The Studies on Micelles. II. The Relation between Surfactant Concentration and Micellar Concentration in Aqueous Surfactant Solutions

By Hiroji SASAKI, Shūji SAITO and Haruhiko OKUYAMA

(Received June 17, 1956)

Introduction

The very important and interesting problem about micelles in aq. surfactant solutions is the relation between micellar concentration and surfactant concentration. Hartley[1] said that in dilute soap solution, the aggregate of paraffin chain salt has a well-marked optimum size and that no picture has given any satisfactory explanation for limitation of the size of aggregates. If this assumption could be applied to the rather concentrated range of surfactants, we should reach the curious conclusion, e. g., of 0.48 molecules of dimethyl amino azobenzene being solubilized in one micelle of dodecyl amine hydrochloride, which consists of 39 surfactant molecules[2], namely, notwithstanding the fact that the surfactant solution was completely saturated with dye, there would be about half of all micelles which were free from the dye molecule. It is generally believed that at about CMC there are small micelles and at high concentration of surfactants there exist large micelles, which consist of several double layers or have branching form in large dimension. But there is no satisfactory explanation about the relation between both kinds of micelles. In order to obtain some information on the relation between the surfactant concentration C_s and the micellar concentration C_m, we have used the following fact on spectroscopy; "in some cases the absorption spectra of associable molecules in solutions change by the effect of association". When such an absorber, whose spectral change by association is great, and which is water-insoluble, is solubilized in an aq. surfactant solution and its spectrum is measured, we should observe some influences of association in the absorption band, so long as there are some micelles which contain more than two absorber molecules in them. Now keeping the concentration of surfactant C_s constant, i. e., the micellar concentration C_m constant, and increasing the concentration of absorber C_a, the number of absorber molecules in solution should exceed at last that of micelles. If we can detect the absorber concentration C_a, upon which the influence of association appears first, this absorber concentration C_a should be equal to the concentration of micelles C_m, i. e., $C_m=C_a$, and further the number of molecules forming every micelle, N_m, is given by the equation

$$N_m=(C_s-C)/C_m \qquad (1)$$

where C is the CMC and the unit of C_s, C and C_m are given by moles per liter; if the surfactant concentration is given by weight percent, C'_s, as is in usual cases, the molar concentration C_s is obtained by $10\times C'_s/M$, where M is the molecular weight of the surfactant.

Materials and Methods

Samples.—*Trans*-azobenzene (AB) is used as a water-insoluble dye. As surfactants we have used sodium dodecyl sulfate (SDS), sodium oleate (SO), trimethyl dodecyl ammonium chloride (TMD), cetyl pyridinium chloride (CPC) and dodecyl polyethylene glycol ether (E120, average molecular weight is 1066). About the purification

---

[1] G. S. Hartley, *Quarterly Reviews* (London), II, 179, (1948).

[2] M. E. L. McBain and E. Hutchinson "Solubilization," Academic Press Inc., Publishers, New York (1955), p. 95.

of AB, SDS, TMD and E120 we have already reported[3]. CPC, manufactured by the L. Light and Co., Ltd. (England), was purified by ether. SO, from the E. Merck Co., is the purest grade and used without special purification.

Methods.—$10^{-3} M/L$ of AB were solubilized in aq. surfactant solutions of certain concentrations and these solutions were used as stock solutions. Every stock solution was diluted in turn by the aq. surfactant solution of the same concentration respectively, and their absorption intensities at certain wave length were measured by the Beckman DU spectrophotometer immediately after dilution.

Results

Fig. 1 is the relation between the absorption intensity of π band and the concentration of AB in CCl_4. Fig. 2 is the relation between absorption intensity at 320 mμ and the concentration of AB in hexane and 10% aq. SDS solution. Figs. 3—7 are the relations between the absorption intensity at a certain wave length and the concentration of AB in various kinds of aq. surfactant solutions of various cocentrations.

