The Surface Activities of Bivalent Metal Alkyl Sulfates. I. On the Micelles of Some Metal Alkyl Sulfates

By Iwao SATAKE, Ichiro IWAMATSU, Shizuko HOSOKAWA and Ryohei MATUURA

(Received September 21, 1962)

Innumerable data have been accumulated by a number of authors in the field of surface chemical studies of long chain alkyl sulfates and sulfonates of monovalent metals, especially of sodium. However, only a little work has been performed on the surface chemical properties of water-soluble detergents containing bivalent metals. The first publications on their surface chemical properties were produced by Lottermoser and Stoll(1), and by Lottermoser and Püschel(2) for various bivalent metal dodecyl sulfates, in which the electrical conductivities and the surface tensions of aqueous solutions were reported. Giers and Boide(3) synthesized zinc, calcium and magnesium dodecyl sulfates and measured the viscosities and contact angles of the solutions against solids. Recently Miyamoto(4-6) has determined the solubilities of various bivalent metal dodecyl sulfates in water and the critical micelle concentration (CMC) of the solutions by the surface tension method. He has found that the CMC values of these detergents are

---

1) A. Lottermoser and F. Stoll, *Kolloid-Z.*, **63**, 49 (1933).
2) A. Lottermoser and F. Püschel, ibid., **63**, 175 (1933).
3) S. Giers and P. Boide, *Soap Chem. Specialties*, **30**, 38, 179 (1954).
4) S. Miyamoto, *Mem. Fac. Sci., Kyushu Univ. Series C, Chem.*, **3**, 93 (1960).
5) S. Miyamoto, This Bulletin, **33**, 371 (1960).
6) S. Miyamoto, ibid., **33**, 375 (1960).

almost independent of the kind of metal ion and are about 1×10^{-3} mol./l. Further discussions on the surface activity of calcium dodecyl sulfate were presented by Lange[7] in connection with the effects of addded electrolytes on the CMC values of detergent solutions, and later by Corkill and Goodman[8] on the micelle formation in an aqueous solution. Tartar and Lelong[9] determined the micellar molecular weight of magnesium dodecyl sulfonate in an aqueous solution. Bone and O'Day[10] have reported the antibacterial activities of various bivalent metal dodecyl sulfates.

It is true that all these works have given us some information on the nature of the surface activity of metal alkyl sulfate, but no deep insight into this surface activity has yet been achieved because of the scarcity of fundamental data on the properties of the solutions of metal alkyl sulfates. The purpose of the present paper is to obtain a knowledge of the micelles of some bivalent metal alkyl sulfates which have not yet been studied fully. As Miyamoto[5] showed, the Krafft point of some metal salts is so high that the determination of the micellar properties is experimentally difficult for them. Therefore, here we have used cobalt, nickel, copper and magnesium salts which had Krafft points near room temperatures.

Experimental

Materials. — The bivalent metal alkyl sulfates were synthesized from pure sodium alkyl sulfate and inorganic salt according to the method used by Lottermoser and Püschel[2]. They were purified by repeated recrystallization. Sodium alkyl sulfate was prepared from the purified fatty alcohol obtained by the fractional distillation of commercial samples, as has been stated earlier[11]. The purity of the metal alkyl sulfates was confirmed by elementary analysis and surface tension measurement. The results of the elementary analysis of these detergents are summarized in Table I.

Method.—The CMC's of the aqueous solutions of bivalent metal dodecyl sulfates were determined by the conductivity method at 30°C using a Yanagimoto conductivity outfit model MY-7. The CMC values of copper tetradecyl and hexadecyl sulfates were determined by the surface tension method at the temperature above each Krafft point; the same surface tension method was adopted for the determination of the CMC's of the detergent solutions with inorganic salts added.

