The Effect of Metallic Ions on Surface Chemical Phenomena. IV. Surface Tension Measurement on Aqueous Solutions of Metal Dodecyl Sulfates

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In the preceding paper[1a], the effect of metal ions on the properties of the emulsion stabilized with sodium dodecyl sulfate was investigated and in connection with it the solubility of various metal dodecyl sulfates was studied[1b]. Metal dodecyl sulfates should be formed in many systems containing sodium dodecyl sulfate and metal ions as a result of a reaction of the former with the latter. They were supposed to constitute also a group of surface active substances from the existence of their Krafft points measured by the temperature change of their solubilities in water. To explain the Krafft point, the presence of micelles of the solute has been assumed. It is therefore expected that metal dodecyl sulfates begin to form the micelles at a relatively narrow concentration range, referred to as critical micelle concentration (abbreviated as cmc) as is the case with sodium dodecyl sulfate.

In the present paper, measurements of surface tension were performed to examine how far they lower the surface tension of their aqueous solution and whether or not they would actually show cmc as expected from the Krafft phenomena. Although Lottermoser and Stoll[2] made the surface tension measurements of aqueous solutions of dodecyl sulfates of silver, magnesium, copper, zinc and iron(II), their data were obtained with the samples synthesized from impure sodium dodecyl sulfate as illustrated from the presence of the minimum in the diagram of surface tension of its aqueous solution versus concentration. So it seems to be necessary to undertake measurements with pure samples in order to obtain further knowledge of properties of metal dodecyl sulfates, on which only

1) (a) S. Miyamoto, *Mem. Fac. Sci. Kyushu Univ., Series C, Chem.*, in press.
(b) S. Miyamoto, This Bulletin, **33**, 371 (1960).

2) A. Lottermoser and F. Stoll, *Kolloid-Z.*, **63**, 49 (1933).

a few studies have been made up to the present[3].

Experimental

Metal dodecyl sulfates were synthesized from pure sodium dodecyl sulfate and then purified as described in the preceding paper[1a,b].

Measurements of surface tension of aqueous solutions of metal dodecyl sulfates were conducted with a Du Noüy's tensiometer at various temperatures kept constant with a water thermostat. The sample solution was contained in a bottle having a narrow neck and this was immersed in the thermostat up to the brim. The solution had been heated to a temperature above the temperature of the measurement of surface tension. In the measurement of surface tension, the ring of the tensiometer was suspended by a thin platinum wire from the bar of the tensiometer and was made to have contact with the surface of the solution prior to the measurement of surface tension. After the attainment of equilibrium of temperature of the solution with that of the thermostat, the measurement was started. At high temperatures, the measurement had to be carried out as rapidly as possible to avoid evaporation of the solvent.

From the data of surface tension, the cmc of each metal dodecyl sulfate solution could be determined and it was compared with the one measured by the dye titration method. The dye titration method was conducted by using pinacyanol chloride and rhodamine 6G and observing the change of their color with the change of the detergent concentration.

Results and Discussion

The values of surface tension of aqueous solutions of various metal dodecyl sulfates at various temperature are shown graphically in Fig. 1—7 as a function of their concentration. It is seen that every curve represents a kink and no minimum near

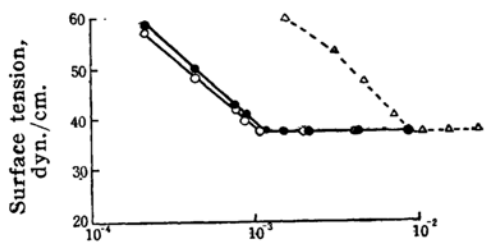

Fig. 1. Relation between surface tension and concentration of magnesium dodecyl sulfate solutions at 40°C (○) and 54°C (●). The dotted line represents the curve obtained with sodium dodecyl sulfate at 54°C.

3) Literatures cited in 1b.

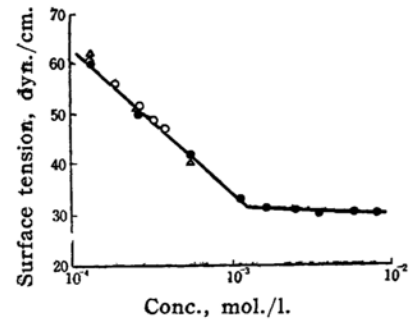

Fig. 2. Relation between surface tension and concentration of calcium dodecyl sulfate. Measurements of surface tension were conducted at 25°C (○), 35°C (△) and 54°C (●).

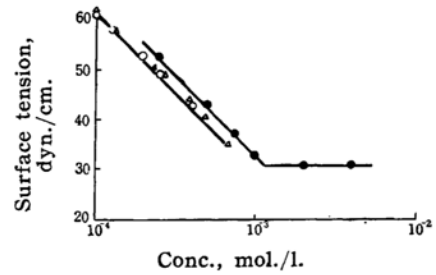

Fig. 3. Relation between surface tension and concentration of strontium dodecyl sulfate. Measurements of surface tension were conducted at 25°C (○), 54°C (△) and 67°C (●).

