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The Effect of Added Salts on the Solubilities and Krafft Points of Sodium Dodecyl Sulfate and Potassium Perfluoro-octanoate

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The solubilities of sodium dodecyl sulfate and potassium perfluoro-octanoate in the presence of added salts have been measured as a function of the temperature. The solubility decrease caused by the added salt was remarkable at temperatures a few degrees higher than the Krafft point of a system which contained no salt. The solubility of the solid agent below the Krafft point decreases approximately inversely proportionally to the concentration of the gegenion as was expected from the solubility product principle, whereas in these experiments the critical micelle concentration (the single-dispersion solubility of a liquid agent), the CMC, decreases inversely proportionally to about the 0.6th power of the gegenion concentration. Hence, the point of the intersection of the solute-solid and solute-liquid equilibrium curves, *i. e.*, the melting point of a hydrated solid agent, shifts to a higher temperature upon the addition of salt. The Krafft-point elevation caused by added salt is explained by the model; the Krafft point is the melting point of a hydrated solid agent, and the formation of the micelle is regarded as a pseudo-phase separation. It is easy to evaluate graphically the Krafft-point elevation in the presence of a 1-1 type salt by applying the above experimental relations.

The solubility of an ionic surfactant is very small below a certain temperature, called the Krafft point,[1)] but above this temperature its increase is so rapid that systems with almost any composition become transparent solutions at temperatures a few degrees above the Krafft point.[2)]

According to the pseudo-phase separation model of micellar solution,[3),4)] the Krafft point is the melting point of a hydrated solid surfactant. Below the Krafft point, the hydrated solid agent separates when the concentration exceeds the saturation concentration of single dispersion, whereas above the Krafft point micelle formation occurs above the saturation concentration of single dispersion. The solute-solid and/or solute-liquid equilibrium curves constitute the solubility curve for ordinary substances. However, since a micellar solution is transparent, the solute-solid and solid-liquid-(micelle) equilibria then form the solubility curve, as may be seen in the case of the ionic surfactant.[3)] Partial molal volume measurements[5)] and calorimetric measurements[6)] above and below the Krafft point clearly support this model. In a previous paper[7)] we found that the Krafft-point depression upon the addition of a small amount of alcohol could be interpreted in terms of this model. From these considerations, it can be concluded that the solubility curve below the Krafft point (the solid-solute equilibrium curve) must intersect with the CMC curve (the liquid-solute equilibrium curve) at its Krafft temperature.

The solubility below the Krafft point will decrease in accordance with the solubility-product principle in the presence of salt. On the other hand, it is experimentally known that the CMC decreases inversely proportionally to about the 0.6th power of the gegenion concentration. From these results, we may expect that the point of intersection of the two curves, *i. e.*, the Krafft point, will shift to a higher temperature upon the addition of salt.

The purpose of this paper is to confirm the above view and to estimate the Krafft-point elevation in salt solutions graphically.

Experimental

The sodium dodecyl sulfate used was the same material as was used in the previous study.[7)] Prefluoro-octanoic acid of the Minnesota Mining and Manufacturing Co. was further purified by recrystallization from carbon tetrachloride. Potassium perfluoro-octanoate was prepared by neutralizing a known amount of perfluoro-octanoic acid with a solution of potassium hydroxide of an extra pure grade. It was further purified by recrystallization from water. The procedures

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1) F. Karfft and H. Wiglow, *Ber.*, **28**, 2566 (1895).

2) R. C. Murray and G. S. Hartley, *Trans. Faraday Soc.*, **31** 183 (1935).

3) K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants," Academic Press Inc., N. Y. (1963), pp. 6—8.

4) K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, **66**, 577 (1962).

5) K. Shinoda and T. Soda, *ibid.*, **67**, 2072 (1963).

6) K. Shinoda, S. Hiruta and K. Amaya, *J. Colloid Interface Sci.*, **21**, 102 (1966).

7) H. Nakayama, K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, **70**, 3502 (1966).

for determining the solubility and CMC have been described in previous papers.[7,8]

Results and Discussion

The solubility and the CMC[8] of potassium perfluoro-octanoate in water in the presence of potassium nitrate, and those of sodium dodecyl sulfate in water in the presence of sodium chloride, are shown in Figs. 1 and 2 respectively.

The solubilities of these ionic surfactants decrease remarkably upon the addition of small amounts of salts. Especially, the decrease in the solubility is most pronounced at temperatures a few degrees higher than the Krafft point of a pure water-surfactant system. For example, in a 0.06 M KNO_3 solution the solubility of $C_7F_{15}COOK$ is reduced to about one-sixth that in pure water at 32°C.

The solid-micelle equilibrium curve, *i. e.*, the solubility curve above the Krafft point, is steeper in the salt solution, because the change in the concentration of gegenions is small in the presence of salt.

It is evident from Figs. 1 and 2 that each Krafft point corresponds to a temperature at which the solute-solid equilibrium curve and the CMC curve intersect with each other; that is, the Krafft point is the melting point of a hydrated solid surfactant.

