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The Effects of Organic Additives on the Solubilities and CMC's of Potassium Alkyl Sulfates in Water. I. The Effects of Several Hydroxy Compounds

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The solubilities and critical micelle concentrations (CMC) of potassium dodecyl sulfate (KDS) and hexadecyl sulfate (KHS) were measured in methanol-, ethanol-, 1-propanol-, ethylene glycol-, 1,2-propanediol-, and glycerol-water mixed solvents over the temperature range from 0 to 40°C. It was found that the higher the hydroxy group density in the solvent, the less the effects on both the solubility and the CMC, and that the presence of an alkyl group in the solvent causes a greater temperature-dependence in the solubility. The solvent effects on the CMC and on the single-ion dispersion were discussed separately. An effect of a net-work structure formed between the hydroxy compound and water on the solubility is suggested. Solvent effects on the alkyl group and the ionic group of a surfactant molecule were separated by considering the difference between the standard free-energy change for the solution process of KHS and that of KDS. The effects on the Krafft point were also discussed in term of the above suggestions.

There are many factors that govern the monomer-micelle equilibrium in the surfactant solution. The solvent effects on the CMC have been studied by many investigators; some additives raise the CMC,[1,5] while others lower it.[2,5] However, no definite conclusion has ever been drawn. These phenomena are considered to be closely related to the structure of water.[3–5] In order to make clear how the addition of an organic substance affects the solution behavior of the micelle and the single ion, which are equilibriated with each other in micellar solution, it was necessary to measure the CMC and the single–ion solubility (not equilibriated with the micelle) of the surfactant in various organic solvent–water mixtures over a wide range of temperature. The potassium alkyl sulfates used in the present work are suitable for determining the solubility and CMC separately, near room temperature, as their Krafft points are about 20°C higher than those of the sodium salt analogs, typical anionic surfactants, the micellar properties of which have been well studied.

In the present paper, we will describe the effects of added hydroxy compounds on the solution properties of the surfactant.

Experimental

Materials. The potassium alkyl sulfates were synthesized by the sulfation of the corresponding long-chain alcohols with concentrated sulfuric acid, followed by neutralization with potassium hydroxide. The crude alkyl sulfates were extracted by butanol, recrystallized from butanol and from water three times each and finally washed with ether in Soxhlet's extractor. The methanol was simply distilled. The ethanol and 1-propanol were refluxed over dried calcium oxide for hours and then distilled. The glycols were distilled under reduced pressure. Glycerol of a G.R. grade was used without further purification.

Measurements of Solubility and CMC. By using an electric conductivity meter outfit, Model CM-1 DB, of the Towa Dempa Kogyo Co., Ltd., solubility and CMC measurements were made with KDS. As the solubilities of KHS were too low to be determined by the electric conductivity method, colorimetry was employed: The supernatant of the saturated solution (a long time was necessary to reach an equilibrium, so the surfactant solution in the presence of the solid phase was shaken mechanically for more than 50 hr and then left to stand for 12 hr in a thermostat) was pipetted through a 4G sintered-glass filter and then extracted as a methylene blue-alkyl sulfate complex into a chloroform phase.[6] The optical density of the blue-colored

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[1] P. F. Grieger and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 3803 (1948).

[2] B. D. Flockhart and A. R. Ubbelohde, *J. Colloid Sci.*, **8**, 428 (1953).

[3] B. D. Flockhart, *ibid.*, **12**, 557 (1957).

[4] P. Mukerjee and A. Ray, *J. Phys. Chem.*, **67**, 190 (1963).

[5] M. F. Emerson and A. Holtzer, *ibid.*, **71**, 3320 (1967).

[6] A simplification and modification of Longwell-Maniece's method (*Analyst*, **80**, 167 (1955)).

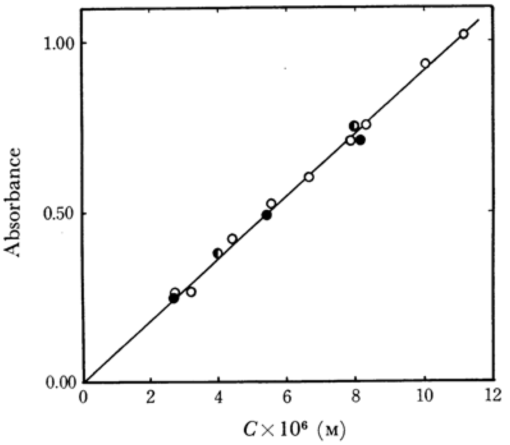

Fig. 1. Absorbance of methylene blue-alkyl sulfate at 650 mμ.
○ hexadecyl, ● tetradecyl, ◐ dodecyl
cell: 1 cm reference: chloroform with blank extraction

chloroform was measured at the wavelength of 650 mμ using a spectrophotometer, Model 139, of the Hitachi Mfg. Co., Ltd. The calibration curve is shown in Fig. 1, where it may be seen that the methylene blue-alkyl sulfate complex shows the same absorbance whatever the length of the alkyl chain.

Results and Discussion

The solubilities and CMC's of KDS are shown as a function of the temperature in Figs. 2—6. A general trend for the solubility to increase slightly in the lower temperature range and to increase markedly in the higher temperature range is apparent. The abrupt change in solubility may be understood as a change in the solution behavior of the surfactant, that is, the micelle formation.

