Studies on Micelles. III. A Check of the New Conclusion from the Spectral Experiments with the Well-known Experimental Facts of Other Authors

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Introduction

From his absorption spectral experiment, the author has discovered[1] that in a certain wide concentration range of surfactants in aq. solutions the micellar concentration C_m is independent of the surfactant concentration C_s and that in this surfactant concentration range only the association number of micelle N_m increases with increasing surfactant concentration.

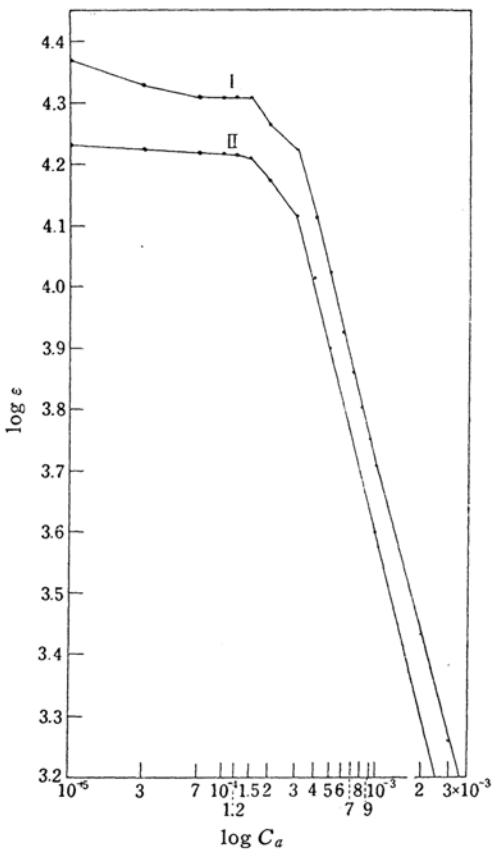

Fig. 1. Absorption intensity of azobenzene at 320 mμ. C_a is the molar concentration of azobenzene. Solvents: I C_2H_5OH, II 10% SDS.

1) H. Sasaki, S. Saito and H. Okuyama, This Bulletin, **30**, 186 (1957).

The facts which have led the author to this conclusion will be discussed briefly.

(**a**) The curve I in Fig. 1 is the absorption intensity of azobenzene at 320 mμ in ethanol. The curve bends remarkably at about azobenzene concentration C_a being 1.2×10^{-4} M. This lowering of absorption intensity is caused by the association of azobenzene. The curve II in Fig. 1 is the absorption intensity of azobenzene in aq. 10% SDS (sodium dodecyl sulfate) solution. The curve is almost parallel to the abscissa until C_a reaches about 1.2×10^{-4} M, which means that azobenzene molecules are mainly in the unassociated state, i. e., until C_a reaches about 1.2×10^{-4} M there are few micelles which contain more than two azobenzene molecules. The curve bends remarkably at about C_a being 1.2×10^{-4} M, which means that the micelles containing more than two azobenzene molecules appear largely at about this concentration. Therefore the micellar concentration C_m can be

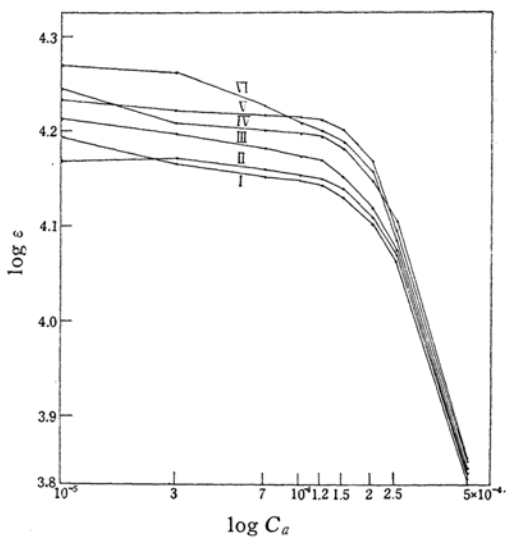

Fig. 2. Absorption intensity of azobenzene at 320 mμ. Solvents: I 0.5% SDS, II 1% SDS, III 2.5% SDS, IV 5% SDS, V 10% SDS, VI 20% SDS.

estimated safely as about 1.2×10^{-4} M in aqueous 10% SDS solution.