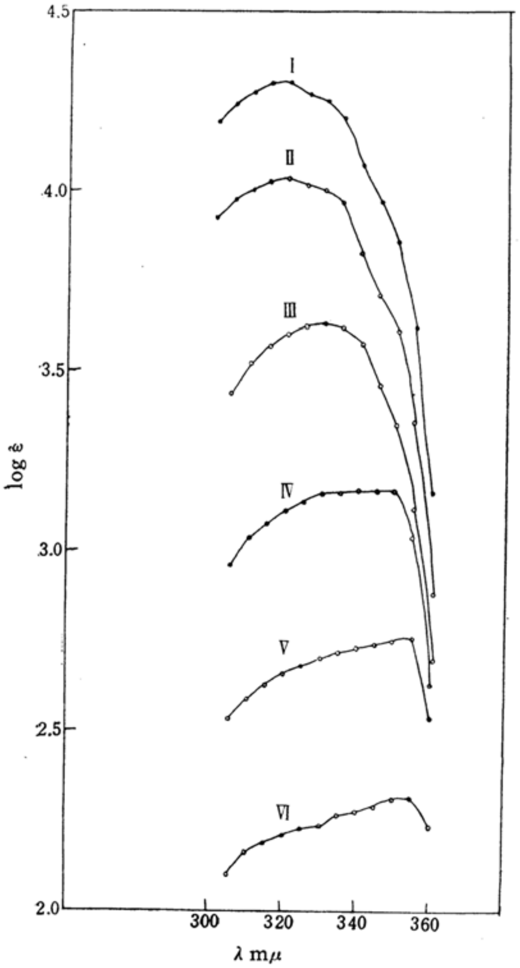

Fig. 1. The π band of azobenzene in CCl_4. Concentration of azobenzene; I : 10^{-4} M, II : 4×10^{-4} M, III : 10^{-3} M, IV : 3.2×10^{-3} M, V : 10^{-2} M, VI : 3.2×10^{-2} M.

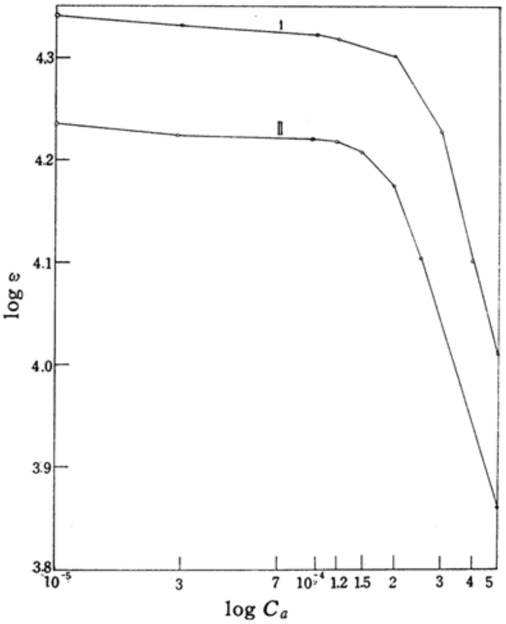

Fig. 2. The absorption intensity of azobenzene at 320 mμ. C_a is the molar concentration of azobenzene. Solvents; I. hexane, II. 10% aq. SDS.

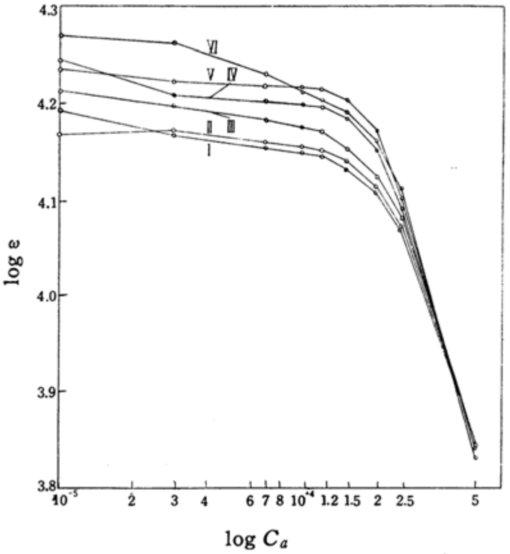

Fig. 3. The absorption intensity of azobenzene at 320 mμ in the aq. SDS solutions. Concentration of SDS; I : 0.5%, II : 1%, III : 2.5%, IV : 5%, V : 10%, VI : 20%.

