9	275.8	−0.7	0	4

[a] Data from references; All compounds are very soluble in *n*-octane. sl, slightly; v, very.
[b] Mainly at the suitable peak.
[c] $0.0001 << CMC < 0.01$.
[d] Ascending order (1; central part, 4; exterior part).
[e] This value seems too high.
[f] Experimental result.

petroleum ether and the white insoluble portions (0.1%) were removed by centrifugation. A white amorphous powder was obtained on drying the remaining solution.

Analysis. Calculated for $(C_8H_{17})_2C_4H_3O_4SO_3Na$: C, 54.04; H, 8.39; S, 7.21; Na, 5.17. Found: C, 53.64; H, 8.55; S, 6.78; Na, 5.23.

Sodium Dodecyl Sulfate. Sodium dodecyl sulfate (SDS) was synthesized from purified dodecyl alcohol by the usual method.

Analysis. Calculated for $C_{12}H_{25}SO_4Na$: C, 49.98; H, 8.74; S, 11.12; Na, 7.97. Found: C, 49.99; H, 8.83; S, 10.50; Na, 7.95.

Polyoxyethylene Cetyl Ether. This compound (15.8 mole condensate, C_{16}-16) was prepared from the previously reported crude polyoxyethylene cetyl ether (21 mole adduct) (4) which was synthesized by the addition of ethylene oxide (EO) to purified cetyl alcohol at atmospheric pressure. The crude product was treated with active carbon and the potassium hydroxide used as catalyst neutralized by hydrochloric acid, dried under vacuum, and one portion was subjected to molecular distillation. For this, a Consolidated Vacuum Corporation type CMS-5 centrifugal molecular still was used and the bp $_{2\times10^{-3}}$ 225 C fraction was collected. The product was a white waxlike solid. The molecular weight calculated from the hydroxy value is 938.5, and the EO addition molar number was 15.8.

Analysis. Calculated for $C_{16}H_{33}O(C_2H_4O)_{15.8}H$: C, 60.92; H, 10.44. Found: C, 60.47; H, 10.25.

In this connection, the EO addition molar number calculated from the integral curve of the NMR spectrum (Varian H-100 NMR spectrometer) was 16.9.

Benzene, *n*-octane and DEA used were of spectral reagent grade, and other compounds used were of chemically pure grade. DEA is oxidized in air, but rectified DEA can be used. Water was purified by ion-exchange and redistillation.

Measurements

UV absorption spectra were measured on a Hitachi recording spectrophotometer type EPS-2, using 10 mm quartz cell at room temperature (20–22 C). The path lengths of the cell were changed from 1 to 10 mm by quartz spacers.

Light scattering was measured on a Shimadzu photoelectric light scattering photometer type PG-21 at room temperature (20–22 C). For the dye adsorption method, pinacyanol chloride, rhodamine 6G, eosine and sodium salt of 2,6-dichlorophenol indophenol were used and the color changes observed visually.

Electric conductivity was measured by a digital conductivity meter, Model CM-ID, made by the Toa Electric Co. Ltd. The measurement was carried out at 30 ± 0.1 C. For surface tension, a du Noüy surface tension meter was used and the measuremenet carried out at 30 ± 0.2 C. The details have been reported previously (3).

Results

Choice of Solubilizate

The shift of λ_{max} of some organic compounds in water, *n*-octane and aqueous solutions of SDEHSS, and attendant data are shown in Table I.

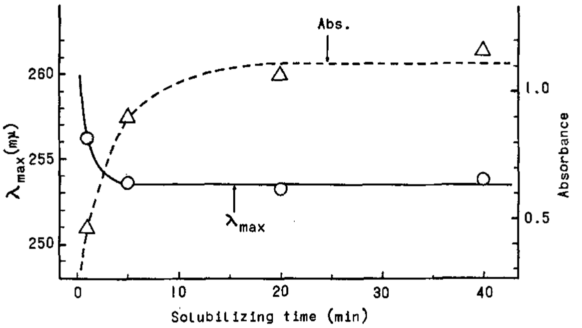

FIG. 1. Effects of solubilizing time on the λ_{max} and absorbance of DEA in 0.002 mol/liter aqueous solution of TDMBAC: DEA, 0.001 ml/3 ml; Reference, 0.002 mol/liter TDMBAC; TDMBAC, tetradecyldimethylbenzylammonium chloride; DEA, N,N'-diethylaniline, 20–22 C.

