The Effect of Metallic Ions on Surface Chemical Phenomena. III. Solubility of Various Metal Dodecyl Sulfates in Water

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In the preceding paper[1] a study was made of the effects of various inorganic electrolytes on the stability and type of emulsions stabilized with sodium dodecyl sulfate. Added polyvalent cations were found to cause phase inversion of the emulsions. These effects can hardly be explained without taking into consideration the properties of corresponding metal dodecyl sulfates formed as the consequence of the reaction of sodium dodecyl sulfate with these cations. In order to understand the nature of the effect of metallic ions in these systems it is, therefore, necessary to investigate fully the properties of various metal dodecyl sulfates, more generally metal alkyl sulfates in aqueous solutions.

Some studies have been reported regarding their properties up to the present. Nishizawa and Tomizuka[2] studied the compositions and crystallographic habits of hexadecyl sulfates of potassium, sodium, ammonium, magnesium and calcium. They also made reference qualitatively to the solubility of these compounds in various solvents. Ueno, Yokoyama and Iwakura[3] found that solubilities of ammonium-, sodium- and potassium dodecyl sulfates and hexadecyl sulfates decrease in this order. They studied also the foam formation, surface tension, interfacial tension at oil-water interface and detergent action of these metal dodecyl sulfates. Yoshizaki and Terashima[4] studied the change of foam volume on aqueous solutions of sodium hexadecyl sulfate with the course of time. Measurement of foam of ammonium-, magnesium- and calcium dodecyl sulfate and hexadecyl sulfate

1) S. Miyamoto, *Mem. Fac. Sci. Kyushu Univ., Series C, Chem.*, in press.
2) K. Nishizawa and T. Tomizuka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **35**, 1368 (1923).
3) S. Ueno, S. Yokoyama and Y. Iwakura, ibid., **38**, 1333 (1935).
4) T. Yoshizaki and H. Terashima, ibid., **55**, 350 (1952).

solutions was made by Nakashima[5]. Lottermoser et al.[6] synthesized metal alkyl sulfates and undertook measurements of conductance, potential, surface tension and interfacial tension of their aqueous solution. These authors gave consideration to the change of dissolved state with the change of concentration of the solution. Further, Giers and Boido[7] measured cloud point, viscosity, pH, contact angle, wetting speed and foaming property of ammonium-, sodium-, potassium-, magnesium-, calcium- and zinc dodecyl sulfates. As regards solubility, sodium dodecyl sulfate, tetradecyl sulfate and hexadecyl sulfate were studied by Hutchinson et al.[8] at various temperatures. On the solubility of metal alkyl sulfates, however, only a few data have been reported. The solubility of calcium dodecyl sulfate was given as 0.03~0.04% at 25°C by Lenher[9], 0.00457 mol./1000 g. H_2O at 50°C by Tartar and Cadle[10] and 0.5 g./l. at 53°C and 1.0~5.0 g./l. at 54°C[11].

In the preceding paper reported by the author[1] values of solubility of sodium-, calcium-, barium-, aluminum-, iron- and thorium dodecyl sulfates were given at 25°C. It seems, however, that further studies are necessary to obtain full knowledge regarding the values of solubility of many other metal dodecyl sulfates. So one has conducted the measurements of solubility of calcium-, strontium-, lead-, barium-, copper, manganese-, magnesium- and cobalt dodecyl sulfates at various temperatures. It is the purpose of the present paper to report the results of the solubility measurement of these metal dodecyl sulfates and to undertake some discussions concerning them.

Experimental

Materials.—Metal dodecyl sulfates were synthesized from pure sodium dodecyl sulfate (abbreviated as SDS) which was synthesized from pure dodecyl alcohol and a guaranteed reagent of concentric sulfuric acid according to the method described in the papers already reported[1,12]. Pure dodecyl alcohol used was obtained by fractional distillations in vacuo. Synthesized SDS was freed from unsulfated dodecyl alcohol by extraction with ethyl ether for about forty hours in a Soxhlet extractor. The purity of the SDS sample was ascertained from the absence of the minimum in the curve representing surface tension of its aqueous solutions versus its concentration and also from results of elementary analysis of the sample. From these results[1], it was found that the SDS sample was highly pure surface-chemically. Metal dodecyl sulfates were precipitated from SDS aqueous solution by adding concentrated aqueous solutions of magnesium-, calcium-, strontium-, barium-, cupric-, lead-, manganous- and cobaltous chlorides. All these electrolytes had been purified before they were used for the preparation of corresponding metal dodecyl sulfates. The precipitated metal dodecyl sulfates were taken out by filtration by a glass filter and then they were recrystallized further three times except in the case of barium salt which was found to be soluble only in small amount even at high temperatures. Washing with water was carried out fully after every recrystallization. Readily soluble metal dodecyl sulfates were washed with cold water. After purification, they were brought into the air-dried state. Elementary analysis and metal content analysis were conducted on these air-dried samples.

