BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3889—3890 (1973)

The Solubilities, Critical Micelle Concentrations, and Krafft Points of Bivalent Metal Alkyl Sulfates

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(Received June 29, 1973)

According to the phase separation model (as well as the mass action model) for a micellar solution,[1] a Krafft point is interpreted as a triple point at which a solid hydrated surfactant, micelles (a liquid state), and a singly-dispersed surfactant are in equilibrium with each other. If so, the CMC values should be smaller than the solubility values above the Krafft point, equal at the Krafft point, while the solubility values should be smaller than the CMC values below the Krafft point. These relations hold for 1–1 ionic surfactants in either the absence or the presence of added salts.[1,2]

Miyamoto[3] has determined the solubilities and CMC's of several bivalent metal dodecyl sulfates. The CMC values of lead, cupric, and manganese dodecyl sulfates he obtained differ considerably from the solubility values at the Krafft points, whereas those of the other metal dodecyl sulfates agree within *ca.* 20%. This raises a serious question as to whether or not the triple point model holds for bivalent metal salts of ionic surfactants. In the present paper, the solubilities, the CMC's, and the Krafft points of various bivalent metal alkyl sulfates will be studied in order to confirm our model.

Experimental

The bivalent metal dodecyl and tetradecyl sulfates have been prepared by adding an aqueous solution of a respective metal chloride to aqueous solutions of sodium dodecyl and tetradecyl sulfates. Extremely pure sodium dodecyl sulfates ($C_{12}>99.9\%$, and no minimum in the surface tension *vs.* concentration curve) and sodium tetradecyl sulfates ($C_{12}=0.2\%$, $C_{14}=99.3\%$, $C_{16}=0.5\%$) were obtained from the Kao Soap Co. through the kindness of Dr. Arai. The metal chlorides were of an extra-pure grade and were used without further purification. The products were recrystallized 4 or 5 times from water and then washed with petroleum ether for 20 hr. No sodium ion was detected by a flame test. It is found from elementary analysis that all the compounds have two surface active anions in each molecule.

The solubility was determined by electrical conductivity measurements. The solutions were stirred for 4—5 hrs in a thermostat controlled within 0.02 °C. Further stirring caused no change in the solubility. The procedures were described in detail in a preceding paper.[4] The solubility was also determined by weighing the dried solution. The two measurements agreed with each other within an error of 1%. The CMC was determined either by conductivity measurements or by a dye method[5] (not by a dye titration method which gives a smaller CMC value, but by observing the color change in a series of solutions of different concentrations after an equilibrium had been reached). The two measurements agreed well with each other.

Results and Discussion

Figure 1 shows the solubilities and the CMC's of bivalent metal dodecyl and tetradecyl sulfates as a unction of the temperature. The supercooled micelles of cupric and manganese salts were fairly stable, the CMC values below the Krafft points were also determined. The solubility data on cupric dodecyl sulfate were less accurate (±3%) than the others (±0.5%) because of the low Krafft point. The concentration was expressed in terms of a molality based on the anhydrous surfactant. It is found from Figure 1 that the solubility increases abruptly at a definite temperature, just as those of 1–1 ionic surfactants do,[1,2] this temperature is the Krafft point above which the micelles are formed. The Krafft points determined from Fig. 1 have been listed in Table 1, together with the CMC values at the Krafft points. The data obtained by Miyamoto[3] and Schwuger[6] are also listed. The CMC values determined by surface tension measurements[3,6] or by conductivity measurements[7] agree well with the present results. It is clear from Figure 1 that the

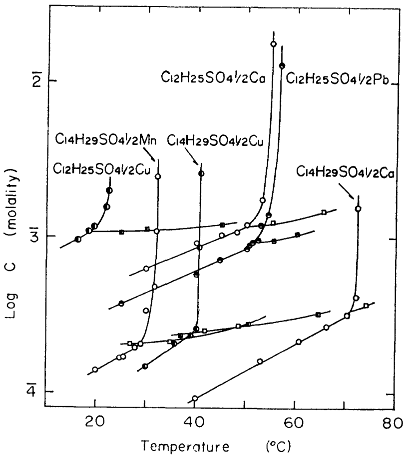

Fig. 1. The solubilities (circles) and the CMC's (squares) of bivalent metal alkyl sulfates as a function of temperature.

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[1] K. Shinoda, Chapter 1 in "Colloidal Surfactants" Academic Press Inc., New York, N. Y., 1963 pp. 6—8; K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, **66**, 577 (1962); R. C. Murray, and G. S. Hartley, *Trans. Faraday Soc.*, **31**, 183 (1935).

[2] H. Nakayama and K. Shinoda, This Bulletin, **40**, 1797 (1967).

[3] S. Miyamoto, *ibid.*, **33**, 371 (1960); S. Miyamoto, *ibid.* **33**, 375 (1960).