---

[3] H. Sasaki, H. Okuyama and S. Saito, This Bull., **29**, 752 (1956).

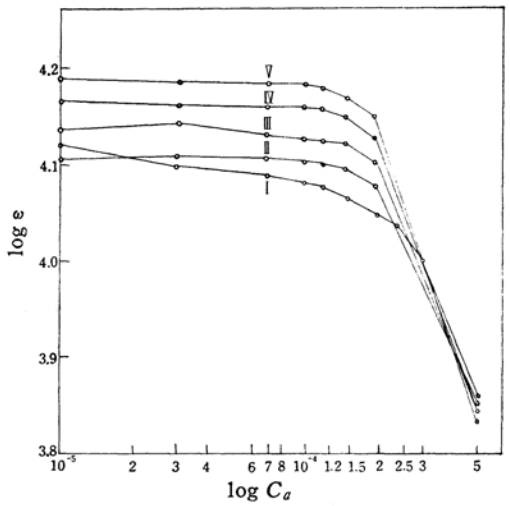

Fig. 4. The absorption intensity of azobenzene at 320 mμ in the aq. TMD solutions. The concentration of TMD; I : 0.3%, II : 0.5%, III : 1%, IV : 2.5%, V : 5%.

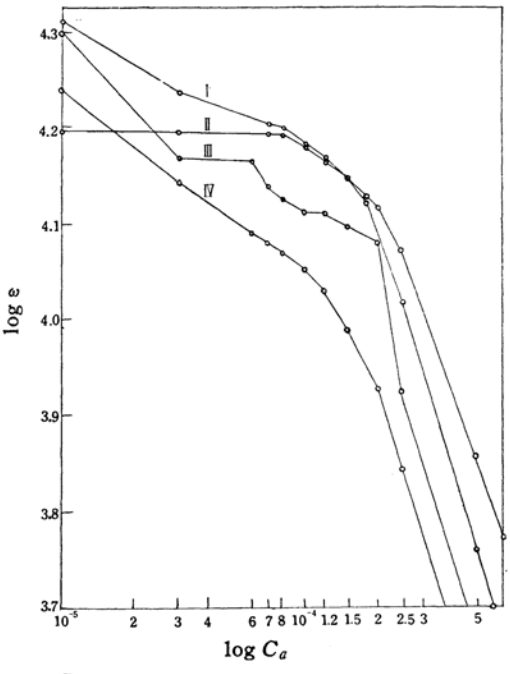

Fig. 5. The absorption intensity of azobenzene at 335 mμ in the aq. SO solutions. The concentration of SO; I : 0.05%, II : 0.5%, III : 1%, IV : 5%.

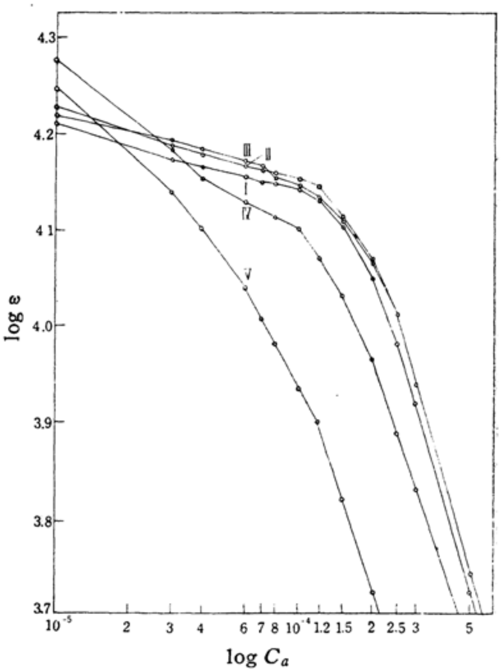

Fig. 6. The absorption intensity of azobenzene at 325 mμ in the aq. E120 solutions. The concentration of E120; I : 0.5%, II : 2.5%, III : 5%, IV : 10%, V : 20%.