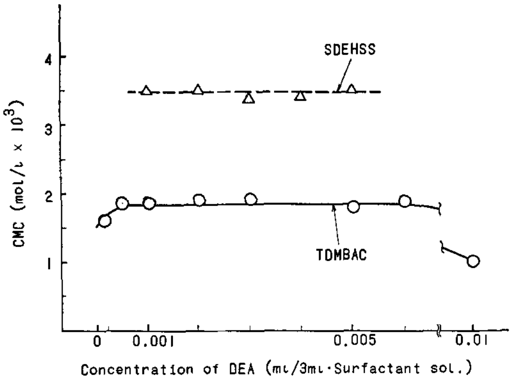

FIG. 2. CMC of TDMBAC and SDEHSS determined by UV method when several amounts of DEA were used: SDEHSS, sodium di-2-ethylhexyl sulfosuccinate; Reference, surfactant solution.

TABLE II

CMCs ($\times 10^3$) Determined by Several Methods

Method	Temp. (C)	Surfactant				
		SDS[a]	SDEHSS	TDMBAC	C_{16}-16	C_{16}-16 : $MgRi_2$[b]
UV absorption spectra[c]	20 – 22	8.1	3.4	1.9	0.13	0.053
Electric conductivity	30 ± 0.1	7.9_6	3.7_1	1.9_2		
Surface tension	30 ± 0.2	8.1			0.16	
Light scattering	20 – 22				0.15	0.05
Dye adsorption	30 ± 0.1		3.5	1.8		

[a] Sodium dodecyl sulfate.

[b] C_{16}-16: Magnesium ricinoleate (5:1 in molar ratio).

[c] DEA was used as a solubilizate.

The organic compounds suited to this measuring method are limited to those which comply with the following conditions: (a) It must exhibit a strong UV absorption; (b) the absorption peaks in *n*-octane and water must be few and sharp; (c) the difference between $\lambda_{\max}$ in water and in *n*-octane must be large; (d) it must have suitable polarity and dissolve well in *n*-octane but only slightly in water (about 0.05–0.5%); (e) the molecular weight must be comparatively small and the molecule must not be bulky; (f) it must be a liquid at room temperature; (g) it must be stable; (h) differences between $\lambda_{\max}$ above and below the CMC with various surfactant solutions must be large, and the absorption peaks must be few and sharp as well.

Condition (d) is necessary in order that the solubilizate can solubilize within the micelle. When the polarity is too strong, the polar section of the molecule is exposed outside of the micelle or adsorbed on the exterior of the micelle. When this happens there is the possibility that the difference in $\lambda_{\max}$ values above and below the CMC is small. Condition (e) is necessary so that solubilization may be easy, and may have as small an effect as possible on the CMC of the surfactant. Condition (f) permits micro amounts to be conveniently obtained, and also facilitates solubilization.

From Table I, DEA is the most suitable compound for the UV method.

Determination of CMC by UV Absorption Spectral Method

The solubilization of DEA in aqueous solution of surfactant is complete in 10 to 15 min with shaking by hand, as shown in Figure 1. No change of $\lambda_{\max}$ of the solution was observed, even after five days. When the solubilization temperature was from 30 to 40 C, the solubilization time was shortened.

The relationship between CMC and concentration of DEA is shown in Figure 2 (cf. Fig. 4). When the concentration of DEA is 0.0005 to 0.005 ml/3 ml solution, the minimum values corresponded with the CMCs determined by other methods, such as electric conductivity. Therefore, 0.002 ml of DEA/3–10 ml of surfactant solution (0.20–0.66 ml/liter) is used for this method (the absorbance of the solution is too large at concentrations above 0.003 ml/3 ml).

Measurements were made in accordance with all the conditions described previously using TDMBAC, SDEHSS, SDS and C_{16}-16. Figure 3 shows the absorption spectra of DEA in water and *n*-octane, as well as of various concentrations of TDMBAC. Figure 4 shows the graphs of $\lambda_{\max}$ of DEA vs. surfactant concentration for each of the surfactants. In all of the curves, break-points are evident.

In Table II, the concentrations of surfactants at these break-points are compared with CMC values obtained by other methods. It can be seen that the CMC values obtained by the surface tension, dye adsorption, electric conductivity and light scattering methods agree well with the concentrations of surfactants at the break-point values in spite of the different ionic characteristics of the surfactants.

The CMC values for several other surfactants were determined and also agreed well with the values obtained by conventional methods. Nearly all graphs of $\lambda_{\max}$ vs. concentration tended to resemble the results in this report (6).

When performing the measurement, it is preferable to keep the amount of DEA used constant for the same material. It is possible to use water or nothing as reference when the sample solution of surfactant has little absorption.

