The Surface Activities of Bivalent Metal Alkyl Sulfates. II. The Solubilization of Some Hydrocarbons in Aqueous Solutions of Bivalent Metal Alkyl Sulfates

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In a previous paper[1], we studied some basic surface chemical properties of bivalent metal alkyl sulfate detergents in aqueous solutions. It was found that the critical micelle concentrations (CMC) of bivalent metal alkyl sulfates are nearly independent of the kind of bivalent metals and considerably smaller than that of corresponding monovalent metal alkyl sulfates; light-scattering experiments indicated that the micellar aggregation number of various bivalent metal dodecyl sulfates lies in the comparatively narrow range from 100 to 120, about 2 to 3 times higher than that of sodium dodecyl sulfate (SDS) reported by some authors[2-4]. In this connection it seemed interesting to study the solubilizing power of the bivalent metal alkyl sulfates, since the phenomenon of solubilization is generally considered to have much to do with the micelle formation in the detergent solution. The solubilization of substances by various detergents has widely been studied by a number of authors, and the general features of the phenomena have been summarized, for example, in the critical reviews of Klevens[5] and Hutchinson[6]. However, no data have been published on the solubilization by the solutions of ionic detergents containing bivalent metals. The purpose of the present paper is to determine the solubilizing powers of some bivalent metal alkyl sulfates towards some typical hydrocarbons, and to discuss the differences, if any, among them.

Experimental

Materials.—The detergents used in the present experiment are copper(II), cobalt(II), magnesium(II) and nickel(II) dodecyl sulfates, and copper(II) tetradecyl sulfate. The preparation and the results of elementary analysis have previously been reported[1]. The values of CMC are 1.2×10^{-3} mol./l. at 30°C for all the bivalent metal dodecyl sulfates used and 2.5×10^{-4} mol./l. at 47°C for copper tetradecyl sulfate. For the sake of comparison, the solubilizing power of sodium dodecyl sulfate (CMC, 7.2×10^{-3} mol./l.) was also measured. Benzene, toluene, *m*-xylene and *n*-hexane were used as solubilizates. They were purified by distillation.

Method.—The maximum amounts of hydrocarbons solubilized at any given temperature and the detergent concentration were determined optically as follows: a series of vessels, each containing

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[1] I. Satake, I. Iwamatu, S. Hosokawa and R. Matuura, This Bulletin, **36**, 204 (1963).

[2] L. M. Kushner and W. D. Hubbard, *J. Colloid Sci.*, **10**, 429 (1955).

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

[4] H. V. Tartar, *J. Colloid Sci.*, **14**, 115 (1959).

[5] H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

[6] M. E. L. McBain and E. Hutchinson, "Solubilization", Academic Press, New York (1955).

10 ml. of a detergent solution of a fixed concentration with an increasing amount of the hydrocarbon added, is shaken at a constant temperature for several hours. It took about six hours for the solubilization to reach an equilibrium. Then the turbidities of the solutions were measured using a Hitachi Photoelectric Photometer **EPO-B** at 430 mμ for copper and magnesium salts, at 610 mμ for cobalt salt, and at 500 mμ for nickel salt. The turbidity of the solution rose sharply when a definite amount of the hydrocarbon was added. Figure 1 shows the typical turbidity curve of benzene in 3×10^{-3} ml./l. copper dodecyl sulfate at 30°C. The apparent amount of hydrocarbon solubilized can be determined by the interpolation of the two linear portions of the turbidity curve. Then the net amount of hydrocarbon solubilized is obtained by subtracting the solubility of hydrocarbon in pure water from the apparent amount of solubilization.

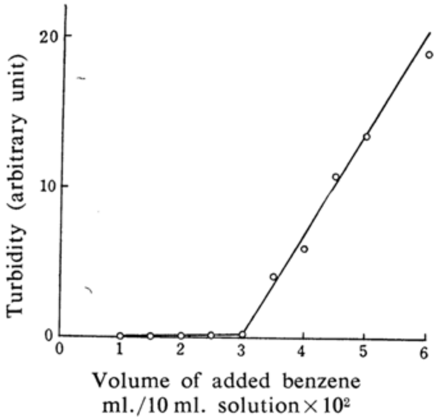

Fig. 1. Typical turbidity curve for benzene in 3×10^{-3} mol./l. copper dodecyl sulfate solution at 30°C.

The measurements were conducted at 30°C or above for bivalent metal dodecyl sulfates and at 40°C for copper tetradecyl sulfate in order to make experiments above the Krafft point of each detergent[1,7].