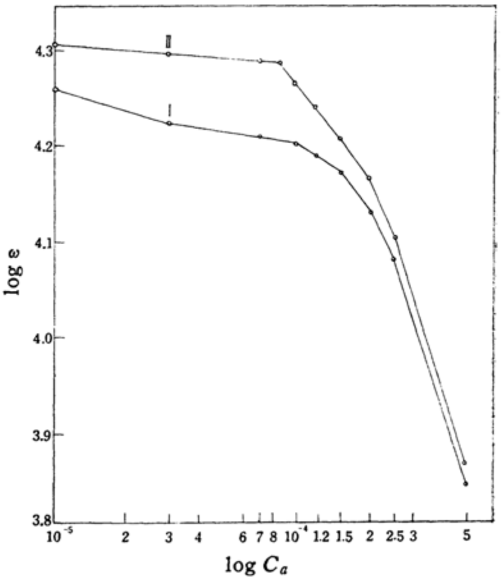

Fig. 7. The absorption intensity of azobenzene at 320 mμ in the aq. CPC solutions. The concentration of CPC; I:0.5%, II:1%.

Discussion

As is shown in Fig. 1, the π band of AB in CCl_4 depends remarkably on its concentration C_a. It is reasonable to think that the cause of this dependence of absorption intensity upon the concentration is association, because AB is a neutral molecule and no dissociation occurs, and in CCl_4 no pH effect occurs, moreover *trans*- and *cis*-azobenzene have no absorption maximum at 355 mμ[4]. From the curve

---

[4] W. R. Brode, J. H. Gould and G. M. Wyman, *J. Am. Chem. Soc.*, **75**, 1856 (1953).

I in Fig. 2 we can observe the relation between the concentration and the absorption intensity of AB at 320 mμ in hexane. The curve is approximately parallel to the abscissa in the range of $C_a \leq 1.2\times10^{-4}M$, which shows that AB molecules are almost in the unassociated state. In the range of $C_a > 1.2\times10^{-4}\,M$, the absorption intensity decreases with increasing C_a, which shows AB molecules are in the associated state. The curve II in Fig. 2 shows the relation between the absorption intensity at 320 mμ and the concentration of AB in aq. SDS solution. As C_s, the surfactant concentration, is kept constant, the micellar concentration C_m is also constant. If we follow the curve II from the left to the right, the number of AB molecules increases and at about $C_a=1.2\times10^{-4}\,M$ both the micellar concentration and the concentration of AB are equal, i. e., $C_m = C_a$, for at this point the curve begins to bend markedly. We will explain this reason again; as the lowering of the absorption intensity of AB in hexane or in CCl_4 is caused by the association, as mentioned above, then from resemblance of curves I and II, this lowering of the absorption intensity of AB solubilized in aq. SDS solution must be also caused by the association of AB molecules in micelles, and in order to cause AB molecules to associate in a micelle, the micelle must contain more than two AB molecules. Therefore the C_a, at this AB concentration where the intensity curve begins to bend markedly, must be equal to the micellar concentration C_m. Beyond this value of C_a, every micelle solubilizes 2, 3, and more AB molecules, therefore, paying the attention to AB molecules, the associate concentration of AB is constant, i. e., equal to C_m, and only the association number of AB increases with increasing C_a. All the curves in Fig. 3 show similar behavior; that is, in the range of $1.2\times10^{-4}\,M \leq C_a \leq 2.5\times10^{-4}M$ the curves bend remarkably, and the concentration of SDS, C_s, is concerned little with this general behavior of the intensity curves. Therefore it is concluded that the micellar concentration of SDS is about $1.2\times10^{-4}M/L$ in the range of $0.5\% < C_s < 20\%$, that is, C_m is constant irrespective of C_s in this range*. Accordingly, the association number of molecules forming every micelle, N_m, of SDS increases with the increase of C_s in the range of C_s being at least above 0.5%, and can be given by equation (1), inserting the value $C=8.12\times10^{-3}M$ (0.234%)[5] and $C_m=1.2\times10^{-4}M$. In the case of $C_s=20\%$ in Fig. 3, the curve differs a little from the others. We shall explain the reason for this afterwards. TMD gives also the similar curves as SDS as observed in Fig. 4, C_m is about $1.2\times10^{-4}\,M$ in the range of $C_s \geq 0.5\%$. At $C_s=0.3\%$, AB is in suspension state (not perfectly solubilized) and this curve is not reliable. The association number of a micelle of TMD is given by equation (1), inserting the value $C=0.016\,M$[6]. In the case of SO, as shown in Fig. 5, the values of C_m is smaller than those of SDS or TMD, that is, C_m is about $8\times10^{-5}M$ in the range of 0.05%—0.5%, and that, with increasing C_s, the bending part of the curves shifts towards the left, i. e., at 1% of C_s, C_m is about $6\times10^{-5}M$ and at 5% we can no longer detect the clear bending part on the curve where AB molecules are in the transitional state from the unassociated to the associated state. The value of association number of every micelle is given by the equation (1), in-