(b) Fig. 2 shows absorption intensity of azobenzene at 320 mμ in aqueous SDS solutions of various concentrations. The bending part of every curve is almost at the same azobenzene concentration, from which it is concluded that the micellar concentration of SDS is almost constant irrespec tive of SDS concentration in the range above 0.5% and below 20%.

(c) The reasonable conclusion deduced from the discussion (a) and (b) is that in a certain wide range of SDS concentration, the association number of SDS-molecules in one micelle increases with increasing SDS concentration.

The author has stated, in his previous report, how a micelle will grow*). The conclusions mentioned there and the natural inference deduced from these conclusions are as follows; (1) above the CMC, micellar concentration C_m increases with increasing surfactant concentration C_s but this range is very limited, meanwhile the range of C_s, where C_m is constant, is very wide: (2) the range of surfactant concentration, where C_m is constant, is dependent upon the size of surfactant molecules, especially upon whether surfactant molecules have unsaturated linkage in them or not. The author thinks that it is necessary to check the above mentioned conclusions from the absorption spectra of aqueous surfactant solutions solubilizing absorber molecules with the known experimental facts of other authors.

The Check of the Conclusions from the Spectral Experiments with the Well-known Experimental Facts

(1) Solubilization. — A curve of solubilization of water-insoluble dye in aqueous surfactant solution, i. e., (the amount of dye solubilized)/(the amount of surfactant C_s) vs. C_s curve bends suddenly after the steep rise above CMC and becomes almost parallel to the abscissa. The curve will begin to rise again when C_s becomes considerably high. Taking the conclusion of constant micellar concentration into consideration, the first rise of the curve must be due to the increase in C_m with increasing C_s. If only C_m continues to increase but N_m is constant with increasing C_s, as are concluded by other authors, the solubilization curve would not show such a sudden bending in a very narrow surfactant concentration range; in this case there is no reason for solubilizing efficiency of micelles to change suddenly with changing surfactant concentration, so the gradient of the curve would be almost constant independent of C_s. An example is shown in Fig, 3, which is the result of Hartley[2] and recalculated in the form of {(the amount of dye solubilized) − (solubility of dye in aq. phase)}/(C_s-CMC) vs. C_s. This curve shows that from CMC to 0.0354% of CPC (cetyl pyridinium chloride) C_m increases and above 0.0354% N_m increases mainly, as at this concentration of CPC the solubilization curve bends remarkably.

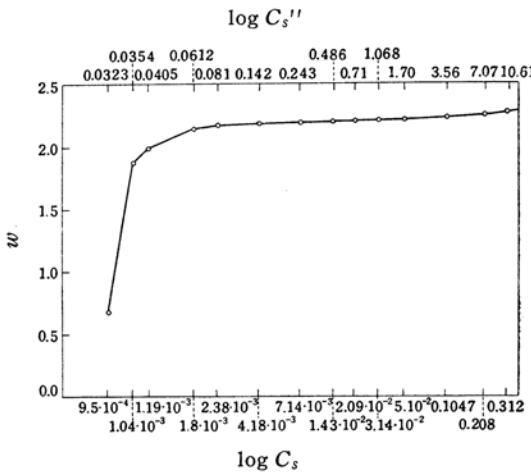

Fig. 3. Solubilization of AB (azobenzene) in aq. CPC (cetyl pyridinium chloride) solution from G. S. Hartley[2] $w=\log\{C_a'/C_s')\times10^3\}$, $C_a'=C_a-2.4\times10^{-5}$, C_a is the molar concentration of AB solubilized, 2.4×10^{-5} M is the solubility of AB in water. $C_s'=C_s-7.2\times10^{-4}$, C_s is the molar concentration of CPC, 7.2×10^{-4} M is the CMC of CPC, C_s'' is the weight percent. of CPC.

That the curve continues to rise slightly in the range of 0.081-3.56% shows the packing density of micelles increasing and the amount of water molecules contained in the inside of micelles[3] decreasing with increasing C_s. Above 3.5% the gradient of the curve begins to increase again, which shows the appearance of larger micelles with several double layers. From the solubilization curves of Green's[4] the concentrations at which the first rising finishes and the second rising begins respectively is as follows;

Surfactant	The concentration at which the first rising finishes	The concentration at which the second rising begins
Na-C_{12}	0.1 M (2.3%)	
Na-Oleate	5×10^{-3} M (0.15%)	0.3 M (9.12%)
$C_{12}NH_3Cl$	0.05 M (1.15%)	
Dodecyl sulfonic acid	0.05 M (1.23%)	0.727 M (16.4%)
Triton X-100	0.1%	10%

*) H. Sasaki et al., op. cit.