Discussion

The dye adsorption method which is often used to measure the CMC is based on the shifts of absorption maxima in the visible region. In the case of ionic surfactants, the color change occurs owing to the conversion of associated dye molecules below the CMC to single molecules on the micellar surface of the surfactant above the CMC (13). On the other hand, it is reported by Nakagawa et al. (14) that for nonionic surfactants the color change occurs by solubilization of the dye molecule into the micelle. The shifts of $\lambda_{\max}$ utilized by the author are based on the solvent effect for the solubilizate between micelle phase and monomolecular phase for not only nonionic but also ionic surfactants.

DEA gives $\lambda_{\max}$ at 261.0 mμ in *n*-octane. However, the position of $\lambda_{\max}$ shifts in water owing to hydrogen bond or the π-electron bond formation. Since the hydrocarbon chains collect in the liquid state inside

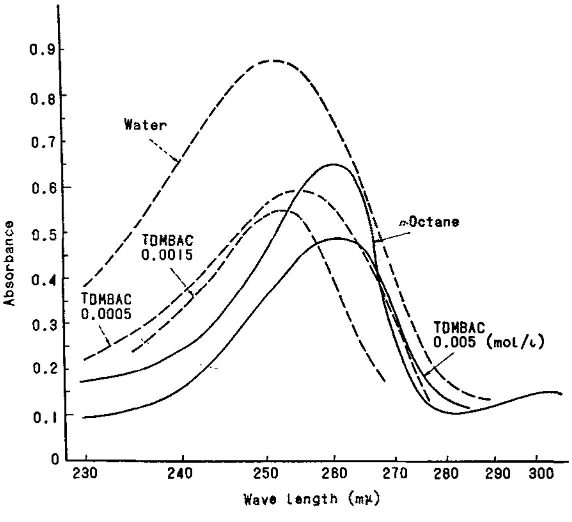

FIG. 3. The UV absorption spectra of DEA in *n*-octane, water and aqueous solutions of TDMBAC: TDMBAC, 0.005 > CMC > 0.0015, 0.0005 (mol/liter); DEA, 0.001 ml/3 ml solution.

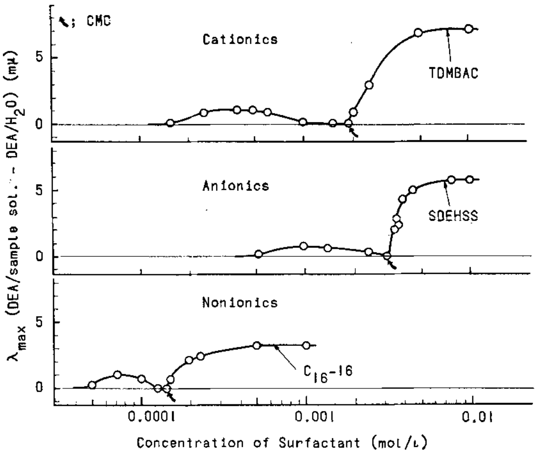

FIG. 4. The CMC of several surfactants by the UV method with DEA: C_{16}-16, polyoxyethylene cetyl ether (15.8 mole adduct).

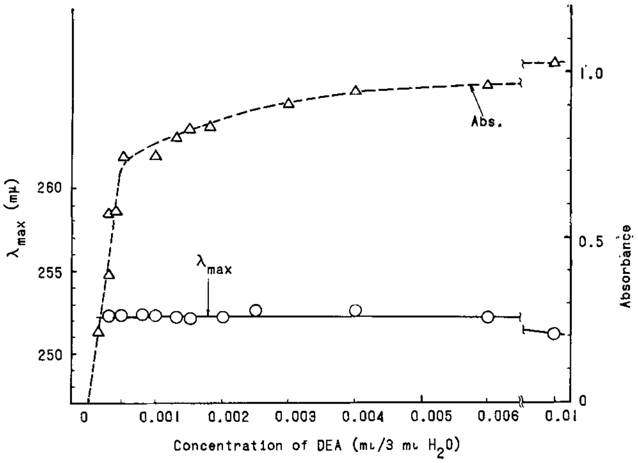

FIG. 5. λ_{max} and absorbance of DEA in water at various concentrations.

the surfactant micelles (15), the condition of the DEA which enters the micelles is similar to the solution in a hydrocarbon solvent. In this case, it would appear that the micelle interior conditions are somewhat different when various types of surfactants, and organic compounds other than DEA, are used.