---

* In these discussions, we take the assumption of approximately monodispersed state of AB molecules solubilized in every micelle, as all micelles are also in the approximately monodispersed state. The reasons to take this assumption are as follows; (1) The facts that the approximately parallel part of the absorption intensity curve of AB in an aq. surfactant solution often shows irregular knicks and decreases with increasing C_a prove that AB molecules in micelles are in some degree in a polydispersed state. But the degree of polydispersity of AB molecules in this range, e. g. in aq. SDS solutions $C_a \leq 10^{-4}M$, is very little. On the other hand, in the range of $C_a > 10^{-4}M$ in SDS, the intensity curves decrease steeply, and this fact shows that when micelles containing more than two AB molecules appear largely, the absorption intensity of solutions decreases markedly. Because this great lowering of the intensity is not observed in the range of $C_a \leq 10^{-4}M$, we can safely say that AB molecules are mainly in a monomer state in the range of $C_a \leq 10^{-4}M$ in SDS. Moreover, it is thought that our assumption is justified, because the values of N_m tabulated in Table 1, which are obtained by the assumption of approximately monodispersed state of AB molecules in micelles, are in good agreement with those obtained by other authors, at least in low values of C_s. (2) If we assume, on the contrary, that at a certain C_s, the micelles were in a polydispersed state (P. A, Thiessen in Zsigmondy, "Lehrbuch der Kolloidchemie." 2, Leipzig (1927), p. 167), instead of approximately monodispersed state, whose solubilizing powers must be different after a different association number, then some possibility would occur that AB molecules might be solubilized also in a polydispersed state. But if so, the degree of polydispersity of AB must be subject to C_s, and the regular form of intensity curves irrespective of C_s, as is observed in Fig. 3, could not be observed. From these reasons mentioned above in (1) and (2), it is understandable that the assumption of the monodispersed state of AB molecules solubilized in micelles as well as surfactant micelles in aq. phase may be allowed in practical meaning, though it can not be admitted in strict meaning.

5) P. Mukerjee and K. J. Mysels, *J. Am. Chem. Soc.*, **77**, 2937 (1955).

6) H. B. Klevens, *J. Phys. Chem.*, **52**, 130 (1948). $0.016\,M/L$ is the CMC of dodecyl trimethyl ammonium bromide and we assume that the CMC of TMD does not differ so much from this value.

serting the value $C=6\times10^{-4}\,M$[7]. In Fig. 6, it is shown the case of E120, C_m decreases also with increasing C_s, i. e., in the range of $0.5\%\leq C_s\leq2.5\%$, C_m is about $1.2\times10^{-4}M$; at 5%, C_m is about $10^{-4}\,M$; at 10%, C_m is about $6\times10^{-5}\,M$; and at 20%, there can not be observed the clear bending point. The number of micellar molecules is given by equation (1), inserting the value $C=0.1\%$* and values of C_m given above. In Fig. 7 shown the experiment on CPC, C_m is about $10^{-4}\,M$ at $C_s=0.5\%$, and about $8\times10^{-5}\,M$ at $C_s=1\%$. N_ms are given by equation (1), inserting the value $C=9\times10^{-4}\,M$ and these values of C_m given above. In Table 1 these calculated values of N_m are tabulated.