2) G. S. Hartley, *J. Chem. Soc.*, **1938**, 1968.
3) H. Sasaki, H. Okuyama and S. Saito, This Bulletin, **29**, 752 (1956).
4) S. A. A. Green, *J. Phys. Chem.*, **51**, 286 (1947).

These concentrations of various kinds of surfactant must have definite physical meaning, and the conclusion obtained by the spectral method agrees well with the behavior of these solubilization curves, as discussed above.

(2) **Diffusion.** — Hartley et. al.[5] have taken the notion that the micellar volume is independent of C_s, from their experimental results of diffusion of surfactants in aqueous salt or alkaline solutions. From the results of diffusion of surfactants in aqueous phase Lamm et. al.[6a] have also reached the same conclusion. M. E. L. McBain recognized that the diffusion coefficients of surfactants in aq. phase decrease with their increasing concentration, and she attributed this to the interaction among the increasing number of micelles[6b]. Stigter et. al.[6c] also accepted the interaction theory, but Abbott et. al.[6d] concluded

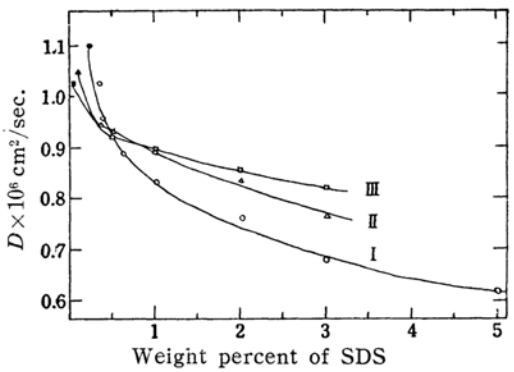

Fig. 4a. Micellar self-diffusion coefficient of SDS at 25°C from D. Stigter et. al.[6c]
Solvents; I. H_2O, II. 0.03 M NaCl, III. 0.1M NaCl.

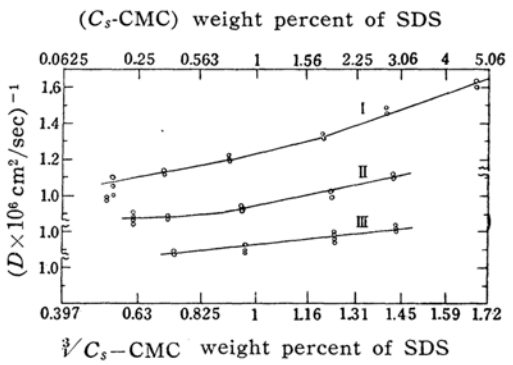

Fig. 4b. Micellar self-diffusion coefficient of SDS at 25°C.
Solvents; I. H_2O, II. 0.03 M NaCl, III. 0.1 M NaCl.

that the micellar radius increases with increasing concentration of the simple salt.

When simple salt is added to aqueous surfactant solution, it is thought that simple salt depresses the dissociation constant of paraffin chain salt[7] and these undissociated molecules are solubilized in the palisade of micelles; accordingly the volume of micelles increases. If so, it is natural to think that when C_s is increased, the surfactant molecules newly added are solubilized in the palisade of the existing micelles, and increase their volume, also depressing their diffusion coefficient. Fig. 4a is the result of Stigter et. al.[6c]. At about 1%, the curve I bends remarkably, which shows that until C_s reaches about 1%, C_m increases and above 1% of SDS, N_m increases mainly with increasing C_s. The curve D^{-1} vs. $(C_s\text{-CMC})^{1/3}$ {D, the diffusion coefficient, is proportional to r, the micellar radius, and also r is proportional to $(C_s\text{-CMC})^{1/3}$} must be linear in the range of $C_s \geq 1\%$, if the conclusion that above 1% of SDS, C_m is constant irrespective of C_s is correct. This is the case as is observed in Fig. 4b {the original paper shows that the curve D^{-1} vs. $(C_s\text{-CMC})^{1/2}$ is straight, but no explanation for this was given}. It must be strictly noted that these discussions mentioned above should be applicable only to the self diffusion coefficient. In usual diffusion experiments, two aqueous surfactant solutions of different concentration, which is above CMC, are used. The diffusion coefficients obtained by such a procedure depend not only on micellar diffusion velocity but also on micellar reconstructing velocity.