TABLE I. THE ELEMENTARY ANALYSIS OF VARIOUS BIVALENT METAL ALKYL SULFATES

Detergent		Metal content %	C, %	H, %
$Cu(DS)_2\cdot4H_2O$	Calcd.	9.61	43.23	8.78
	Found	9.55	43.29	8.87
$Co(DS)_2\cdot6H_2O$	Calcd.	8.45	41.29	8.96
	Found	8.62	41.56	9.33
$Ni(DS)_2\cdot6H_2O$	Calcd.	8.41	41.33	8.96
	Found	8.76	41.55	9.16
$Mg(DS)_2\cdot6H_2O$	Calcd.	3.77	43.48	9.35
	Found	3.73	43.45	9.39
$Cu(TS)_2\cdot4H_2O$	Calcd.	8.88	46.66	8.88
	Found	8.58	46.70	9.28
$Cu(HS)_2\cdot4H_2O$	Calcd.	8.24	49.48	9.27
	Found		49.22	9.48

DS: Dodecyl sulfate radical; TS: Tetradecyl sulfate radical; HS: Hexadecyl sulfate radical

The micellar molecular weights were estimated by the light scattering method, using a Shimadzu photoelectric light-scattering photometer and a Brice Phoenix universal light scattering photometer at 436 and 546 mμ with a semi-octagonal cell. The dependence of the refractive indices on the concentration of the detergents were measured by a Brice Phoenix differential refractometer at the same wavelength. The measurements were performed in the salt free and 0.1 M metal sulfate solutions.

The micellar charge was evaluated from the data of conductivity and light scattering using the equation previously reported[12].

Results and Discussion

The CMC's of Various Bivalent Metal Dodecyl Sulfates.—The critical micelle concentration is one of the most fundamental quantities in determining the surface activity of the detergent solution. Table II shows the CMC values of various bivalent metal alkyl sulfates. The CMC values obtained are almost the same within the range of experimental error, and no differences can be observed among various metal dodecyl sulfates. The CMC value of about 1.2×10^{-3} mol./l. obtained for various bivalent metal dodecyl sulfates in the present experiment is in good agreement with the value of 1.7×10^{-3} mol./l. at 40°C obtained by Lottermoser and Püschel[2] and the value of 1×10^{-3} mol./l. at various temperatures obtained by Miyamoto[6].

These CMC values are quite small compared with those of the corresponding monovalent metal dodecyl sulfates, e. g., sodium salt, indicating the increased surface activity of bivalent

---

[7] H. Lange, *Kolloid-Z.*, **121**, 66 (1951).

[8] J. M. Corkill and J. F. Goodman, *Trans. Faraday Soc.*, **58**, 206 (1962).

[9] H. V. Tartar and A. L. M. Lelong, *J. Phys. Chem.*, **59**, 1185 (1955).

[10] J. N. Bone and D. W. O'Day, *J. Am. Pharm. Assoc.*, **47**, 795 (1958).

[11] R. Matuura, H. Kimizuka, S. Miyamoto and R. Shimozawa, This Bulletin, **31**, 532 (1958).

[12] H. Kimizuka and I. Satake, ibid., **35**, 251 (1962).

TABLE II. THE CRITICAL MICELLE CONCENTRATIONS OF VARIOUS BIVALENT METAL ALKYL SULFATES

Detergent	Temp. °C	CMC mol./l.	Method
$Cu(DS)_2$	30	1.20×10^{-3}	Conductivity
$Mg(DS)_2$	30	1.25×10^{-3}	Conductivity
$Co(DS)_2$	30	1.23×10^{-3}	Conductivity
$Ni(DS)_2$	30	1.24×10^{-3}	Conductivity
$Cu(TS)_2$	47	2.5×10^{-4}	Surface tension
$Cu(HS)_2$	47	5.8×10^{-5}	Surface tension

salts. Miyamoto[5,6] reported that quite similar CMC values are also obtained for calcium, lead and strontium dodecyl sulfates; however, their Krafft points are 50, 53 and 64°C respectively, which are considerably higher than those of copper, cobalt and magnesium salts, which are 24, 23 and 25°C respectively. Also, the solubility of these salts is quite different from each other. Nevertheless, the CMC values are nearly identical for all these bivalent metal dodecyl sulfates. This means that the fundamental factor responsible for determining the CMC value of a detergent is the valency of the metal ion; varying the kind of metal ion having the same valency has little or no detectable effect on the CMC value, provided that the anionic group is the same.