With compounds such as benzene or ethylbenzene, which solubilize near or in the central part of the micelle, the chain length and shape of the alkyl radical of the surfactant will probably not have much effect. With the relatively polar DEA, or naphthalene, etc., it is thought that solubilization occurs in the palisade layer of hydrocarbon chains; in this case the influence of alkyl radicals is considerable. Therefore, if the alkyl chain is of sufficient length, the situation will probably be the same as in octane, decane, etc.; however, when there are two short and bulky 2-ethylhexyl chains such as in SDEHSS, the situation should be somewhat different, and with short chains such as in sodium alkylnaphthalene sulfonate, it will be considerably different. From these results, there should also be a shift between λ_{max} in high micellar concentrations and that in *n*-octane. Compounds of higher polarity such as cresol and *o*-nitroaniline do not penetrate deeply between the hydrocarbon chains so that the outer water layer and polar radical of the surfactant have considerable influence. With compounds such as dimethyl phthalate, where adsorption occurs on the exterior of the micelle, this tendency should be even stronger. These differently solubilized states should be clear from the results in Table I, as well from earlier work (10,16–19).

TABLE III

Correlations Between DEA Molecule and Surfactant Molecule at Several Points in the Curves of λ_{max} vs. Concentrations of Surfactants in Aqueous Solution With DEA[a] (cf. Fig. 4)

Surfactant	Concentration mol/liter	DEA/ Surfactant (mole ratio)	$\Delta \lambda_{max}$
Constant point[b] (above CMC)			
SDEHSS	0.008	0.52	2.6[c]
TDMBAC	0.005	0.83	1.1
C_{16}-16	0.0008	5.23	4.7
Minimum point (CMC)			
SDEHSS	0.0034	1.23	0[d]
TDMBAC	0.0019	2.20	0
C_{16}-16	0.00013	32.2	0
Maximum point (below CMC)			
SDEHSS	0.0008	5.23	0.7[d]
TDMBAC	0.0004	10.5	1.1
C_{16}-16	0.00007	59.7	1.0

[a] The solution was a mixture of 3 ml of aqueous solution and 0.001 ml of DEA.

[b] Minimum concentration which reached to the constant value (λ_{max}).

[c] $\Delta \lambda_{max} = \lambda_{max}$ in *n*-octane-λ_{max} in surfactant solution.

[d] $\Delta \lambda_{max} = \lambda_{max}$ in surfactant solution $-\lambda_{max}$ in water.

However, the existence of a small shift in λ_{max} cannot always be taken as evidence that solubilization occurs near or at the outside of the micelle; for example, the λ_{max} shift for benzene is quite small. By the same token, a large shift cannot be taken as evidence of solubilization in the interior of the micelle.

Shifts of λ_{max} in respect to changes in the overall concentration of the aqueous surfactant solution are still more complex. When the concentration of the surfactant solution is below the CMC, single molecules of the surfactant are present and it is possible that they associate with solubilizate by hydrogen or π-electron bond. When the concentration of the surfactant solution is above the CMC, the concentration and the number of the micelles increase along with the increase in the overall concentration, while the monomolecular concentration is held constant in the surfactant of a single system (20). Therefore, the composite value (λ_{max}) corresponding to small amounts of DEA in micelles and the value corresponding to the monomolecular phase at lower micelle concentrations, as well as of the value for large amounts of DEA in micelles and the value for monomolecular phase at higher micelle concentrations, can be determined.

In UV absorption, Lambert-Beers law ($\log_{10} I_0/I = \epsilon cl$) is well known with respect to the amount of absorption. It holds good even when two kinds of molecules exist unless there are reciprocal actions and the superimposed results of the spectra of the components are obtained with respect to λ_{max} of the absorption peaks. The problem in this study, unlike previous ones, is a variation of a shift of a compound in a mixed solvent, which are not mutually soluble and are in variable ratios. There is no clear general rule concerning this phenomenon. It is assumed that various results are produced owing to several reciprocal actions between solubilizate and solvent, plus those of solvents with each other. From experiments, it is assumed that the shift of λ_{max} of DEA in the total phase is probably the arithmetical average of that in micellar and monomolecular phase, above the CMC.

Table III shows (a) the minimum concentrations required to reach a constant value of λ_{max} on the higher concentration side, the concentrations at the minimum points (*i.e.,* the CMC) at the maximum points on the lower concentration side (below CMC) of the graphs for three surfactants in Figure 4; (b) molar ratios of DEA to the surfactant; and (c) differences of λ_{max} between those at the above mentioned concentrations and in water or *n*-octane. In the curve of Figure 4, the overall shape is almost the same in spite of the various ionic characteristics of the surfactants. The amounts of DEA in solutions are all the same. However, there are evident differences in the numerical values. These differences are: (a) The differences of λ_{max} in *n*-octane and in high concentrations of surfactants were in the order of C_{16}-16 > SDEHSS > TDMBAC. (b) The molar ratios at the maximum points in low concentrations were in the order of C_{16}-16 > TDMBAC > SDEHSS.

