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Krafft Temperatures of Perfluoro-Octanoic Acid and of Its Salts

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The Krafft temperatures of perfluoro-octanoic acid and of its alkali metal and ammonium salts have been determined from the solubility measurements. The heats of solution and of wetting of dry solid surfactants have also been measured. The solubility decreases in the order; Li-salt$>$ Na-salt$>$K-salt, and then increases in the sequence; Rb-salt$<$Cs-salt. Ammonium salt is more soluble than sodium salt. Acid is least soluble. The heats of wetting depend markedly on the kind of counterions, but the heats of solution of hydrated solids, which are calculated from the temperature-dependence of single-dispersion solubility, are almost independent of the counterions. The order of Krafft temperatures for alkali metal salts is; Li$<$Na$<$K$>$Rb$>$Cs, just the reverse of that of the solubility. It is concluded that the Krafft temperature of each substance is mainly determined by the magnitude of the non-micellar solubility, and that the increasing order of the solubilities of salts can reasonably be estimated by comparing it with the solubility order of ordinary organic or inorganic salts which have the same chemical properties as the surfactants. This sequence of solubility is markedly determined by the strength of the acids from which the salts are derived.

From various solubility data[1-8)] for ionic surfactants in water, it is widely known that, below a well-defined temperature called the Krafft point,[9)] the solubility of an ionic surfactant is quite small, and that it increases in a normal manner, slowly, with the temperature, while above the Krafft temperature it increases drastically as a result of the formation of a micelle. The Krafft temperature characterizes the solubility of ionic surfactants so strikingly that it is of particular importance to study it comprehensively not only from the point of view of scientific interest, but also from the practical point of view.

Tartar and Wright[2)] measured the solubilities of sodium salts of straight-chain alkyl sulfonates of 10, 12, 14, 16, and 18 carbon atoms, and observed that the Krafft points increased with an increase in the alkyl chain length. On the other hand, Murray and Hartley[1)] measured the solubilities of cetyl sulfonic acid and of its lithium, sodium and potassium salts and found the interesting fact that the Krafft temperature varied with the kind of counterion. Miyamoto[6)] obtained similar results for the several dodecyl sulfates with bivalent cations.

Therefore, we can expect that changing the counterions of surfactants provides an important way to control the Krafft points, although the Krafft points may also be varied by the addition of a small amount of a tertiary substance.[7,8)]

Many investigations[10-17)] have been carried out into the effect of counterions on the critical micelle concentration (CMC). However, so far as we know, regarding the effect of changing counterions on the Krafft points, no conclusion has yet been obtained even for the simple case of alkali metal ions.

In this paper, the solubilities of perfluoro-octanoic acid and of its several salts were determined in order to see the effect of counterions on the Krafft temperatures. Some experiments were also carried out regarding the heats of solution and of wetting of these substances in order to ascertain the thermal

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nature of hydrated solid surfactants; we hoped that the results would throw new light on this problem.

Perfluoro-octanoic acid and its salts were chosen because: (1) the solubilities of these substances had not been measured, (2) various salts can be obtained easily by neutralizing the acid, and (3) it is important to know some fundamental properties, such as the solubility, of these fluorocarbon surfactants, since they are highly surface-active.[18]

Experimental

Materials. Perfluoro-octanoic acid ($C_7F_{15}COOH$) manufactured by the Minnesota Mining and Manufacturing Co. was further purified by two recrystallizations from carbon tetrachloride and one from redistilled water. $C_7F_{15}COONa$, $C_7F_{15}COOK$, and $C_7F_{15}COONH_4$ were prepared by neutralizing perfluoro-octanoic acid solutions with solutions of extra pure hydroxide, NaOH, KOH, and NH_4OH respectively. These salts were subjected to two additional recrystallizations from redistilled water, and dried at 60—70°C under reduced pressure. $C_7F_{15}COORb$ was obtained by neutralization with RbOH (99% purity) and two recrystallizations from pure water. It was difficult to obtain crystal samples of $C_7F_{15}COOLi$ and $C_7F_{15}COOCs$ because of their large solubilities in water. Hence, we obtained these salts by the following methods. An acid solution, which had been neutralized with a corresponding hydroxide solution, was dried up. The residue was extracted with ethyl alcohol to remove the carbonate. The purity of these salts might be lower than that of other salts.