When the alkyl chain length of the anionic group increases for the same metal salt, copper salt in the present case, the CMC value varies according to the formula:

$$\log(\mathrm{CMC}) = AN + B \tag{1}$$

as is the case with usual monovalent detergents. Here N is the number of carbon atoms in the alkyl chain, and A and B are constants. Figure 1 shows the relation between log (CMC) and N in the copper alkyl sulfates. The value of -0.32 is obtained for A, which is in good agreement with the value of -0.3 obtained for various alkyl sulfates of sodium.

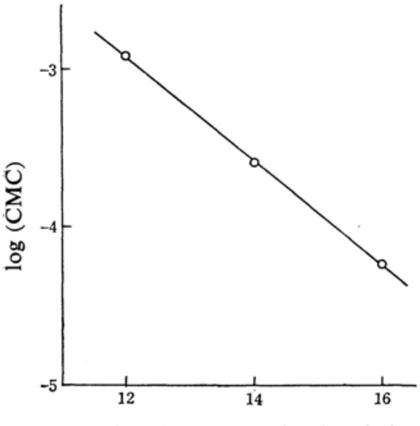

Fig. 1. Relation between log (CMC) and the number of carbon atoms in the chain of copper alkyl sulfates.

Effects of the Added Electrolytes on the CMC Value.—The effects of added electrolytes on the CMC value of the detergent have been widely studied by many authors. Especially, Corrin and Harkins[13] have investigated the effects of added electrolytes on the CMC values of various detergents and have found the following empirical equation between the CMC value and the total gegen-ion concentration:

$$\log(\mathrm{CMC}) = a \log m^{+} + b \tag{2}$$

Here a and b are constants, and $m^{+} = (\mathrm{CMC}) + C'$, where C' is the concentration of added electrolytes. Subsequent investigation of this problem was carried out by Lange[7], who obtained the same empirical relation when the valencies of the ion of the added electrolyte and the detergent gegen-ion are identical. However, he pointed out that Eq. 2 is not applicable if the valency of the ion of the added electrolyte is different from that of the gegen-ion, although he suggested that when the concentration of the added electrolytes is higher than that of detergent gegen-ions, a similar type of equation can be applied, one in which the concentration of added electrolytes, C, is substituted for m^{+} in Eq. 2:

$$\log(\mathrm{CMC}) = a \log C + b \tag{3}$$

Theoretical considerations of these empirical relations have been undertaken by Stainsby and Alexander[14], Hobbs[15] and Shinoda[16,17].

The effects of added copper sulfate and sodium sulfate on the CMC values of sodium dodecyl sulfate (SDS) and copper dodecyl sulfate ($Cu(DS)_2$) are shown in Figs. 2 and 3. The general features of the curves shown in Figs. 2 and 3 are quite similar to those obtained by Lange[7] for calcium dodecyl sulfate. At first the CMC value of SDS rapidly decreases with the addition of copper sulfate to about one fourth, and thereafter it gradually decreases as the concentration of copper sulfate increases. In the case of $Cu(DS)_2+Na_2SO_4$, the CMC value of $Cu(DS)_2$ decreases gradually compared with the case of $SDS+CuSO_4$.

In the solutions with the excess salt added, the CMC curve of the $SDS+CuSO_4$ system has a tendency to approach the curve of the $Cu(DS)_2+CuSO_4$ system, and the curve of $Cu(DS)_2+Na_2SO_4$ approaches that of $SDS+Na_2SO_4$. These facts suggest that the nature

---

[13] M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

[14] G. S. Stainsby and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 587 (1950).

[15] M. E. Hobbs, *J. Phys. Chem.*, **55**, 675 (1951).

[16] K. Shinoda, This Bulletin, **26**, 101 (1953).

[17] K. Shinoda, ibid., **28**, 340 (1955).