The fact that when C_s increases largely, C_m decreases, and that at last the clear bending point disappears seems to be due to the general phenomenon about surfactant micelles. The values of N_m, given in Table I, at the low values of C_s, are in good agreement with what are obtained by other methods, for example, 75 for aq. SDS solution by the light scattering[8]. The range of C_s, where C_m is kept constant, seems to be subject to the volume of surfactant molecules, and to whether the unsaturated part exists or not in surfactant molecules; this upper limiting concentration seems to be 20%** in SDS, 5% in SO and 10% in E120.

TABLE I

THE VALUES OF MICELLAR CONCENTRATION, C_m, AND THE NUMBER OF SURFACTANT MOLECULES, N_m, IN THE CERTAIN CONCENTRATION OF SURFACTANTS, SUCH AS SODIUM DODECYL SULFATE (SDS), TRIMETHYL DODECYL AMMONIUM CHLORIDE (TMD), SODIUM OLEATE (SO), LAURYL POLYETHYLENE OXIDE ETHER (E120) AND CETYL PYRIDINIUM CHLORIDE (CPC)

Surfactants		C_m M/L	N_m
SDS	0.5%	1.2×10^{-4}	77
	1.0	〃	220
	2.5	〃	650
	5.0	〃	1380
	10.0	〃	2800
TMD	0.5%	1.2×10^{-4}	50
	1.0	〃	230
	2.5	〃	800
	5.0	〃	1740
SO	0.05%	8×10^{-5}	13
	0.5	〃	198
	1.0	6×10^{-5}	550
E 120	0.5%	1.2×10^{-4}	32
	1.0	〃	70
	2.5	〃	188
	5.0	1.0×10^{-4}	460
	10.0	6×10^{-5}	1550
CPC	0.5%	10^{-4}	138
	1.0	8×10^{-5}	358

Summary

From the spectral change of π band, caused by the association of azobenzene solubilized in aq. surfactant solutions, we have reached the conclusion that in a certain wide range of surfactant concentration, the micellar concentration is constant and only the number of surfactant molecules forming every micelle increases with increasing surfactant concentration. These values of the number of micellar molecules, obtained by spectral method, are in good agreement with those reported previously, in low concentration of surfactants.

The authors wish to express their sincere thanks to Prof. N. Sata for his encouragement.

Department of Chemistry, Faculty of Science, Osaka University, Osaka

---

[7] I. M. Kolthoff and W. Stricks, ibid., **53**, 424 (1949).

* This value is estimated from the solubilization of AB and not the precise value.

[8] E. Hutchinson and J. G. Melrose, *Z. physik. Chem., Neue Folge* **2**, 363 (1954).

** Suppose that $C_m=1\,2\times10^{-4}M/L$ and volume of 1000 cm^3 is divided by the sphere of NC_m (N is the Avogadro's Number), the radius of this sphere is given by the equation $(4/3)\Pi r^3NC=(10^{27})$ Å^3, i. e., $r=150$ Å. According to Debye's opinion (P. Debye and E. W Anaker, *J. Phys. Chem.*, **55**, 644 (1951)). the size of micelle does not exceed 300 Å, and Hess et. al. (K. Hess and H. Kiessig, *Ber.*, **81**, 327 (1948)). reported that the shape of large micelles is blade-like. A micelle which consists of less than one hundred surfactant molecules might be spherical, but a large micelle consisting of some hundreds of molecules can not be spherical, so we assume that this large micelle is a disk-like shape, which consists of one double layers. As one surfactant molecule occupies 25 Å^2, (J. W. McBain, in R. E. Burk and O. Grumitt "Frontiers in Colloid Chemistry," New York (1950), p. 133). the radius of this disk, r, at 10% of SDS is given be the equation $\Pi r^2=25\times(2800/2)$, i. e., $r=105$ Å, where 2800 is N_m tabulated in Table I. If this micelle continues its growth until 20% of SDS concentration, then $N_m=5720$, which is obtained by the equation (1), and $r=151$ Å. It is understandable easily that the micelles, even if they have a different shape, will combine wrth each other and form larger micelles when C_S exceeds some limiting value, given above.