Method.—Measurements of solubility were performed as usual by weighing the amounts of solute contained after drying up known weights of the saturated solution at 50°C. It was found that long periods of time were necessary to attain true equilibrium of solubility, so the bottle containing the sample was shaken to accelerate the attainment of equilibrium. The process of attainment of equilibrium is shown in Fig. 1 with magnesium-, calcium-, strontium-, lead- and barium dodecyl sulfates.

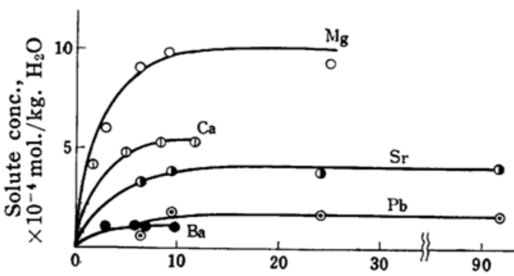

Fig. 1. Attaiment of equilibrium of the solubility in solution of Mg-, Ca-, Sr-, Pb- and Ba dodecyl sulfates in water with the course of stirring time.

Results

At first, elementary analyses of carbon, hydrogen and metal contents of air-dried metal dodecyl sulfates were carried out.

5) H. Nakashima, ibid., **56**, 611 (1953).
6) A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933); A. Lottermoser and F. Stoll, ibid., **63**, 49(1933).
7) S. Giers and D. Boido, *Soap Chem. Specialities*, **30**, 38, 179 (1954).
8) E. Hutchinson, K. E. Manchester and L. Winslow, *J. Phys. Chem.*, **58**, 1124 (1954).
9) S. Lenher, *Am. Dyestuff Reptr.*, **22**, 663 (1933).
10) H. V. Tartar and R. D. Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).
11) K. Kanamaru, "Surface Active Agents (Kaimen Kassei Zai)", Maki Shoten, Tokyo (1955), p. 47.
12) R. Matuura, H. Kimizuka, S. Miyamoto and R. Shimozawa, This Bulletin, **31**, 532 (1958).

TABLE I. RESULTS OF ELEMENTARY ANALYSIS AND METAL CONTENT ANALYSIS OF AIR-DRIED METAL DODECYL SULFATES

Metal		Metal content %	Elementary analysis C, %	H, %
Ca	Found	9.33	49.10	8.65
	Calcd. as $Ca(DS)_2$	9.38	49.19	8.60
Sr	Found	14.22	46.95	8.11
	Calcd. as $Sr(DS)_2$	14.18	46.59	8.15
Ba	Found	20.53	43.36	7.77
	Calcd. as $Ba(DS)_2$	20.57	43.12	7.55
Pb	Found	28.04	38.90	6.89
	Calcd. as $Pb(DS)_2$	28.09	39.04	6.83
Mn	Found	9.33	49.10	8.65
	Calcd. as $Mn(DS)_2$	9.38	49.19	8.60
Mg	Found	3.67	43.43	9.47
	Calcd. as $Mg(DS)_2 \cdot 6H_2O$	3.77	43.48	9.35
Co	Found	8.65	41.23	8.95
	Calcd. as $Co(DS)_2 \cdot 6H_2O$	8.45	41.29	8.96
Cu	Found	—	43.09	8.86
	Calcd. as $Cu(DS)_2 \cdot 4H_2O$	—	43.23	8.78

TABLE II. VALUES OF SOLUBILITY (mol./1000 g. H_2O) OF METAL DODECYL SULFATES AT VARIOUS TEMPERATURES (THOSE OF GREATER SOLUBILITY)