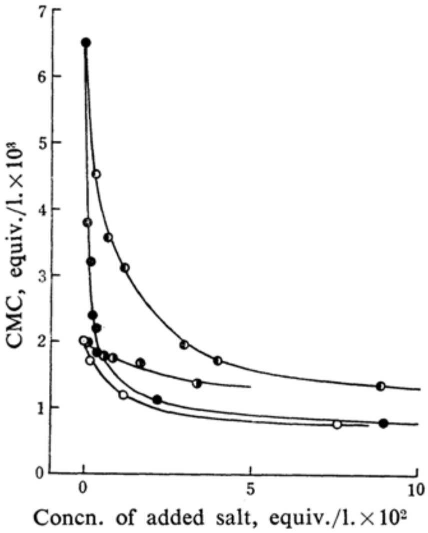

Fig. 2. Effects of the added salts on the CMC's of sodium dodecyl sulfate and copper dodecyl sulfate.
○ : $Cu(DS)_2+CuSO_4$ ◑ : $Cu(DS)_2+Na_2SO_4$
● : $SDS+CuSO_4$ ◐ : $SDS+Na_2SO_4$.
The CMC data of the system $SDS+Na_2SO_4$ was taken from the data reported by Corrin and Harkins[13].

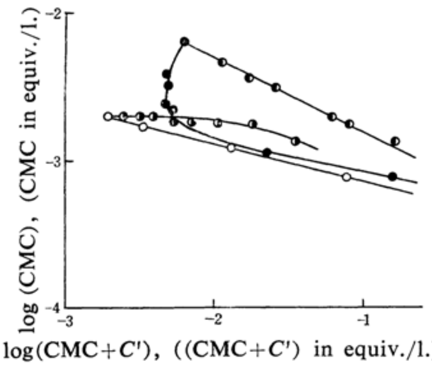

Fig. 3. Effects of the added salts on the CMC's of sodium dodecyl sulfate and copper dodecyl sulfate.
○ : $Cu(DS)_2+CuSO_4$ ◑ : $Cu(DS)_2+Na_2SO_4$
● : $SDS+CuSO_4$ ◐ : $SDS+Na_2SO_4$
The CMC data of the system $SDS+Na_2SO_4$ was taken from the data reported by Corrin and Harkins[13].

of the detergent in excess salt solutions is characterized by the added cations and that there occurs a rearrangement of the detergent micelle, i. e., the variation of the micellar aggregation number and the formation of a new, surface, gegen-ion layer of the micelle caused by the exchange between salt cations and the surface layer gegen-ions of the original detergent micelle. In both cases in which the gegen-ion is different from the added salt cation, there are no linear relationships between log (CMC) and log m^+, as is shown in Fig. 3. On the contrary, for the $Cu(DS)_2+CuSO_4$ system a good linearity is found to exist. Shinoda[17] derived an equation which expresses the effect of added electrolytes on the CMC value of the detergent solution. Using this equation we found that the degree of dissociation of micelle forming ion of copper dodecyl sulfate is 0.52. The degree of dissociation can also be determined by conductivity measurement, as will be described later.

The Determination of Micellar Molecular Weight by the Light-scattering Techinique.—The light-scattering technique is one of the most useful methods of estimating the molecular weight of the colloidal aggregate. However, the effect of micellar charge must be taken into cosideration in the application of this method to the charged system, as has already been pointed out by, for instance, Dosher and Mysels[18] and Hutchinson[19]. Dosher and Mysels[18] pointed out that Eq. 5 should be employed for charged systems in place of the usual scattering formula, Eq. 4.

$$(HC/\tau)_{C\to 0}=1/M \qquad (4)$$

$$(HC/\tau)_{C\to 0}=(1+P)/M \qquad (5)$$

Here, P is the number of simple ions associated with one charged, colloidal ion, M is the molecular weight of the colloidal particle, τ is the turbidity of the solution, C is the concentration in g./ml., and

$$H=32\pi^3n^2(\mathrm{d}n/\mathrm{d}c)^2/3N\lambda^4$$

where n is the refractive index of the solution and λ is the wavelength of the incident light. The true molecular weight of the solute particle can be obtained from the scattering experiment in an excess salt solution because P in Eq. 5 tends to zero in this condition. The measurements were conducted at 436 and 546 mμ and at 30°C. The values of micellar molecular weight obtained at 436 and 546 mμ were approximately the same within the range of experimental error. The scattering was observed by using a semi-octagonal cell at the angle of 45 90 and 135° with relation to the incident light, but the dissymmetries of the scattering can not be detected. Thus, the limiting condition in the application of Eqs. 4 or 5, that the dimension of the solute particle must be smaller than $\lambda/20$, is considered to be quite satisfied.