In (a), it is possible that the oleophilic radicals of surfactants resemble *n*-octane when differences are small, or the effects of λ_{max} of DEA molecules in monomolecular phase to those in the overall phase is relatively small, or both, but it is not always clear. It is possible that the difference is small in C_{16}-16 because hydrogen bonding arises between the POE chain which penetrates slightly into the palisade of the hydrocarbon chain in the micelle, and the solubilizate molecules (11). For high concentrations, it is thought that the extent to which λ_{max} decreases in all phases is due to the fact that the values in the monomolecular phase are small. This naturally depends on the number of DEA molecules which are present in the monomolecular phase of a surfactant and in equilibrium with DEA molecules in the micelles at high concentrations. It is reported by Riegelman et al. (10) that, among the solubilizates, those which are only slightly soluble in water (such as benzene and ethylbenzene) may be present in a monomolecular phase as only one to several hundred parts in the micelles, and this ratio may be somewhat smaller in reasonably soluble compounds such as *o*-nitroaniline and *p*-nitroaniline. In the case of more-or-less soluble benzoic acid in water, it was found that the ratio was about 10 in aqueous solution of cetomacrogal (POE cetyl ether) (11,21). In DEA, it is thought that the ratio approaches the case of nitroaniline. If so, the value of DEA in the monomolecular phase can be disregarded as compared to that in the micelle phase when considering the arithmetical average.

In (b), surfactants with low CMC values are necessarily the largest by far, but the relations among the surfactants and certain reasons for the occurrance of maximum points below the CMC are not yet clear. At any rate, it is supposed that the state of the surfactant molecule or of the interaction of DEA molecule and surfactant molecule varies in this concentration range.

The time of solubilization and the progress of the dissolution can be seen from the increase in absorbance, but λ_{max} becomes constant in a time shorter than this. As mentioned previously, λ_{max} above the CMC is the composite of λ_{max} of DEA in the micelle phase and in the monomolecular phase of surfactant. Differences of the values of λ_{max} in the early and later stages in solubilization were observed, because the dissolution rate in the two phases differed. In this case, the initial value was high, but it decreased and became constant after about 5 min. This means that the DEA solubilized more quickly in the micelle phase than in the monomolecular phase. It is highly preferable for the UV spectral method that λ_{max} of the solubilized solution reach a fixed value in a short time.

The appropriate range of DEA concentration is 0.0005–0.005 ml/3 ml as shown in Figure 2. This range is limited only by the amount of the solution and not by the concentration or the type of surfactants. Since concentration is generally chosen mainly around the CMC, the micelle concentration will probably be in about the same range for surfactants with both high and low CMC values. When large excess amounts of DEA are used, the breakpoints appear rather low and are not clear. The absorbance and λ_{max} were measured under the same CMC-measuring conditions by adding DEA to water. The graph in respect to DEA concentration is shown in Figure 5. Even when a large excess amount of DEA (0.01 ml/3 ml) is used (part forms oil drops and the water phase is cloudy) there is little change in λ_{max} of absorption maxima. The increase of the absorbance above the soublity is thought to be due to turbidity. When the CMC is measured using large excess amounts of DEA, it might be supposed that the low value is obtained because the same effect as the UV absorption in micelles is caused by the emulsified droplets of DEA itself, but previous examples prove this to be wrong. When oleophilic compounds are solubilized, the CMC values are often decreased (22,23), but since the optimum DEA concentration range is rather wide, this has little influence on the solubilization. Therefore, it is thought that the decrease in the CMC values when large excess of DEA is used is due to some other reason.

Consequently, further theoretical and experimental studies are necessary particularly for such problems as the fact that λ_{max} of the compound at CMC and in water are almost the same; a maximum portion in the curve of λ_{max} occurs at concentrations below the CMC. It is believed that these results will lead to the solution of solubilization problems.

In the case of mixed systems of surfactants and surfactants with strong absorption characteristics, it has been clear that the measurement of CMC is possible on the same principle (cf. Table II). Details will be published in the future.

ACKNOWLEDGMENTS

M. Nagamine assisted in the experiments. NMR spectra by O. Yamamoto; instructive advice by T. Toyoda, H. Narasaki, A. Kato, A. Kuboyama and T. Goto.

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[Received July 3, 1969]