Temp., °C	$Cu(DS)_2 \cdot 4H_2O$	$Mn(DS)_2$	$Co(DS)_2 \cdot 6H_2O$	$Mg(DS)_2 \cdot 6H_2O$
5.0	1.99×10^{-2}	2.12×10^{-3}	—	—
10.0	2.46×10^{-2}	4.15×10^{-3}	—	6.39×10^{-4}
13.0	—	5.26×10^{-3}	—	—
15.0	3.48×10^{-2}	6.35×10^{-3}	8.08×10^{-4}	8.06×10^{-4}
16.0	—	1.75×10^{-2}	—	—
17.0	—	8.92×10^{-1}	—	—
20.0	—	8.99×10^{-1}	9.01×10^{-4}	9.27×10^{-4}
23.0	4.12×10^{-2}	—	9.78×10^{-4}	9.58×10^{-4}
25.0	6.53×10^{-2}	—	2.53×10^{-3}	9.58×10^{-4}
25.8	9.30×10^{-1}	—	—	—
26.5	9.68×10^{-1}	—	—	—
28.0	—	—	9.81×10^{-3}	4.98×10^{-3}
31.0	—	—	4.17×10^{-2}	4.46×10^{-2}

TABLE III. VALUES OF SOLUBILITY (mol./1000 g. H_2O) METAL DODECYL SULFATES AT VARIOUS TEMPERATURES (THOSE OF SMALLER SOLUBILITY)

Temp., °C	$Ca(DS)_2$	$Sr(DS)_2$	$Pb(DS)_2$	$Ba(DS)_2$
25.0	4.61×10^{-4}	4.05×10^{-4}	1.76×10^{-4}	1.15×10^{-4}
35.0	7.31×10^{-4}	5.39×10^{-4}	1.21×10^{-4}	1.74×10^{-4}
40.0	9.33×10^{-4}	—	—	—
45.0	—	8.10×10^{-4}	2.81×10^{-4}	2.55×10^{-4}
50.0	1.62×10^{-3}	—	—	—
51.0	2.09×10^{-2}	—	—	—
52.6	2.30×10^{-2}	—	—	—
54.0	—	—	1.18×10^{-3}	—
55.0	2.45×10^{-2}	1.09×10^{-3}	3.43×10^{-3}	—
58.0	—	—	6.37×10^{-2}	—
60.0	—	1.40×10^{-3}	6.54×10^{-2}	—
65.0	—	3.59×10^{-3}	7.82×10^{-2}	5.06×10^{-4}
65.5	—	3.59×10^{-2}	—	—
66.0	—	6.25×10^{-2}	—	—
67.0	—	7.46×10^{-2}	—	—
70.0	—	—	—	6.74×10^{-4}
75.4	—	—	—	8.02×10^{-4}
100.0	—	—	—	1.66×10^{-3}

and the results are shown in Table I. From these results the compositions of metal dodecyl sulfates were determined. That is, they were found to have the following formulae. $Ca(DS)_2$, $Sr(DS)_2$, $Ba(DS)_2$, $Pb(DS)_2$, $Mn(DS)_2$, $Mg(DS)_2 \cdot 6H_2O$, $Co(DS)_2 \cdot 6H_2O$ and $Cu(DS)_2 \cdot 4H_2O$, where the abbreviation DS represents the dodecyl sulfate radical.

Values of solubility of these metal dodecyl sulfates were obtained at various temperatures and they are shown in Table II (greater solubility) and Table III (smaller solubility).

It has been well known that soaps have the Krafft point above which their solubilities increase enormously. The Krafft point has also been observed generally with the surface active agents such as sodium alkyl sulfates[8], sodium alkyl sulfonates[13], anisidine sodium sulfonates, alkyl pyridinium halides and alkyl trimethylammonium halides[14]. Metal dodecyl sulfates are considered to be surface active agents also, so they are expected to have a Krafft point. To examine whether they have a Krafft point or not, plots of logarithms of solubility versus reciprocals of temperature were drawn as shown in Fig. 2. In this figure, the intersections of two straight lines are seen, which show the Krafft points. The values of Krafft points thus obtained are shown in Table IV.