(3) **Electrical Conductivity.**— Hartley et. al.[8] pointed out that the association number of micelles can not be determined by the equivalent conductivity, Λ, alone. McBain asserted that when micelles are formed from free ions, Λ should increase[9]. But Hartley et. al. suspected McBain's theory from the consideration that after the lowering of Λ due to the secondary effect (the inclusive and the atmospheric effects) outweighing the primary effect (McBain's effect), the equivalent conductivity Λ should again increase owing to the occurence of the reverse case of both the effects with increasing C_s[8], and they presented the desorption theory[10]. McBain et. al.[11] explained the behavior of Λ vs. $C_s^{1/2}$ curves by the hypothesis of ionic micelle and neutral colloid, but Schmid et. al.[12] were doubtful about this hypothesis from their experimental results of high frequency effect. On the other hand, in the author's opinion, when n unassociated paraffin chain ions form one aggregate, Λ would decrease owing to the secondary effect overcoming the primary effect. But if we compare a smaller micelle with a larger micelle, i. e., if we

5) G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc.*, **A168**, 420 (1938); O. Lamm, *Kolloid-Z.*, **98**, 45 (1942); G. Jander and K. F. Weitendorf, *Angew. Chem.*, **47**, 197 (1934).

6) (a) O. Lamm and H. Högberg. *Kolloid-Z.*, **91**, 10 (1940); (b) M. E. L. McBain, *J. Am. Chem. Soc.*, **55**, 545 (1933); (c) D. Stigter, R. J. Williams and K. J. Mysels, *J. Phys. Chem.*, **59**, 330 (1955); (d) A. D. Abbott and H. V. Tartar, ibid., **59**, 1193 (1955).

7) H. V. Tartar, *J. Phys. Chem.*, **59**, 1195 (1955).

8) J. L. Moilliet, B. Collie, C. Robinson and G. S. Hartley, *Trans. Faraday Soc.*, **31**, 120 (1935).

9) J. W. McBain, ibid., **9**, 99 (1913).

10) G. S. Hartley, B. Corrie and C. S. Samis ibid., **32**, 795 (1936).

11) J. W. McBain and C. S. Salmon, *J. Am. Chem. Soc.*, **42**, 426 (1920).

12) G. Schmid and E. C. Larsen, *Z. Electrochem.*, **44**, 651 (1938).

compare an aq. paraffin chain salt solution at different concentrations, the secondary effect would be almost constant for the both surfactant concentrations but the primary effect should increase with increasing micelle size. So that it is the strong evidence of constant C_m irrespective of C_s for Λ to increase with C_s. Stigter[13] mentioned that the curve $\kappa - C_s$ (κ is the specific conductivity) consists of, in a typical case, two straight lines in an unassociated and an associated region. But taking the conclusion of constant micellar concentration into account, the curve $\kappa - C_s$ must have, at least, three knicks, that is, at CMC, at the point where the increase of C_m finishes and at the point where the larger

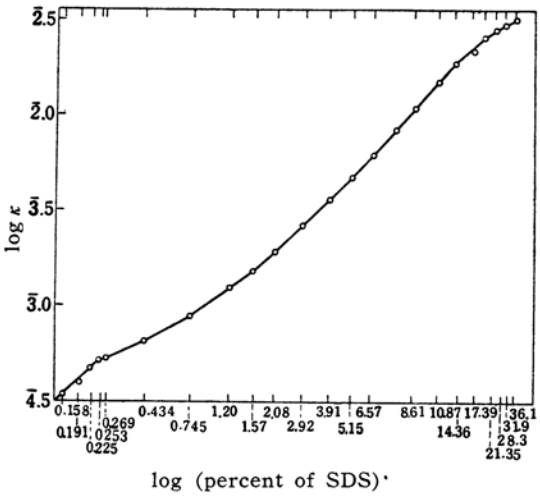

Fig. 5. Specific conductivity κ of SDS in aq. phase from A. F. H. Ward[14].