In Fig. 4, the typical scattering curve of copper dodecyl sulfate is given. The abscissa represents the micellar concentration $C-C_o$, where C_o is the CMC value. Table III shows the micellar molecular weights of nickel,

---

[18] T. M. Dosher and K. J. Mysels, *J. Chem. Phys.*, **19**, 254 (1951).
[19] E. Hutchinson, *J. Colloid Sci.*, **9**, 191 (1954).

TABLE III. MICELLAR MOLECULAR WEIGHTS OF VARIOUS METAL DODECYL SULFATES AT 30°C

Solute	Solvent	CMC $\times 10^3$ (mol./l.)	MMW	AN	P
Ni(DS)$_2$	H_2O	1.1	24400	92	0.16
	0.1 M $NiSO_4$	0.3	28200	106	
Co(DS)$_2$	H_2O	1.2	27400	103	0.11
	0.1 M $CoSO_4$	0.3	30300	114	
Cu(DS)$_2$	H_2O	1.2	22700	85	0.13
	0.1 M $CuSO_4$	0.3	25600	97	
Mg(DS)$_2$	H_2O	1.2	26300	99	0.19
	0.1 M $MgSO_4$	0.3	31300	118	

MMW: Micellar molecular weight; AN: Aggregation number

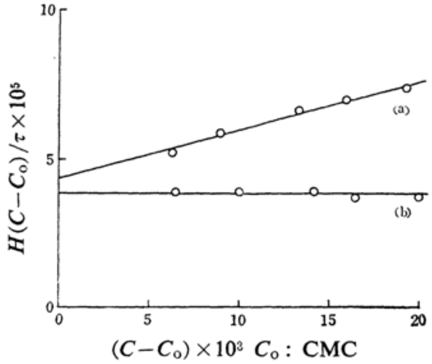

Fig. 4. $H(C-C_o)/\tau\sim(C-C_o)$ curves for copper dodecyl sulfate in H_2O at 436 mμ (a), and in 0.1 M $CuSO_4$ at 546 mμ (b), at 30°C.

cobalt, copper and magnesium dodecyl sulfate in salt free solutions and in corresponding metal sulfate solutions. For the salt free solutions, Eq. 4 was also assumed to hold.

Only small differences are found among the micellar molecular weights of the various bivalent metal dodecyl sulfates studied. The values of the micellar molecular weight in salt free solutions fall in the comparatively narrow range between 23000 and 27000, and those in salt solutions, in the range between 25000 and 31000. The micellar molecular weights of the detergents in salt solutions are slightly larger than those in salt free solutions. The ***P*** values calculated from Eq. 5 by using the data of micellar molecular weight in Table III are of the order of 0.1 to 0.2, indicating the almost complete screening action of the bivalent metal ions, even in salt free solutions. The micellar aggregation number, i. e., the number of dodecyl chains in a micelle, of bivalent metal dodecyl sulfates is about 100, which is almost twice the value (41) for SDS[20]. The same order of aggragation number was reported by Tartar and Lelong[9], who obtained the micellar molecular weight of 28500 and the aggregation number of 107 for magnesium dodecyl sulfonate in a salt free solution.

Thus, the marked increase in surface activity, especially the solubilizing power of the bivalent metal dodecyl sulfates, may be expected because of the increased micellar aggregation number of the micelle and their decreased CMC value. The solubilizing power of these detergents will be reported on in another paper.

The Estimation of Micellar Charge from Conductivity Data.—The micellar charge of the detergent can be evaluated from the conductivity of the aqueous solution and from the micellar aggregation number obtained by the light-scattering technique, as has been reported[12].

Using some basic assumptions[12], the following equations can be derived:

$$[(\Lambda_o-\Lambda)/(\Lambda_o-\Lambda_m)]^2=\{(Z_d-Z_c)+(Z_g+Z_c)C/C_m\}/(Z_d+Z_g) \qquad (6)$$

$$Z_c=\{Z_m{}^2-Z_g(nZ_d-Z_m)\}/nZ_d \qquad (7)$$

Here, Λ_o is the equivalent conductivity of the detergent at infinite dilution, Λ_m is the equivalent conductivity at the CMC value, and Z_d and Z_g are the valencies of the detergent ion and gegen-ion respectively. The value of Z_c can be evaluated from the slope of the straight line by plotting the quantity $[(\Lambda_o-\Lambda)/(\Lambda_o-\Lambda_m)]^2$ as the function of the reduced concentration, C/C_m. Moreover, the value of the micellar charge, Z_m, can be calculated from Eq. 7 by using the micellar aggregation number, n, obtained by the light-scattering experiment. Figure 5 shows one of the typical relations between $[(\Lambda_o-\Lambda)/(\Lambda_o-\Lambda_m)]^2$ and C/C_m for copper dodecyl sulfate. The calculated micellar charge, Z_m, and the dissociation degree of the micellar ion, α, are given in Table IV.