The relation between the CMC and the gegenion concentration may be expressed experimentally by the following equation;

$$X_2 \cdot X_3^{K_g} = \text{const.} \tag{1}$$

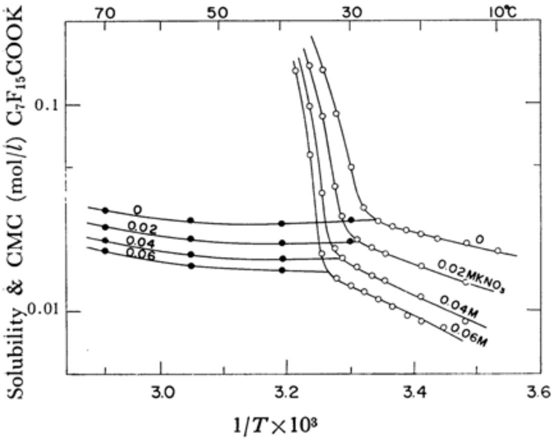

Fig. 1. The solubility and the CMC of potassium perfluoro-octanoate in aqueous potassium nitrate solution close to the Krafft point. The points of intersection of the solubility curves and the CMC curves are the Krafft points in respective solutions.
○, Solubility; ●, CMC

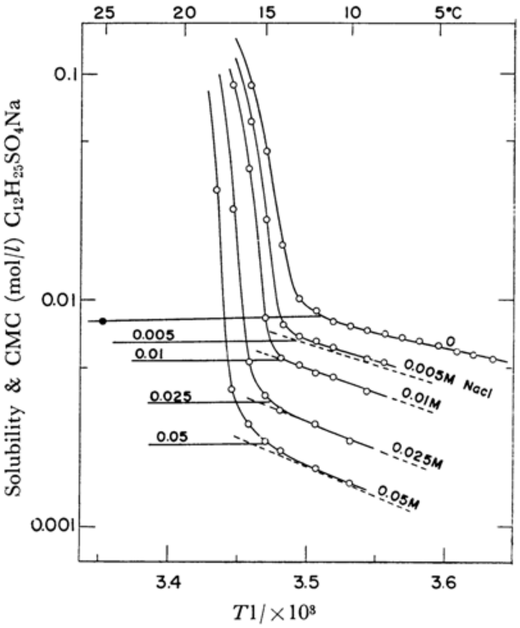

Fig. 2. The solubility and the CMC of sodium dodecyl sulfate in aqueous sodium chloride solution close to the Krafft point. The points of intersection of the solubility curves and the CMC curves are the Krafft points in respective solutions.
○, Solubility; ●, CMC

where X_2 is the concentration of the surface-active ion in single dispersion; X_3, the total concentration of gegenions, and K_g, an experimental constant which is usually about 0.5—0.7 but which varies slightly with the temperature.[8] The numerical values of K_g are found to be 0.52 (at 30°C) for $C_7F_{15}COOK$ and 0.68[9,10] (at 25°C) for $C_{12}H_{25}SO_4Na$. Thus, the CMC decreases inversely proportionally to about the 0.6th power of the total gegenion concentration.

On the other hand, the solid-solute solubility follows the solubility-product principle below the Krafft point just as an ordinary salt; that is, the solubility of a surfactant, X_2, should change approximately inversely proportionally to the concentration of gegenions, X_3. In fact, it was found in our laboratory that the slope of $\ln X_2$ *vs.* $\ln X_3$ was -0.98[8] in the case of the $C_7F_{15}COOK$-KNO_3 system at 25°C. Using the mean activity coefficient, $f_\pm$, the solubility-product principle can be expressed as follows:

$$X_2 \cdot X_3 \cdot f_\pm{}^2 = K(T, p) \tag{2}$$

in which $K(T, p)$ is a constant at a given temperature and pressure. The dotted lines in Fig. 2 show

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[8] K. Shinoda and K. Katsura, *ibid.*, **68**, 1568 (1964).

[9] R. J. Williams, J. N. Phillips and K. J. Mysels *Trans. Faraday Soc.*, **51**, 728 (1955).

[10] E. Matijevic and B. A. Pethica, *ibid.*, **54**, 587 (1958).

the solubility as calculated by the aid of Eq. (2). The mean activity coefficient, $f_{\pm}$, was estimated by the Debye-Hückel limiting law:

$$\log f_{\pm} = -\frac{1.824\times 10^{6}}{(DT)^{3/2}}\cdot\sqrt{I} \tag{3}$$

where I is the ionic strength (mol/l), D, the dielectric constant of water, and T, the absolute temperature. The calculated lines coincide with the experimental results. Thus, it is possible to calculate the solubility of a surfactant in the presence of a known amount of an added salt. As the solute-solid curve below the Krafft point follows Eq. (2) and as the CMC curve follows Eq. (1), the point of intersection, that is, the Krafft point, is raised by the addition of salt in water. This fact is in striking contrast with the effect of added alcohols, in which case the Krafft point is depressed by the formation of mixed micelles.⁷⁾ It can thus be concluded that the addition of salt or alcohol is an effective way to control the solubility of an ionic surfactant.

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