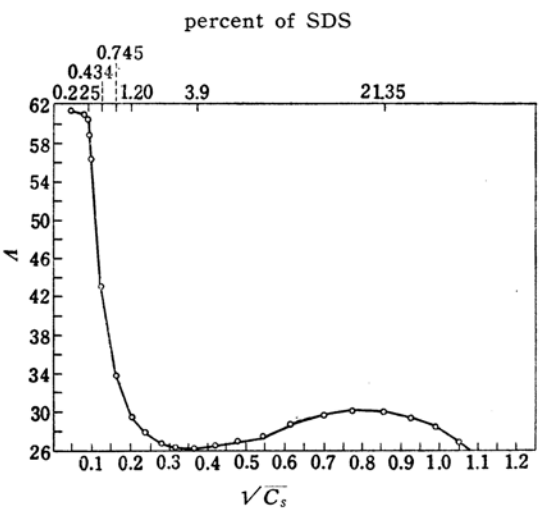

Fig. 6. Equivalent conductivity Λ of SDS in aq. phase from A. F. H. Ward[14].
C_s is the molar concentration of SDS.

13) D. Stigter, *Rec.trav. chim. Poy-Bas*, **73**, 611 (1954).
14) A. F. H. Ward, *Proc. Roy. Soc*, **A176**, 412 (1940).

micelle appears. Fig. 5 is the results of Ward[14] recalculated to the form $\log \kappa$ vs. $\log C_s$. At 0.25%, 0.75% and 17.5% there are definite changes in the curve. These three concentrations can be made to correspond to those points mentioned above respectively. The gradient of the curve, κ', decreases rapidly when the curve proceeds across the CMC, which is caused by the secondary effect, but gradually recovers with increasing C_s, which is caused by the primary effect, and at 3.9% κ' is 1, and still continues to increase with increasing C_s. In these regions κ' is higher than even that in the unassociated region. In concordance with these changes of κ' there appears the minimum in the curve Λ vs. $C_s^{1/2}$ ($\Lambda = 1000\,\kappa/C_s$) as observed in Fig. 6. The importance is not the minimum itself but the increase of κ' in the range from 0.75% to 17.5%. In the range of 3.9-17.5% κ' is greater than the unit, and above 21.5% κ' is less than the unit, therefore there appears maximum in the vs. $C_s^{1/2}$ curve, and this maximum (17.5-21.5%) is the concentration at which the larger micelle consisting of several double layers appears as mentioned above. It is easily understandable that when the larger micelle appears Λ, begins to decrease again owing to the higher viscosity. In conclusion the fact that the vs. $C_s^{1/2}$ curve has the minimum and the maximum is the proof that C_m is constant and N_m increases with increasing C_s.

(4) Light Scattering. — The most direct method to determine the micellar volume is light scattering, but the micellar molecular weight obtained by this method is generally at CMC[15] and there are few systematic investigations about the relation between the micellar volume and C_s. On the other hand, there are many studies about the charge effect[16] and different views are presented[15a, b, c]. It is desirable that some attentions are paid to nonionic surfactants (which have no charge) and also to the relation between the micellar volume and the surfactant concentration.

(5) X-Ray. — Corrin[17] pointed out that the micellar shape can not be determined decisively by X-Ray diffraction alone. Therefore very different micellar models have been presented by many X-Ray investigators, e. g., some authors have the idea of a larger micelle consisting of several double layers[18]. Others hold a small spherical model; especially Brady[19] has reported that the micelle of SDS is spherical even in such a high concentration as 14.71% and 29.42%, and some have explained the relation between the

15) (a) P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949); *J. Phys. Chem.*, **53**, 1 (1949); (b) H. V. Tartar, ibid., **59**, 1185 (1955); J. N. Phillips and K. J. Mysels, ibid., **59**, 325 (1955); (c) E. Hutchinson, *Z. physik. Chem.*, neue Folge **2**, 363 (1954).
16) J. J. Hermans, *Rec. trav. chim. Poy-Bas*, **68**, 859 (1948); T. M. Doscher and K. J. Mysels, *J. Chem. Phys.*, **19**, 254 (1951); E. Hutchinson, *J. Colloid Sci.*, **9**, 191 (1954). K. J. Mysels, *J. Phys. Chem.*, **58**, 303 (1954).
17) H. L. Corrin, *J. Chem. Phys.*, **16**, 844 (1948).
18) E. W. Hughes, W. M. Swayer and J. R. Vinograd, *J. Chem. Phys.*, **13**, 131 (1945); J. Stauff, *Kolloid-Z.*, **96**, 244 (1941); H. K. Kiessig, ibid., **96**, 252 (1941).
19) G. W. Brady, *J. Chem. Phys.*, **19**, 1547 (1951).