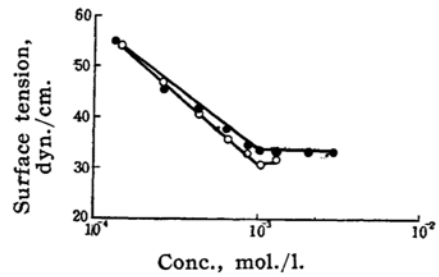

Fig. 4. Relation between surface tension and concentration of lead dodecyl sulfate. Measurements of surface tension were conducted at 54°C (○) and 67°C (●).

the kink point. The absence of the minimum is considered to show the absence of more surface active impurities than these metal dodecyl sulfates. The value of cmc can be obtained as the concentration at the kink point of every curve. These values of cmc of various metal dodecyl sulfates at various temperatures are shown in Table I. It can be seen from Table I that the temperature dependence of the value of cmc of each

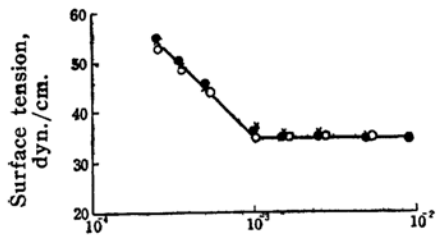

Fig. 5. Relation between surface tension and concentration of manganese dodecyl sulfate. Measurements of surface tension were conducted at 25°C (×), 40°C (○) and 54°C(●).

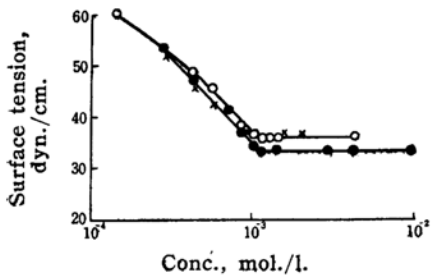

Fig. 6. Relation between surface tension and concentration of cobaltous dodecyl sulfate. Measurements of surface tension were conducted at 25°C (×), 40°C (○) and 54°C (●).

metal dodecyl sulfate of divalent cation is not so remarkable and also the values of dodecyl sulfates of various cations are almost the same, independent of the kind and type of cations contained in the molecules of these metal dodecyl sulfates.

These metal dodecyl sulfates were found to have their Krafft points as already reported[1b]. It is generally accepted with surfactant solutions that only at the temperatures above the Krafft point the micelles are formed. It seems true for some metal dodecyl sulfates studied in the

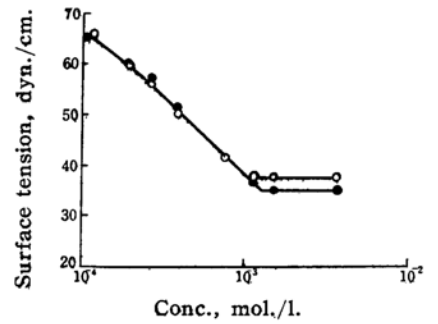

Fig. 7. Relation between surface tension and concentration of cupric dodecyl sulfate. Measurements of surface tension were conducted at 25°C (○) and 40°C (●).

present experiment. For example, calcium dodecyl sulfate was found to show its cmc at 54°C, as illustrated by the kink point of the surface tension-concentration curve (Fig. 2), but at 35°C which is below its Krafft point 50°C, the solution was saturated before its cmc had been reached. Referring to the diagram of Fig. 2 in the preceding paper[1b], it is found that the solubility of magnesium-, calcium-, strontium- and cobalt dodecyl sulfates at each Krafft point is nearly equal to the cmc of each solution which has been determined in the present experiment. In the case of lead salt, however, the solubility at its Krafft point is a little smaller than its cmc, and copper- and manganese salts show considerably larger solubilities than their corresponding value of cmc. It is not clear at the present why these metal dodecyl sulfates show anomalous behaviors. It will be necessary to make measurements of the existence of micelles over a much wider range of temperatures in order to elucidate the relation between the Krafft point and the micelle formation with these metal dodecyl sulfates.