Results and Discussion

In Figs. 2 and 3, the amount of benzene solubilized in grams per liter of solution is plotted against the detergent concentration at 30 and 40°C respectively. For the sake of comparison, the amount of benzene solubilized by the SDS solution is also shown. The amount of benzene solubilized by bivalent metal dodecyl sulfates is found to be much larger than that by SDS, and only small differences in solubilizing power can be observed among the different bivalent salts. As has previously been reported[1], the nature of bivalent metal has no detectable effect on CMC. Thus, all the bivalent salts used had the identical CMC value of 1.2×10^{-3} mol./l., which is quite small compared with the value of 8×10^{-3} mol./l. for SDS. In addition, the micellar aggregation numbers of bivalent salts determined by a light-scattering experiment[1] are 97 for copper, 114 for cobalt, 118 for magnesium and 106 for nickel, aggregation numbers which are 2 to 3 times those for SDS[2-4]. The marked increase in the solubilizing power of bivalent metal dodecyl sulfates may reasonably be explained in terms of the increased micellar aggregation numbers.

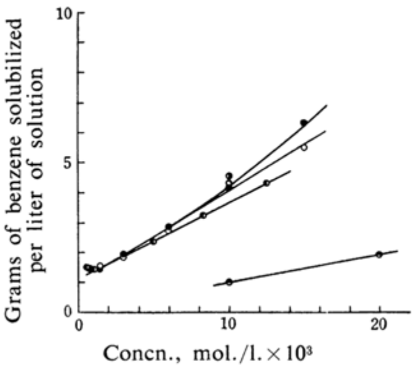

Fig. 2. Solubilization of benzene in aqueous solutions of bivalent metal dodecyl sulfates at 30°C.

○ ; Copper ● ; Cobalt ◐ ; Magnesium
◑ ; Nickel ◓ ; Sodium

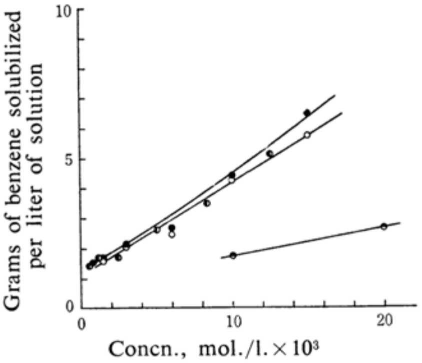

Fig. 3. Solubilization of benzene in aqueous solutions of bivalent metal dodecyl sulfates at 40°C.

○ ; Copper ● ; Cobalt ◐ ; Magnesium
◓ ; Sodium

A nearly linear relation is observed between the amount of benzene solubilized and the detergent concentration. Mankowich[8] has pointed out that there are linear relations between log of solubilized amount and log of concentration for dye solubilization by various detergents,

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[7] S. Miyamoto, This Bulletin, **33**, 371 (1960).

[8] A. M. Mankowich, *J. Colloid Sci.*, **14**, 131 (1959).

but he has given no theoretical considerations. In a narrow concentration range as in the present experiment, the micellar aggregation number and the micellar size may be assumed to be independent of the detergent concentration, as is shown by the light-scattering experiment[1]. If this is true, a linear relation between the amount of benzene solubilized and the detergent concentration is most probable. The slope of these lines indicates the amount of benzene solubilized per mole of micelle-forming detergent molecules. The available volume, v, for the solubilization in a micelle of a solubilized state can be evaluated from the micellar aggregation number, n, and the slope of these lines, provided that the partial molar volume of the solubilizate is assumed to be nearly identical with the molar volume of its pure state. The value of v is given by nmV/ZN, in which V is the molar volume of benzene; m, the number of moles of benzene solubilized per mole of micelle-forming detergent molecules; Z, the valency of gegen ions, and N, the Avogadro number. The values of v thus calculated are about $(3\sim4)\times10^4$ Å^3 for bivalent metal dodecyl sulfates and about $(7\sim9)\times10^3$ Å^3 for SDS, when we use the values of m taken from Figs. 2 and 3. In the calculation of the v for the SDS micelle, we take the micellar aggregation number of 40. Then the available volume for solubilization in a micelle of bivalent metal dodecyl sulfates is about four times that of the SDS micelle.

Now, we assume the spherical micellar models for both SDS and bivalent metal dodecyl sulfates; further, the area, s, which is occupied at the micellar surface by a polar head of a micelle-forming detergent molecule is assmed to be nearly independent of the micellar aggregation number and the nature of gegen ion. Therefore, the geometrical volume of a spherical micelle is given by $(ns)^{3/2}/6\pi^{1/2}$. If, therefore, the micellar aggregation number, n, is increased, the volume of the spherical micelle will be increased being proportional to $n^{3/2}$. Thus, the ratio of the available volume for solubilization in a micelle may be expected to be proportional to $(n_1/n_2)^{3/2}$, because the available volume for solubilization would be proportional to the total micellar volume. Here n_1 and n_2 are the micellar aggregation numbers of SDS and of bivalent salt respectively. In the present case, the ratio of the micellar aggregation number is taken to be about 2.5 to 3.0, from which the ratio of the micellar volume may be estimated to be 4 to 5. Thus, the experimental results obtained above may approximately be explained by the simple spherical micellar model of the detergent.