smaller micelle and the larger micelle[20] but as yet have not ascertained it experimentally. Many authors, e. g. Philippoff[21], have discussed the X-Ray CMC. Although the values of X-Ray CMC given by these authors are not always in agreement with each other, generally X-Ray CMC is detectable in 10-20% of surfactant concentration range[21]. The concentration at which the solubilization curve for dye begins to rise again is 9.12% for sodium oleate and 16.4% for dodecyl sulfonic acid; the conductivity curve reaches its maximum at 17.5-21.5% for SDS. It is an interesting problem whether these concentrations at which larger micelles appear have any relation with the X-Ray CMC.

(6) Density, Viscosity and Osmotic Coefficient.—Fig. 7 is the curve of density-concentration and Fig. 8 is that of viscosity-concentration in aq. SDS solution derived from Wright et. al.[22].

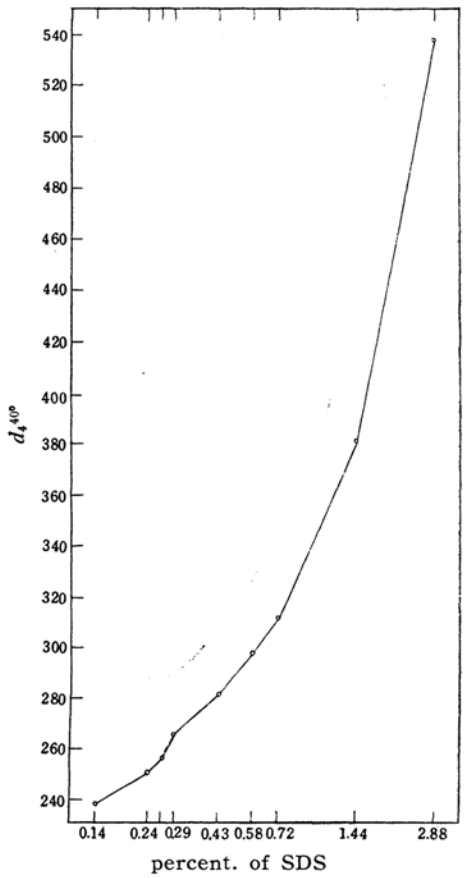

Fig. 7. Density $d_4^{40°}$ of aq. SDS solution from K. A. Wright et. al.[22].

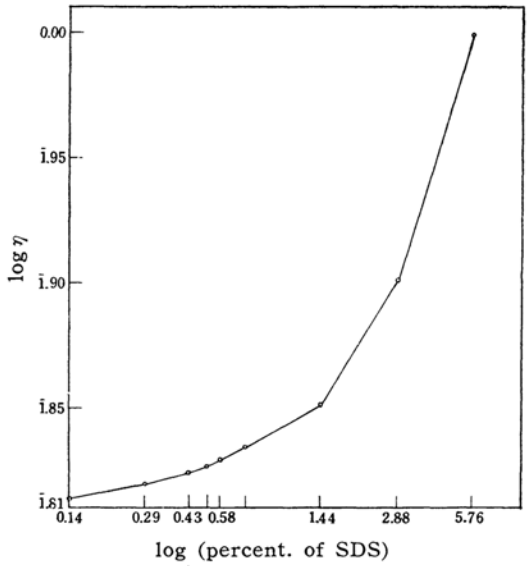

Fig. 8. Viscosity η of aq. SDS solution from K. A. Wright et. al.[22].

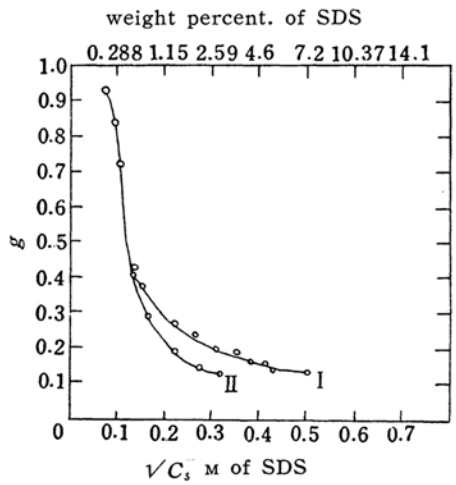

Fig. 9. Osmotic coefficient of aq. SDS solution from H. Huff et. al.[23]. Temperature; I. 30°C, II. 50°C.