As mentioned above, the dependence of

TABLE I. VALUES OF cmc (mol./l.) OF METAL DODECYL SULFATES AT VARIOUS TEMPERATURES DETERMINED BY SURFACE TENSION MEASUREMENTS

Subst.	cmc (mol./l.)			
	25°C	40°C	54°C	67°C
NaDS	7.4×10^{-3}	—	9.2×10^{-3}	—
$Mg(DS)_2\cdot6H_2O$	8.8×10^{-4}	1.1×10^{-3}	1.1×10^{-3}	—
$Ca(DS)_2$	—	—	1.3×10^{-3}	—
$Sr(DS)_2$	—	—	—	1.1×10^{-3}
$Pb(DS)_2$	—	—	1.0×10^{-3}	9.8×10^{-4}
$Mn(DS)_2$	1.1×10^{-3}	1.1×10^{-3}	1.1×10^{-3}	—
$Co(DS)_2\cdot6H_2O$	8.3×10^{-4}	9.7×10^{-4}	1.1×10^{-3}	—
$Cu(DS)_2\cdot4H_2O$	1.0×10^{-3}	1.2×10^{-3}	—	—

the values of cmc of various metal dodecyl sulfates on the kind of divalent cations contained in them is not explicitly found, the cmc being all nearly 1×10^{-3} mol./l. On the contrary, the values of cmc of alkali metal dodecyl sulfates measured by the electrical conductance method have been reported by Meguro et al.[4] to vary with the kind of alkali metal cations; i. e. they reported 7.8, 8.9 and 10.5 millimol./l. as the values of cmc of potassium-, sodium- and lithium dodecyl sulfates, respectively. These authors explained the dependence of cmc on the kind of monovalent cations as being due to the difference in hydration of these monovalent cations. This explanation might be applied also to the case of the metal dodecyl sulfates having the divalent cations examined in this experiment, but actually this effect seems so small that it can hardly be detected in this experiment. Metal dodecyl sulfates having divalent cations show far smaller values of cmc than those of the metal dodecyl sulfates having monovalent cations. This fact shows that the former sulfates have a less hydrophilic nature because of the two hydrocarbon chains for a metal, than the latter ones, and thus they have a tendency to form their micelles in solutions more easily. This may be a reason for the independence of their cmc's on the kind of divalent gegenions.

The value of surface tension of the solution above cmc is nearly constant. It ranges only from 31 to 37 dyn. per cm., depending on the temperature and the kind of metal dodecyl sulfates. In general a salt which is more soluble in water shows a larger value of saturation surface tension.

The cmc of a surface active substance has well been known to be obtained by the dye titration method as well as by the surface tension measurement. To examine the possibility of obtaining the values of cmc of the metal dodecyl sulfates by the dye titration method, measurements were conducted using pinacyanol chloride or rhodamine 6G as the indicator of the dye titration method. It was found that this method can also be applied to metal dodecyl sulfates. The values of cmc of the various metal dodecyl sulfates thus obtained are shown in Table II.

From Table II, the values of cmc obtained by pinacyanol chloride and rhodamine 6G are seen to be in good agreement with each other.

TABLE II. VALUES OF cmc (mol./l.) OF VARIOUS METAL DODECYL SULFATES* AT 40°C OBTAINED BY THE DYE TITRATION METHOD USING PINACYANOL CHLORIDE AND RHODAMINE 6G

Subst.	cmc (mol./l.) By pinacyanol chloride	cmc (mol./l.) By rhodamine 6G
NaDS	6.1×10^{-3}	6.1×10^{-3}
$Mg(DS)_2\cdot6H_2O$	1.0×10^{-3}	1.1×10^{-3}
$Ca(DS)_2$	1.3×10^{-3} (at 54°C)	—
$Mn(DS)_2$	1.2×10^{-3}	1.1×10^{-3}
$Co(DS)_2\cdot6H_2O$	1.0×10^{-3}	1.3×10^{-3}
$Cu(DS)_2\cdot4H_2O$	1.2×10^{-3}	1.3×10^{-3}
$Zn(DS)_2\cdot6H_2O$	1.1×10^{-3}	1.1×10^{-3}

* Measurements were not performed on strontium- and lead dodecyl sulfates because of their high Krafft points.

Comparing the values obtained by the dye titration method with those shown in Table I, obtained from surface tension measurements, it is found that these two methods of measuring cmc give values approximately coinciding with each other.

As described above, metal dodecyl sulfates with divalent cations are found to lower the surface tension of their solutions exceedingly and have far smaller cmc values than those of the salts of monovalent cations. Relatively soluble salts such as cupric-, manganese-, cobaltous- and magnesium dodecyl sulfates, therefore, may be useful for many purposes based on their strong surface activity.

Summary

The surface tension of aqueous solutions of various metal dodecyl sulfates with divalent cations was measured at various temperatures with a Du Noüy's tensiometer. The values of surface tension were observed to decrease steeply with the increase of their concentrations up to their cmc's, which are all nearly equal to 1×10^{-3} mol./l. These values of cmc of the metal dodecyl sulfates with divalent cations were found to be practically independent of temperature and the kind of these cations. Further, the dye titration methods were also performed to obtain the values of cmc of these metal dodecyl sulfates using pinacyanol chloride and rhodamine 6G. The values of cmc obtained by these methods were found to coincide with those from the surface tension measurements.

4) K. Meguro, T. Kondo, O. Yoda, T. Ino and N. Ohba, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, 77, 1236 (1956).

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