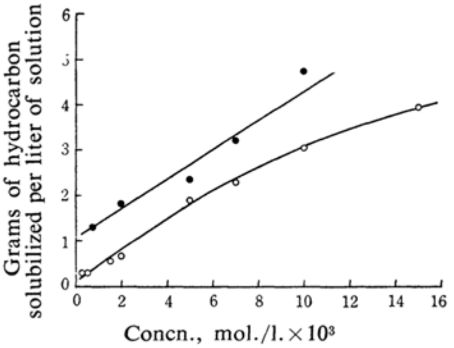

Fig. 4. Solubilization of toluene and n-hexane in aqueous solution of coopper dodecyl sulfate at 40°C.

○ ; Toluene ● ; n-Hexane

The increase in the molar volume of the solubilizate has the normal effect of decreasing the solubilization. Figure 4 shows the amounts of toluene and n-hexane solubilized by copper dodecyl sulfate at 40°C. Table I gives the effect of the size of the solubilizate on the solubilization by metal dodecyl sulfates at 30°C. The effect of the molar volume of the solubilizates on the extent of solubilization has been investigated by several authors[5,9,10]. Especially, Harkins et al.[9] pointed out, on the basis of their solubilization experiments on a number of hydrocarbons using potassium laurate and myristate, that the amount of hydrocabon solubilized is inversely proportional to the molar volume of the solubilizate so far as the same homologous series is concerned. In the present experiment, however, one can find no such simple relationships between the molar volume and the amount of hydrocarbon

TABLE I. THE EFFECT OF THE SIZE OF THE SOLUBILIZATE ON THE SOLUBILIZATION OF HYDROCARBONS BY VARIOUS METAL DODECYL SULFATES AT 30°C

Detergent	Concn. mol./l.	Grams of hydrocarbon solubilized per litre of solution		
		Benzene	Toluene	m-Xylene
$Cu(DS^*)_2$	1×10^{-2}	4.31	2.94	2.30
$Co(DS)_2$	1×10^{-2}	4.15	3.13	2.82
$Ni(DS)_2$	1×10^{-2}	4.55	2.95	2.22
$Mg(DS)_2$	8.3×10^{-3}	3.22	2.07	2.22**
NaDS	2×10^{-2}	1.93	1.46	

* DS; Abbreviation of the dodecyl sulfate radical.

** By 10^{-2} mol./l. solution

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[9] R. S. Stearns, H. Oppenheimer, E. Simon and W. D. Harkins, *J. Chem. Phys.*, **15**, 496 (1947).

[10] J. W. McBain and P. H. Richards, *Ind. Eng. Chem.*, **38**, 642 (1946).

TABLE II. THE EFFECT OF TEMPERATURE ON THE SOLUBILIZATION OF HYDROCARBONS IN GRAMS PER LITER OF SOLUTION OF BLVALENT METAL DODECYL SULFATES

Solubilizate	Detergent	Concn., mol./l.	Temp., °C			
			30	40	45	50
Benzene	$Cu(DS)_2$	1.5×10^{-2}	5.48	5.72	5.92	6.63
	$Mg(DS)_2$	1.25×10^{-2}	4.34	5.10	4.78	4.87
Toluene	$Cu(DS)_2$	1.0×10^{-2}	2.94	2.80		2.77
	$Co(DS)_2$	1.0×10^{-2}	3.13	3.16		2.78

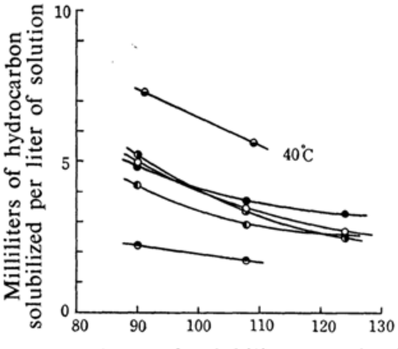

Fig. 5. Relation between the molar volume of solubilizate and the amount of hydrocarbon solubilized by 10^{-2} mol./l. metal alkyl sulfates at 30°C.
○; $Cu(DS)_2$ ●; $Co(DS)_2$ ◐; $Mg(DS)_2$
◑; $Ni(DS)_2$ ◒; $Cu(TS)_2$ ◓; NaDS(2×10^{-2} mol/l.).