Solubility Measurements. The solubilities of $C_7F_{15}COONa$, $C_7F_{15}COOK$, $C_7F_{15}COORb$, and $C_7F_{15}COONH_4$ were determined by drying up a known volume of saturated solutions at 50—60°C under reduced pressure. The details of the procedures were similar to those reported in previous papers.[7,8] For $C_7F_{15}COOH$, the saturated solution was dried in a desiccator over a long period of time at room temperature under atmospheric pressure until the weight became constant, because it had low melting point (56.4—57.9°C)[18] and slightly sublimed even at 40°C. Only for the acid solution was gel formation observed above 45°C. The solubilities of $C_7F_{15}COOCs$ were determined by sealing up weighed amounts of the salt and water in a test tube, heating it until the contents dissolved to give a clear solution, and then cooling it until a solid solute appeared. The mean values of the two temperatures were regarded as the temperatures at which the mixtures became saturated solutions. $C_7F_{15}COOLi$ was very soluble, so it was difficult to measure its solubility because of the solvent freezing.

Calorimetry. A Tian-Calvet type micro-calorimeter, which was designed by Amaya[19] and manufactured by Ōyōdenki Kenkyujo (CM-502), was used. The details of the mechanism of this model and its precise operations in the measurements have been described by Koishi.[20]

The heat of solution of a dry solid surfactant was measured by dissolving 0.2—0.4 g of completely dried salts into 30 m*l* of redistilled water. The final concentration was about 80% of the solubility of a single dispersion. The heat of wetting was the heat evolved when a known amount of dried salt was further immersed into a saturated solution in which an excess amout of hydrated solid solute was already present. All the measurements were carried out in an air thermostat at 25°C. The values tabulated in Table 1 are averages of two or three determinations. Taking account of the experimental error introduced by the several steps and of the experimental restriction that the total heat is only 1—3 cal, the results may be in error as much as 10% at worst.

Results and Discussion

Solubility and Thermal Data. The solubilities of perfluoro-octanoic acid and of its sodium, potassium, rubidium, caesium, and ammonium salts have been determined as a function of the temperature. Typical examples of the temperature dependence of the solubilities for sodium and potassium salts are shown in Fig. 1. For a series of alkali metal salts, the increasing order of solubilities does not show any intimate correlation with the order of the atomic numbers of the counterions; at first it decreases in the order: Li-salt > Na-salt > K-salt, and then it increases in the sequence: Rb-salt < Cs-salt.

Below the Krafft point which is regarded as the temperature from which the solubility curve deviates from the straight line, an equilibrium has been attained between singly-dispersed ions and the hydrated solid surfactant. Therefore, the heat of solution of the hydrated solid solute, ΔH_s^*, can

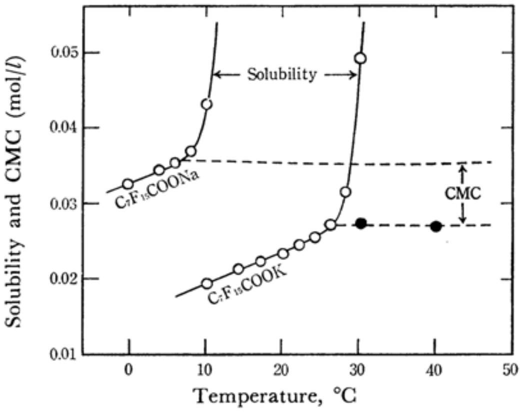

Fig. 1. The solubility (○) and CMC (●) curves for $C_7F_{15}COONa$ and $C_7F_{15}COOK$ close to the Krafft points. CMC curve for potassium salt is taken from Ref. 24 and that of sodium salt is drown with the assumption that it behaves like potassium salt.