At about 1.44%, the gradients of both curves increase remarkably. Huff et. al.[23] have shown that the osmotic coefficient of aqueous SDS solution vs. $C_s^{1/2}$ curve bends remarkably at about 0.023 M (0.66%) as is shown in Fig. 9. These concentrations must be those at which the increase of C_m finishes. But such properties of aqueous surfactant solutions as density[24], viscosity[25], osmotic coefficient or vapor pressure depression and

20) R. W. Mattoon, R. S. Stearns and W. D. Harkins, ibid., **15**, 209 (1947); W. D. Harkins, ibid., **16**, 156 (1948); J. Stauff, *Naturwiss.*, **27**, 213 (1939); *Kolloid-Z.*, **89**, 224 (1939); J. W. McBain, *Nature*. **145**, 702 (1940).

21) W. Philippoff, *Disc. Faraday Soc.*, NO. **11**. 96 (1951).

22) K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 544 (1939).

23) H. Huff, J. W. McBain and A. P. Brady, *J. Phys. Chem.*, **55**, 311 (1951).

24) R. G. Paquette, E. C. Lingafelter and H. V. Tartar, *J. Am. Chem. Soc.*, **65**, 686 (1943); A. B. Scott and H. V. Tartar, ibid., **65**, 692 (1943); C. R. Bury and G. A. Parry, *J. Chem. Soc.*, **1935**, 626.

25) W. Philippoff and K. Hess, *Ber.*, **70**, 1808 (1937).

cryoscopic behavior[26] can not sensitively reveal the relation among C_s, C_m and N_m.

Conclusion

By no experimental method other than spectral, can we obtain any intimate relationship among the surfactant concentration, the micellar concentration and association number of molecules forming every micelle; there therefore exists some space of alternative explanations for these experimental results. In the author's present paper, it is proved that the conclusion from the spectral experiments coincides well with many results obtained by various other experimental methods. Contrariwise the assumptions on the relation between micellar volume and surfactant concentration, having been presented by many authors, fail to prove any explanation of the various experimental results uniformly, especially they fail to explain the behavior of absorption intensity and solubilization curves in wide range of surfactant concentrations. For example, in aqueous SDS solution, the solute concentration, at which the micellar concentration becomes constant first, exists in the range from 0.5% to 1.5%, which is obtained by the spectral method and is not contradicted with solubilization, diffusion, conductivity, viscocity and osmotic coefficient data (here it is assumed that solubilization curve of sodium dodecyl sulfate for dye does not so much differ from that of dodecyl sulfonic acid). If we took an alternative explanation, e. g., of micellar interaction to elucidate the behavior at the minimum in the curve of equivalent conductivity or to elucidate the decrease in self diffusion coefficient at about 1% in aqueous SDS solution, there would remain some inexplicable points, e. g., why the solubilization curve bends so rapidly at about this concentration. Also the author has determined the SDS concentration at which the larger micelle appears first to be 17.5–21.5%. If we took the desorption theory of Hartley's, some doubts would remain, e. g., why the solubilization curve of SDS for dyes begins to rise again at about this concentration, where the equivalent conductivity curve reaches its maximum.

26) J. W. McBin and M. M. Barker, *Trans. Faraday Soc.*, **31**, 149 (1935); J. W. McBain and M. D. Bety, *J. Am. Chem. Soc.*, **57**, 1909 (1935); E. Gonick and J. W. McBain, ibid., **69**, 334 (1947); M. H. Norris *J. Chem. Soc.*, **121**, 2161 (1922); M. N. Fineman and J. W. McBain, *J. Phys. Chem.*, **52**, 881 (1948); A. Smits, *Z. Physik. Chem.*, **45**, 608 (1903); H. Okuyama and k. Tyuzyo, *Bull. Chem. Soc. Japan*, **27**, 259 (1954); J. W. McBain, "Colloid Science," D. C. Heath and Co., San Francisco (1950), p. 243.

Summary

The conclusion, which is obtained by the spectral experiments on aqueous surfactant solutions, that the micellar concentration in aqueous surfactant solution is constant irrespective of surfactant concentration in the range which is from a little above the CMC to a considerably high surfactant concentration, coincides well with many other experimental results such as solubilization of dye, conductivity, self diffusion, X-Ray diffraction, density, viscosity and osmotic coefficient or cryoscopic behavior.

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