[4] K. Shinoda, M. Hatō, and T. Hayashi, *J. Phys. Chem.*, **76** 909 (1972).

[5] K. Shinoda, *ibid.*, **58**, 1136 (1954).

[6] M. J. Schwuger, *Kolloid-Z. Z. Polym.*, **233**, 979 (1969).

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

TABLE 1. KRAFFT POINT, CMC AND HEAT OF SOLUTION ΔH_s (FROM HYDRATED SOLID TO SINGLY DISPERSED STATE), OF MICELLE FORMATION ΔH_m AND OF FUSION ΔH_f (FROM HYDRATED SOLID TO MICELLAR STATE) OF BIVALENT METAL ALKYL SULFATES

Compound	Krafft point (°C)	CMC at K.P. (molality)[c]	ΔH_s	ΔH_m (kcal/mol)	ΔH_f
$(C_{12}H_{25}SO_4)_2Mn$	16±1	0.0011_5 (25 °C)	—	—	—
$(C_{12}H_{25}SO_4)_2Cu$	19±1	0.0010_8	—	$0._0$	—
$(C_{12}H_{25}SO_4)_2Co$[a]	23	0.00083 (25 °C)	—	—	—
$(C_{12}H_{25}SO_4)_2Mg$[a]	25	0.00088	—	—	—
$(C_{12}H_{25}SO_4)_2Ca$	50.0±0.5	0.0011_8	$19._1$	$-1._1$	18±1
$(C_{12}H_{25}SO_4)_2Pb$	52.0±0.5	0.00092	$19._0$	$-1._8$	17±1
$(C_{12}H_{25}SO_4)_2Sr$[a]	64	0.0011 (67 °C)	—	—	—
$(C_{12}H_{25}SO_4)_2Ba$	105[d]	—	—	—	—
$(C_{14}H_{29}SO_4)_2Mn$	29.0±0.5	0.00020_4	$23._2$	$-2._4$	21±2
$(C_{14}H_{29}SO_4)_2Mg$[b]	38.5	0.00025 (38 °C)	—	—	—
$(C_{14}H_{29}SO_4)_2Cu$	39.8±0.5	0.00024_5	$27._5$	$-3._5$	24±2
$(C_{14}H_{29}SO_4)_2Ca$	71±1	0.00034	$27._0$	$-5._0$	22±2
	67[b]	0.00034 (80 °C)[b]			

a) Ref. 3. b) Ref. 6. c) Moles of anhydrous salts/10^3 g of H_2O, the values from references 3 and 6 are expressed in mol/l. d) A value estimated from the solubilities of 0.5 and 1 wt% aqueous solutions.

CMC and solubility curves of all the compounds examined intersect exactly at the Krafft point, and that the CMC values of supercooled micelles are larger than the corresponding solubility values. This is in accord with the model.[1] No anomalous behavior has been observed in the cases of cupric and lead dodecyl sulfates. Similar results have been obtained in the case of fluorinated surfactants, $C_9F_{19}SO_3 1/2Mg 2H_2O$.[4,8] From the foregoing discussion, the heats of fusion, ΔH_f (from a hydrated solid to a micellar state), of the bivalent metal alkyl sulfates can be calculated from the temperature dependence of the solubility or CMC by the aid of the following equations[9] (the values are listed in Table 1),

$$\Delta H_f = \Delta H_s + \Delta H_m \qquad (1)$$

$$\Delta H_s = 3RT^2(\partial \ln C_2/\partial T) \qquad (2)$$

$$\Delta H_m = -(2+K_g)RT^2(\partial \ln CMC/\partial T) \qquad (3)$$

where ΔH_s is the heat of solution of a hydrated solid agent; ΔH_m, the heat of micelle formation; C_2, the solubility, and K_g the experimental constant. K_g is 0.57_2 for calcium dodecyl sulfate[10] and is assumed to be 0.57_2 for the other surfactants. As these hydrated solids have a vapor pressure very close to that of pure water, the anhydrous solid was equilibrated with an aqueous solution of potassium chloride (0.001 mol/l and $P/P^\circ > 0.997$) in order to determine the number of hydrated water at 26.5±0.3 °C. Calcium dodecyl and tetradecyl sulfates were found not to take up the water of hydration. After a lapse of 5 days (for manganese tetradecyl sulfate) or of 20 days (for cupric tetradecyl sulfate), the salts come to a constant weight, giving a value of 6±0.4 H_2O. The lower Krafft point of manganese (or cupric) tetradecyl sulfate than that of calcium tetradecyl sulfate may result from the larger entropy of fusion of the former, which is partly attributable to the entropy change in hydrated water.

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[8] M. Hatō and K. Shinoda, *Nippon Kagaku Zasshi*, **91**, 27 (1970).

[9] K. Shinoda, S. Hiruta, and K. Amaya, *J. Colloid Interfac. Sci.*, **21**, 102 (1966).

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