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TABLE 1. THE KRAFFT TEMPERATURE, CMC, HEAT OF SOLUTION OF HYDRATED SOLID SOLUTE (ΔH_s^*), HEAT OF SOLUTION (ΔH_s) AND OF WETTING (ΔH_w) OF DRY SOLID SOLUTE

Surfactant	Krafft temp. °C	CMC mol/l	ΔH_s* from Eq. (1)	ΔH_s	ΔH_w
			kcal/mol		
$C_7F_{15}COOLi$	below 0	—	—	2.6 ± 0.2	—
$C_7F_{15}COONa$	8.0	0.036	7.3	3.5 ± 0.3	-3.8 ± 0.3
$C_7F_{15}COOK$	25.6	0.027	7.3	6.0 ± 0.4	-0.9 ± 0.1
$C_7F_{15}COORb$	20.2	0.028	7.2	6.3 ± 0.4	-0.9*
$C_7F_{15}COOCs$	below 0	—	—	4.4 ± 0.3	—
$C_7F_{15}COOH$	20	0.009	3.6	—	—
$C_7F_{15}COONH_4$	2.5	0.033	*ca.* 7.3	5.0 ± 0.4	-2.3*

* See text.

be calculated from the well-known thermodynamic relation:[21]

$$\Delta H_s^* = -2\boldsymbol{R}\frac{\partial \ln S}{\partial(1/T)}\left(1+\frac{\partial \ln \gamma_\pm}{\partial \ln S}\right) \tag{1}$$

in which S is the solubility below the Krafft point; T, the absolute temperature; $\boldsymbol{R}$, the gas constant, and $\gamma_\pm$, the mean activity coefficient, which can be approximately estimated from the Debye-Hückel limiting law. It was found from the measurements of the temperature dependence of the solubility that the slope of $\ln S$ *vs.* $1/T$ was not only linear for each substance below the Krafft point; the slopes for sodium, potassium, rubidium, and presumably for ammonium salts were also almost the same. The identical values of the heats of solution of hydrated solids were, therefore, obtained from Eq. (1) for these salts, assuming that Debye-Hückel law held up to the solubility range studied.

For each substance investigated, the Krafft point and the CMC (at its Krafft temperature) are tabulated in Table 1. Table 1 also includes the values of the observed heats of solution, ΔH_s, and of wetting, ΔH_w, of dry solid solutes, and the heats of solution of hydrated solid solutes, ΔH_s^*, calculated using Eq. (1).

The following scheme, which gives the relation between ΔH_s^*, ΔH_s and ΔH_w, can be constructed, and Eq. (2) is obtained from Hess's law.

$$\begin{tikzcd}
\text{Dry solid solute} \arrow[rr, "\Delta H_w"] \arrow[dr, "\Delta H_s"'] & & \text{Hydrated solid solute} \arrow[dl, "\Delta H_s^*"] \\
& \text{Singly-dispersed solute} &
\end{tikzcd}$$

$$\Delta H_s^* = \Delta H_s - \Delta H_w \tag{2}$$

For sodium and potassium salts, Table 1 reveals that Eq. (2) holds within the limits of experimental error at ionic strengths of 0.02—0.03 mol/l. Other data[5,7,21] also show that this is true for $C_{12}H_{25}SO_4$-Na. Therefore, the heats of wetting of rubidium and ammonium salts were estimated by inserting the experimentally-obtained ΔH_s^* and ΔH_s values into Eq. (2); these heats are listed in Table 1.

Referring to Table 1, it can be seen that the property of perfluoro-octanoic acid differs markedly from those of its salts. This indicates that some specific factors such as a strong hydrogen bond cause its anomalous behavior. Only for the acid solution was bulky gel formation observed above 45°C.