The dissociation degrees of the micellar ion, α, obtained in the present experiment are comparatively small, suggesting that about half of the micelle-forming detergent molecules are undissociated. The value of α decreases

---

[20] H. V. Tartar, ibid., **14**, 115 (1959).

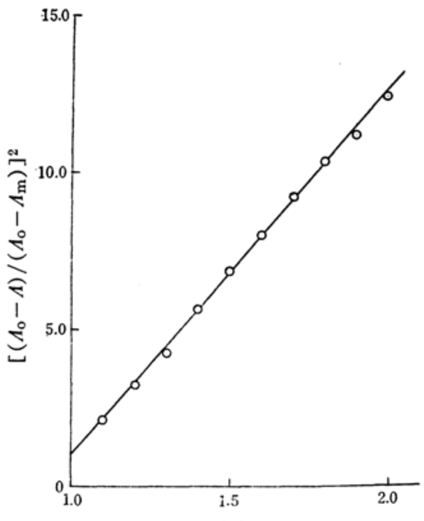

Fig. 5. Typical relation between $[(\Lambda_o-\Lambda)/(\Lambda_o-\Lambda_m)]^2$ and C/C_m for copper dodecyl sulfate at 30°C.

TABLE IV. THE MICELLAR CHARGE AND THE DISSOCIATION DEGREE OF THE MICELLAR ION OF VARIOUS METAL DODECYL SULFATES AT 30°C

Solute	n (In a salt solution	Z_c	Z_m	α
$Co(DS)_2$	114	47	75	0.66
$Cu(DS)_2$	97	34	58	0.60
$Mg(DS)_2$	118	20	50	0.42

Here α equals Z_m/nZ_d.

in the order cobalt>copper>magnesium, but the difference among them is said to be not very large. The value of 0.60 for copper dodecyl sulfate micelle is approximately the same as the value of 0.52 obtained from the effect of the added electrolyte on the CMC value mentioned above.

These experimental results suggest that, above the CMC value, the micelle of the bivalent metal dodecyl sulfate must be treated as a weak electrolyte. The bivalent metal dodecyl sulfates are composed of a weak base and a strong acid; therefore, the effect of the hydrolysis of the bivalent gegen-ion must be considered. This problem will, in the near future, be treated in another paper in connection with the change in the pH value of the detergent solutions with concentration.

Summary

Dodecyl sulfates of bivalent nickel, cobalt, copper and magnesium were synthesized, and studies were carried out on the CMC values of these detergents, the effects of the added electrolytes on these CMC values, on micellar molecular weights, and on micellar charges. The CMC values of the detergents were independent of the kind of metal, and the CMC value of 1.2×10^{-3} mol./l. was obtained. The micellar aggregation numbers of bivalent metal dodecyl sulfates were of the order of 100, which is about twice that of sodium dodecyl sulfate. The dissociation degrees of the micelles were also evaluated from the conductivity data. The α values obtained were 0.66 for cobalt, 0.60 for copper and 0.42 for magnesium. The dissociation degree of the copper dodecyl sulfate micelle was also estimated to be 0.52 from the depression of the CMC value by the added electrolyte; this figure is approximately the same as the value of 0.60 obtained from the conductivity data. These results suggest that the fundamental factor responsible for determining the surface activities of bivalent metal dodecyl sulfates is the valency of the gegen-ion and that the kind of metal has little or no detectable effect on them.

The authors wish to thank to Professor Tomoo Oyama in the Faculty of Technology and to Professor Satoru Akune in the Faculty of Agriculture, both of Kyushu University, for helping in the light-scattering experiment.

Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka