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The Solubilities and Kraft Points of Fatty Acid Soaps of Odd Carbon Numbers

Keizo Ogino and Yukinori Ichikawa

Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278

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The solubilities of sodium soaps of odd carbon-number fatty acids were measured at various temperatures and the Kraft points[1)] of the soaps were determined from the phase diagrams showing the temperature dependence of equilibria among monomers, micelles, and hydrated solid. It was found that the Kraft points were related with the carbon numbers of the fatty acids in a zig-zag curve.

The solubility of sodium soaps of fatty acids at room temperature usually decreases with increasing alkyl chain length. The only soaps that do not require elevation of temperature for dissolution are sodium oleate (sodium *cis*-9-octadecanoate) and some soaps of the less saturated fatty acids. The solubilities of most sodium soaps containing long alkyl chains in water at room temperature are lower than those of unsaturated fatty acid soaps. Many reports have been presented on the solubility of sodium soaps, but they are concerned with the fatty acid soaps of even carbon numbers originating from natural fatty oils.[2–6)]

Recently, the advance of organic synthesis makes the fatty acids of odd carbon numbers readily available for technical uses. For the current industrial activity, it is necessary to investigate the properties of sodium soaps of odd carbon-number fatty acids. Thus the solubilities in water and the Kraft points have been determined for the sodium soaps of fatty acids of odd carbon numbers in this study.

Experimental

Materials. The sodium soaps of pentanoic (C_5), heptanoic (C_7), nonanoic (C_9), undecanoic (C_{11}), tridecanoic (C_{13}), and pentadecanoic (C_{15}) acids were prepared by neutralizing these acids with ethanolic sodium hydroxide. These soaps were purified by recrystallization and stored in a dessicator at room temperature. The fatty acids were supplied from Ajinomoto Co., Ltd.; their properties have been listed in a previous work.[7)]

Determinations of Solubility. The solubility was determined in 200 × 15 mm Pyrex test-tubes in which 40 ml of water and a sufficient amount of a sodium soap were mixed so as to precipitate the solid phase. The equilibrium was ascertained by the approach in two directions, from the unsaturated and from the supersaturated states. The tubes were stoppered and thermostatted within ±0.02 °C for 24 h. The solution was permitted to stand until the suspended crystals settled. The crystals were filtered by a small glass filter fastened to the inlet of a 25 ml pippet. During the transfer of the solution from the test tube to a weighing bottle through the pippet, the weighing bottle was kept cold in an ice-bath and covered to prevent loss of water vapor. Then the bottle containing the solution was heated to evaporate the water and the residual soap was dried in vacuum at 60 °C for 24 h. The content of the weighing bottle was weighed before and after the evaporation and drying. The dried soap was stored in a dessicator at room temperature before use. The solubility was calculated as the weight of soap (grams) dissolved in 100 g of water.

Determination of CMC. CMC was determined by measuring the specific conductivity of a soap solution at various temperatures. The specific conductivity was measured with a Conduct Meter Model CH-IDB of the Toa Electric Wave Co., Ltd.

Results and Discussion

The solubilities of sodium salts of pentanoic, heptanoic, nonanoic, undecanoic, tridecanoic, and pentadecanoic acids obtained from the experiments are given in Table 1.

The solubilities presented in weight percent have been plotted in Fig. 1. The plots showing the solubilities of sodium pentanoate and heptanoate are presented at the upper right corner in Fig. 1. From the results, it is clear that these two alkyl soaps dissolve appreciably at room temperature. The Kraft points for these soaps were not determined because these soaps freeze at −5 °C. It should be noticed that the melting points of pentanoic and heptanoic acids are −34.5 and −10.5 °C respectively, which are far lower than the freezing points of the corresponding soaps.

On the other hand, the solubilities of all the soaps of the larger carbon numbers are small at room temperature, and increase as a linear function of the temperature until the concentrations reach the critical values. When either the concentration or the temperature goes beyond this critical threshold, the ionic soap species in a monomolecularly dispersed state seem to undergo some kind of aggregation, accompanied by an enormous increase in the solubility. This is a well-defined critical micelle concentration (CMC). That is, the maximum solubility of the monomer ions or molecules appears at CMC; if this saturation point is exceeded, a new phase, the micelles, appears. This point can be clearly detected when the maximum solubility (presented in molarity) is plotted against $1/T$, as shown in Fig. 2.

In Table 2 the critical concentration C_K have been given with the corresponding temperatures.

In order to determine the Kraft point, the critical micelle concentration (CMC) was measured at different temperatures. For the determination of CMC, the electric conductivity method was applied, though many other methods might be applicable.[8–11)]

Figure 3 shows the specific conductivity, κ, of aqueous solutions of sodium pentadecanoate at various concentrations at 55 and 65 °C. As shown in Fig. 3, the relations of the specific conductivity with the concentration slightly bend at certain concentrations of the soap solution, that is, at the CMC.

Shinoda *et al.* have mentioned that the Kraft point can be compared to the phase diagram of the ice-water system. In solutions of soaps, the concentration

TABLE 1. SOLUBILITIES OF THE SODIUM SOAPS OF ODD FATTY ACIDS

Temp °C	g/100 g-H$_2$O	Volume normality (mol/l)	Temp °C	g/100 g-H$_2$O	Volume normality (mol/l)	Temp °C	g/100 g-H$_2$O	Volume normality (mol/l)	Temp °C	g/100 g-H$_2$O	Volume normality (mol/l)
Sodium pentanoate C_5						24.00	1.65	79.1×10^{-3}	7.00	0.41	19.6×10^{-3}
6.00	15.98	12.88	2.01	8.00	6.45	23.00	1.25	79.0×10^{-3}	5.00	0.26	12.7×10^{-3}
5.02	13.81	11.13	0.00	5.99	4.83	22.00	1.20	57.7×10^{-3}	3.02	0.13	12.7×10^{-3}
4.00	12.00	9.67	−1.01	4.69	3.78	20.00	0.77	46.6×10^{-3}			
3.00	9.30	7.50	−2.00	4.00	3.25	Sodium tridecanoate C_{13}					
Sodium heptanoate C_7						45.00	1.298	54.92×10^{-3}	35.00	0.258	10.92×10^{-3}
5.02	12.70	8.34	0.00	5.50	3.62	43.00	0.796	33.70×10^{-3}	35.00	0.229	9.70×10^{-3}
4.00	10.75	7.07	−1.01	3.50	2.40	42.01	0.649	27.49×10^{-3}	30.00	0.200	8.50×10^{-3}
3.00	9.00	5.91	−2.00	3.40	2.32	40.00	0.441	18.69×10^{-3}	25.01	0.185	7.85×10^{-3}
2.01	5.85	3.84				39.01	0.390	16.52×10^{-3}	23.00	0.166	7.04×10^{-3}
Sodium nonanoate C_9						38.00	0.339	14.37×10^{-3}	20.00	0.126	5.33×10^{-3}
14.00	7.05	391.3×10^{-3}	9.02	1.16	64.6×10^{-3}	35.98	0.246	10.44×10^{-3}	15.00	0.124	5.25×10^{-3}
12.99	4.46	258.7×10^{-3}	8.00	1.12	62.1×10^{-3}	Sodium pentadecanoate C_{15}					
12.01	3.86	214.2×10^{-3}	7.00	1.06	58.9×10^{-3}	57.00	1.230	46.59×10^{-3}	40.00	0.068	2.59×10^{-3}
11.00	1.90	105.6×10^{-3}	6.01	0.99	55.0×10^{-3}	55.01	0.487	18.41×10^{-3}	38.00	0.067	2.53×10^{-3}
10.50	1.59	88.5×10^{-3}	5.00	0.93	51.7×10^{-3}	54.02	0.469	17.73×10^{-3}	35.98	0.064	2.44×10^{-3}
10.00	1.21	66.9×10^{-3}	4.00	0.94	52.1×10^{-3}	53.01	0.418	15.80×10^{-3}	35.00	0.062	2.33×10^{-3}
9.50	1.17	65.2×10^{-3}				52.00	0.126	4.77×10^{-3}	33.00	0.060	2.27×10^{-3}
Sodium undecanoate C_{11}						50.00	0.116	4.38×10^{-3}	30.01	0.059	2.22×10^{-3}
28.00	7.53	245.9×10^{-3}	19.00	0.72	34.6×10^{-3}	47.02	0.110	4.16×10^{-3}	25.01	0.058	2.20×10^{-3}
27.00	3.27	156.8×10^{-3}	18.04	0.69	32.6×10^{-3}	45.00	0.086	3.25×10^{-3}	23.00	0.056	2.10×10^{-3}
26.01	2.29	109.9×10^{-3}	15.00	0.63	30.2×10^{-3}	42.01	0.069	2.63×10^{-3}	20.00	0.052	1.98×10^{-3}
25.01	2.25	107.8×10^{-3}	10.00	0.51	24.8×10^{-3}						

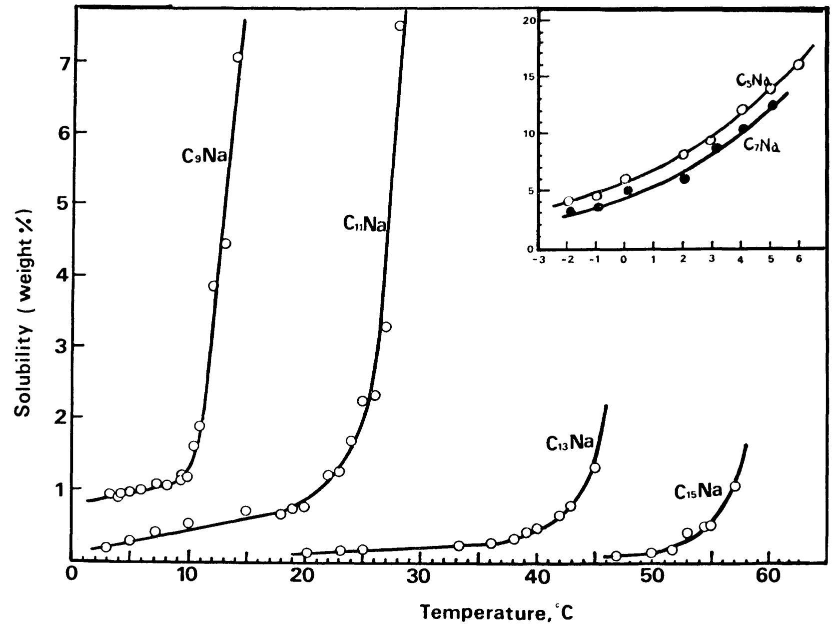

Fig. 1. Solubilities of soaps of the fatty acids with odd carbon numbers.

of monomeric soap molecules plays a role similar to the vapor pressure in the vapor-liquid equilibrium of a one-component system.[12,13] According to Shinoda's analogy, we depicted the phase diagram in the vicinity of the Kraft point of sodium pentadecanoate as shown in Fig. 4.

The Kraft point here can be interpreted as the point at which the solid hydrated soap and the micelles are in equilibrium with the monomers: in terms of the phase rule for three phase systems composed of two components, the equilibrium among the three phase (hydrated solid$\rightleftarrows$monomers$\rightleftarrows$micelles) is univariant, so that at a given pressure the point is fixed. The concept of the Kraft point as a freezing point of the micelles is also supported by Shinoda.

Hydrolysis is the main source of error in studies of

Table 2. Critical concentrations of sodium soaps

Sodium soap	Temperature °C	Critical concentration $C_k \times 10^3$ (mol/l)
C_5	—	—
C_7	—	—
C_9	10.5	63.91
C_{11}	26.2	40.12
C_{13}	39.8	11.70
C_{15}	52.8	4.05

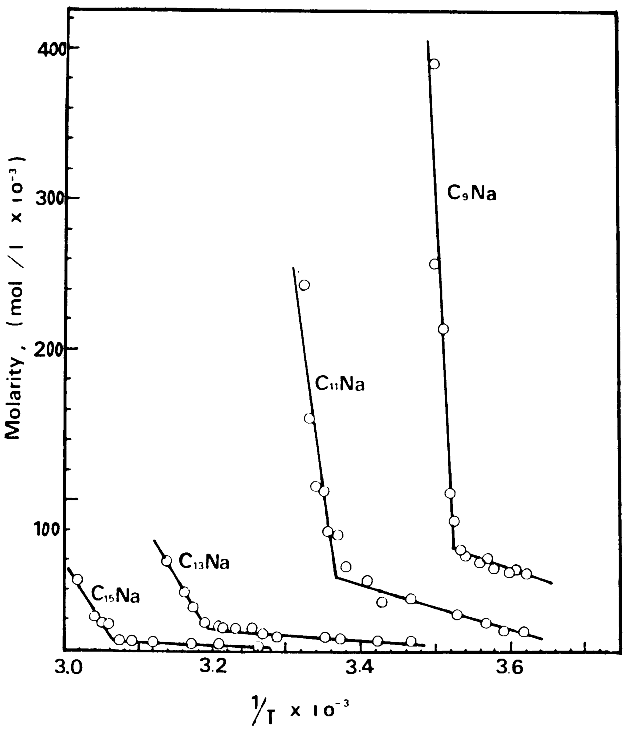

Fig. 2. Solubilities of soaps of the fatty acids with odd carbon numbers showing breaks in the curves for higher alkyl soaps.

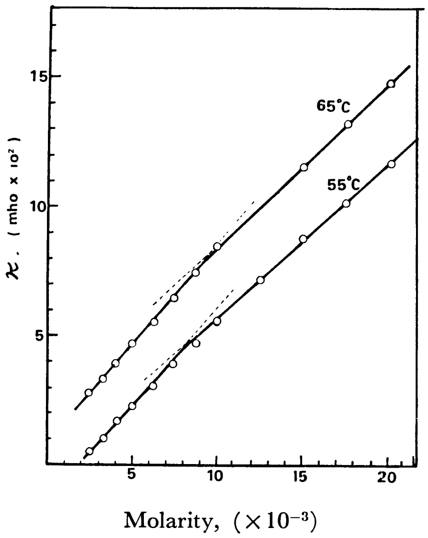

Fig. 3. Specific conductivity-concentration curves for sodium pentadecanoate.

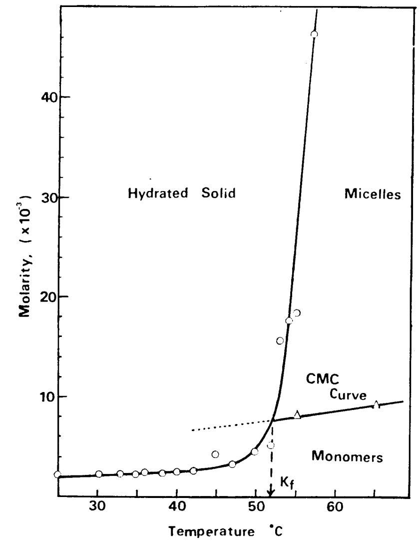

Fig. 4. Phase diagram in the vicinity of the Kraft point of sodium pentadecanoate.

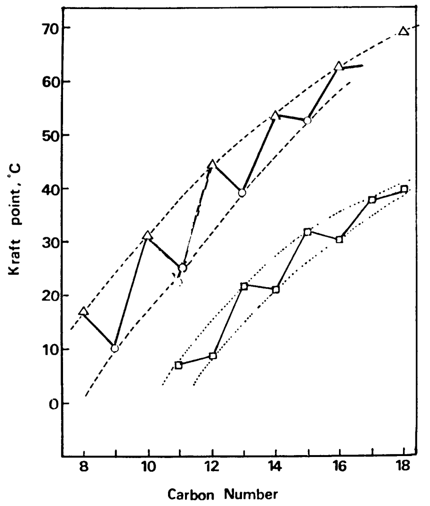

Fig. 5. Kraft points of sodium soaps.
△ ○: Sodium soaps, □: sodium alkylsulfates.

soap solutions. Therefore, in most of the works performed on the solubilities of soaps, alkaline solutions have been used as the solvent in place of pure water to prevent hydrolysis. In this work, we used distilled water free from carbon dioxide as the solvent, thus minimizing the effect of hydrolysis. From the results, the measurements of the Kraft points seemed to be little influenced by the hydrolysis product, fatty acid.

Similar results were also obtained for the soaps of the other fatty acids, and it was found that the Kraft points agree closely with the melting points of the corresponding fatty acids. When one plots the Kraft points of soaps of saturated fatty acids against the number of carbon atoms, a zig-zag curve (high at even carbon numbers and low at odd) is obtained, as shown in Fig. 5. Here the Kraft points of soaps of even carbon number are cited from McBain's report.[14] Figure 5 shows also the Kraft points of sodium normal alkylsulfates.[15]

In a previous work, we studied the melting behavior of binary and ternary mixtures of odd carbon-number fatty acids. Those results would be useful for the determination of the Kraft points of commercial soaps consisting of mixed soaps of various fatty acids.

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