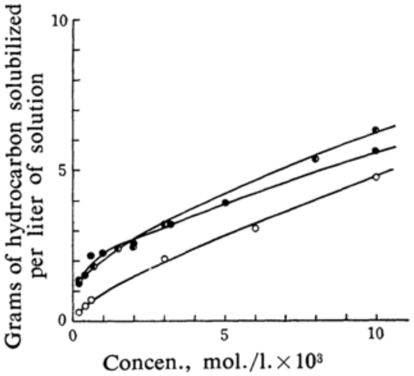

Fig. 6. Solubilization of hydrocarbons in aqueous solution of copper tetradecyl sulfate at 40°C.
◐; Benzene ○; Toluene ●; *n*-Hexane

solubilized, as is shown in Fig. 5. It can only be said that the extent of solubilization decreases as the molar volume of the solubilizate increases; no unique and quantitative relation has been found between them.

Table II shows the effect of temperature on the solubilization of benzene and toluene by bivalent metal dodecyl sulfates. The temperature change has no appreciable effect on the extent of the solubilization of benzene or toluene, as may be seen from Table II, suggesting that the heat of the solubilization of benzene or toluene in these detergent micelles is negligibly small. This is not unreasonable if the micellar interior is assumed to be of a liquid hydrocarbon-like structure.

In Fig. 6 the solubilization of benzene, toluene and *n*-hexane by copper tetradecyl sulfate is plotted against the concentration at 40°C. The considerable increase in the solubilizing power of copper teradecyl sulfate is to be noted. At the same detergent concentration, say at 10^{-2} mol./l., the ratio of the amount of hydrocarbons solubilized by copper tetradecyl sulfate to that by copper dodecyl sulfate is found to be 1.5 for benzene, 1.6 for toluene and 1.4 for *n*-hexane. The effect of chain length on the solubilizing power of the detergent has already been studiend by several authors. Harkins et al[9], for example, have shown in their study of the solubilization of benzene and *n*-hexane that the solubilizing power of potassium myristate is about twice that of potassium laurate. The same order of increase in solubilizing power was reported by Klevens[5] for the solubilization of ethylbenzene by the same detergents as above. If the above-mentioned spherical micellar model can also be applied to the copper tetradecyl sulfate micelle, meaning that the increase in the solubilizing power of copper tetradecyl sulfate may be ascribed to the increase in micellar volume caused by the change in micellar aggregation number, we can estimate the micellar aggregation number of this detergent to be 127.

It is to be noted that a small number of hydrocarbons can be solubilized at quite low concentrations of the detergents, as may be seen in Figs. 2, 3, 4 and 6. It is really a well-known fact that the CMC value of the detergent solution decreases with the solubilization of hydrocarbons[11,12], but, for example, the depression of the CMC value caused by the addition of hydrocarbons has been found to lie only within the range of 10 to 30 per cent for sodium alkyl sulfonate[11]. If this is the case with the metal dodecyl sulfates, the

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[11] H. B. Klevens, *J. Phys. & Colloid Chem.*, **54**, 1012 (1950).
[12] W. C. Lin, This Bulletin, **28**, 227 (1955).

solubilization of hydrocarbons at very low concentrations of these detergents could not be due to their micelles. It seems that a small amount of some hydrocarbons is bound with singly-dispersed detergent molecules or ions in order to be soluble in the solution. The scheme of this binding is a problem to be examined in the future.

Summary

The solubilizing power of the bivalent copper, cobalt, nickel and magnesium dodecyl sulfates, and of copper tetradecyl sulfate towards benzene, toluene, *m*-xylene and *n*-hexane has been determined over the concentration range from 10^{-3} to 1.5×10^{-2} mol./l. at various temperatures. There were approximately linear relationships between the amounts of hydrocarbons solubilized and the detergent concentration. No fundamental difference could be observed among the solubilizing powers of the various bivalent salts studied, in accordance with such other micellar properties as CMC or micellar aggregation number. The solubilizing power, in moles of hydrocarbon solubilized per equivalent detergent, was found to be about 2.0 for the solubilization of benzene by bivalent metal dodecyl sulfates, which is about 1.5 times that by sodium dodecyl sulfate. This increased solubilizing power of bivalent salts was ascribed to the increased micellar volume and to the increased micellar aggregation number compared with that of sodium dodecyl sulfate. The increasing chain length causes a normal increase in solubilizing power. The ratio of the amount of hydrocabons solubilized by copper tetradecyl sulfate to that solubilized by copper dodecyl sulfate was about 1.5.

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