We can see from Table 1 that the heats of solution of dry solid solutes widely change from salt to salt. However, as has been mentioned above, the heats of solution of hydrated solid solutes as calculated from the solubility data using Eq. (1) are almost the same for sodium, potassium, rubidium and ammonium salts. Although it is not obvious whether this is the case for lithium and caesium salts as well, we might reasonably expect the same ΔH_s^* values for these salts. Therefore, it is clear that the effect of counterions mainly rests in the difference in the heats of wetting. Because of such features as the heats of wetting, it seems that the enthalpy change from the hydrated solid state to the singly-dispersed state, ΔH_s^*, is almost independent of the kind of counterion. The relatively small difference in the solubilities for a series of salts, compared with those of a group of corresponding inorganic salts, for example, chlorides, is presumably due to such a characteristic equilibrium between hydrated solid and singly-dispersed ions.

The Relation between the Krafft Point and the Non-micellar Solubility. From Table 1, we can see the interesting fact that the sequence of the Krafft points, Li$<$Na$<$K$>$Rb$>$Cs, is just the reverse of that of the solubilities. This suggests that the Krafft point is mainly determined by the magnitude of (non-micellar) solubility. This will be interpreted from the pseudo-phase separation model[17,22] for micelle formation, and from the

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experimental fact that the $\partial \ln S/\partial(1/T)$ slope is almost independent of the kind of counterion.

According to the pseudo-phase separation model, the Krafft point may be regarded as the melting point of the hydrated solid solute. Hence, the solubility curve of singly-dispersed ions (the hydrated solid—singly-dispersed solute equilibrium curve) must intersect with the CMC curve (liquid solute (micelle)—singly-dispersed solute equilibrium curve) at the Krafft point. This has been experimentally confirmed for several systems.[8] In general, the CMC is not markedly dependent on the type of counterion.[12,14,17] Especially for a series of alkali metal ions, the difference in the effect of the counterion on the CMC is quite small.[11,12,16] On the other hand, the solubility (below the Krafft point) changes from salt to salt.[23] As a result, we may expect that a point of the intersection of the solubility curve and the CMC curve, that is, the Krafft point, is almost entirely determined by the solubility curve. Figure 1 shows the above relation explicitly for sodium and potassium salts. The solubility of sodium salt is about twice that of potassium salt, whereas the CMC ratio of sodium salt to potassium salt is only 1.3. Therefore, the more soluble sodium salt has a lower Krafft point.

Comparison of the Solubilities of Ionic Surfactants with Those of Ordinary Salts. If we compare the solubilities of alkali metal salts of perfluoro-octanoic acid with those of alkali metal chlorides, which behave as the typical strong 1-1 electrolytes,[25] we can see the same sequence, Li$>$Na$>$K$<$Rb$<$Cs, for both systems. This not only suggests that the dissolution processes for both systems are essentially the same; it also indicates that an explanation or to an estimation of the difference in solubilities (and therefore Krafft points) of a series of surfactants with different counterions can be based on an estimation of solubilities of a group of suitable ordinary salts. By "suitable" we mean that we must use for comparison the solubilities of salts which have the same chemical properties as those of the surfactants. Thus, the reverse order of solubility, Na$<$K, which was found for the salts of higher carboxylic acids,[4] such as myristates, palmitates, and stearates, would correspond to that of the salts which have anions derived from weak acids. In fact, if we examine the solubilities of acetates, carbonates and bicarbonates, it can be seen that the potassium salts are more soluble than sodium salts. Therefore, here again we can see an intimate correlation between ionic surfactants and ordinary salts, and we may reasonably expect that the sequence of the solubility is markedly influenced by the strength of the acid from which the salts are derived.

The reversal in order, Na$<$K, for the salts of weak acids may be ascribed to some ionic association, not of the Bjerrum type,[26] but one due to interaction between the polarized water molecules in the hydration sheath around the cations and proton-accepting anions[25] ("localized hydrolysis"). Because this type of ionic association depends on the intensity with which the cation polarized the water molecules, the extent of association decreases in the order; Li$>$Na$>$K$>$Rb$>$Cs. The same trend has been found for the counterion binding in the solutions of polyacrylic acid,[27] polymethacrylic acid,[27] and polyphosphates,[28] and for the selective adsorptivity of cations on the methacrylic acid[29] and crosslinked carboxylic acid[30] resins.

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