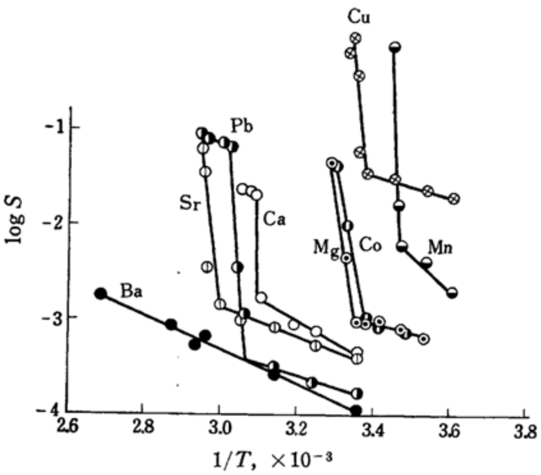

Fig. 2. Relation between the logarithms of solubility of various metal dodecyl sulfates and the reciprocals of absolute temperature.

13) H. V. Tartar and K. A. Wright, *J. Am. Chem. Soc.*, **61**, 539 (1939).
14) N. K. Adam and K. G. A. Pankhurst, *Trans. Faraday Soc.*, **42**, 523 (1946).

TABLE IV. KRAFFT POINTS OF VARIOUS METAL DODECYL SULFATES

Substance	Krafft point, °C
$Mn(DS)_2$	16
$Co(DS)_2 \cdot 6H_2O$	23
$Cu(DS)_2 \cdot 4H_2O$	24
$Mg(DS)_2 \cdot 6H_2O$	25
$Ca(DS)_2$	50
$Pb(DS)_2$	53
$Sr(DS)_2$	64
$Ba(DS)_2$	—*

* Krafft point of $Ba(DS)_2$ was not observed below 100°C.

Discussion

From the results of the composition of various metal dodecyl sulfates shown in Table I it is confirmed that calcium-, barium, magnesium- and cupric dodecyl sulfates have the same formulae as those already given by Lottermoser et al.[6] It is noted that some of them have crystalline water. All metal dodecyl sulfates examined were found to have the two dodecyl sulfate radicals in their molecules, presumably showing no hydrolysis of the cations contained in them throughout the process of preparation.

The values of solubility of metal dodecyl sulfates examined were found to increase rapidly with the increase of temperature above the respective Krafft point, except for the case of barium dodecyl sulfate as shown in Fig. 2. The Krafft point could be obtained as the intersect of two straight lines in the diagrams of logarithms of solubility versus the reciprocals of temperature. This method of obtaining the Krafft point has been known to be applicable to many surface active substances in general. From their behaviors in solution, metal dodecyl sulfates are considered to be also a group of the surface active substances.

The values of solubility of magnesium-, calcium-, strontium- and barium dodecyl sulfates in water below the respective Krafft point decrease in this order, which is the same order as that of the values of solubility in water of the inorganic metal sulfates having these cations and also the same as the order of increase of ionic radii of these cations. This series of gegenions is also applied to the values of Krafft point of these metal dodecyl sulfates. These correspondences are, however, not to be extended to manganese-, lead-, cobalt- and copper dodecyl sulfates. As a whole, the Krafft points of various metal dodecyl sulfates seem to become higher as their solubilities decrease. At a temperature above the Krafft point the micelles of a surface active substance may be formed in the aqueous solution as explained by Murray and Hartley[15]. It has been found from the surface tension vs. concentration diagrams that the critical concentration for micelle formation of the solution of metal dodecyl sulfates of divalent cations is almost the same irrespective of the difference in the kind and type of gegenions. (The details of the surface tension measurement will be reported in a separate paper.) A sparingly soluble metal dodecyl sulfate can let its concentration reach the critical concentration for micelle formation at higher temperatures than more soluble metal dodecyl sulfate.

15) R. C. Murray and G. S. Hartley, ibid., 31, 183 (1935).

Summary

Calcium, strontium-, barium-, lead-, manganese-, magnesium-, cobalt- and copper dodecyl sulfates were synthesized and their compositions were determined from the results of their elementary analysis and metal content analysis. Further, the solubility of these metal dodecyl sulfates was measured at various temperatures. From these data, these metal dodecyl sulfates except barium salt were found to have the Krafft points, values of which were shown also.

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