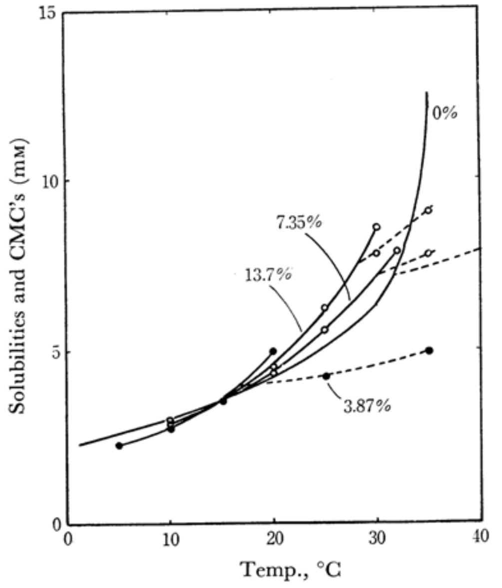

Fig. 2. Solubilities and CMC's of KDS in propanol-water mixtures ●, and in methanol-water mixtures ○.
solid line: solubility, dotted line: CMC

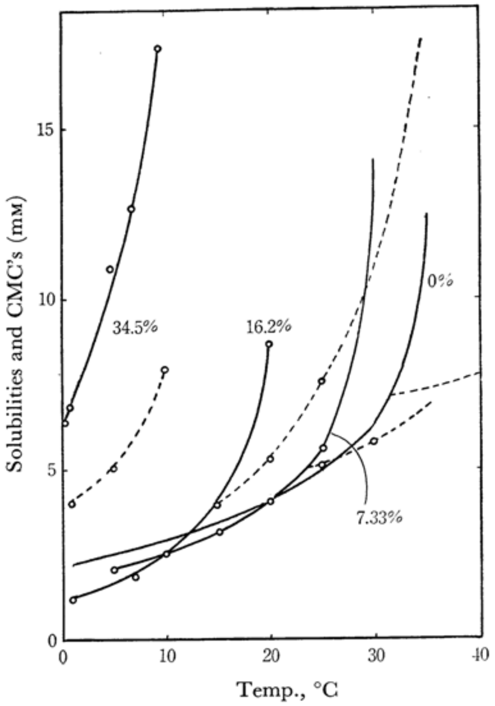

Fig. 3. Solubilities and CMC's of KDS in ethanol-water mixtures.

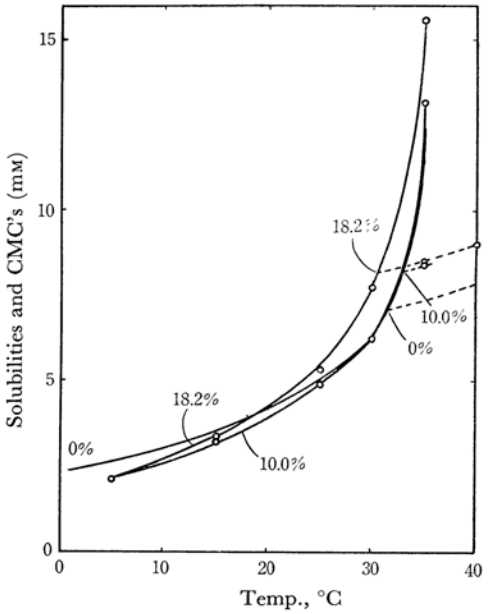

Fig. 4. Solubilities and CMC's of KDS in ethylene glycol-water mixtures.

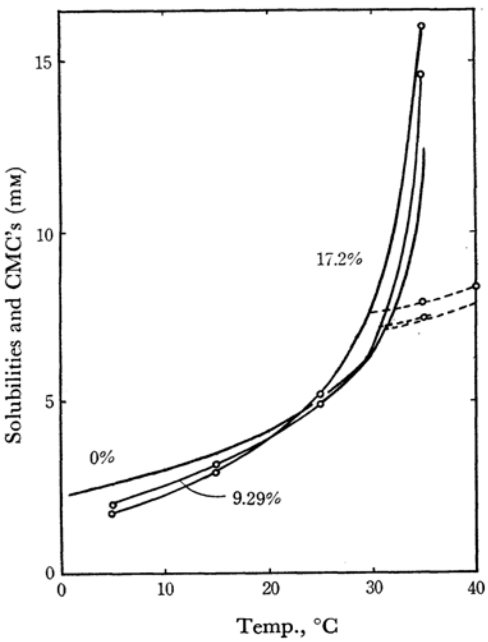

Fig. 5. Solubilities and CMC's of KDS in propylene glycol-water mixtures.

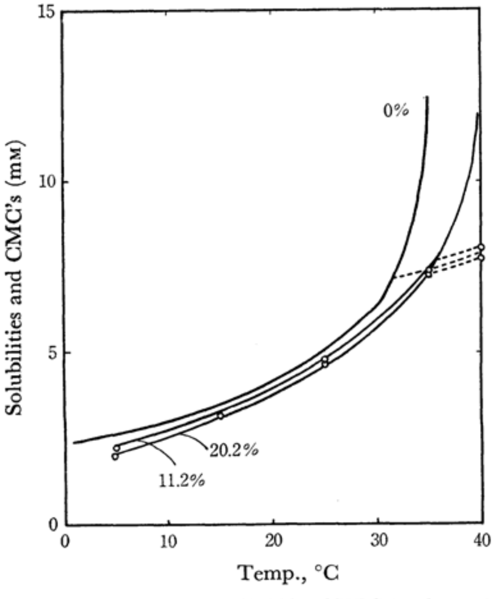

Fig. 6. Solubilities and CMC's of KDS in glycerol-water mixtures.

Thus, a temperature at which the solubility curve intersects the CMC curve is defined as the Krafft point. Therefore, it will be convenient to discuss the solvent effects on micelle formation and on single-ion dispersion separately.

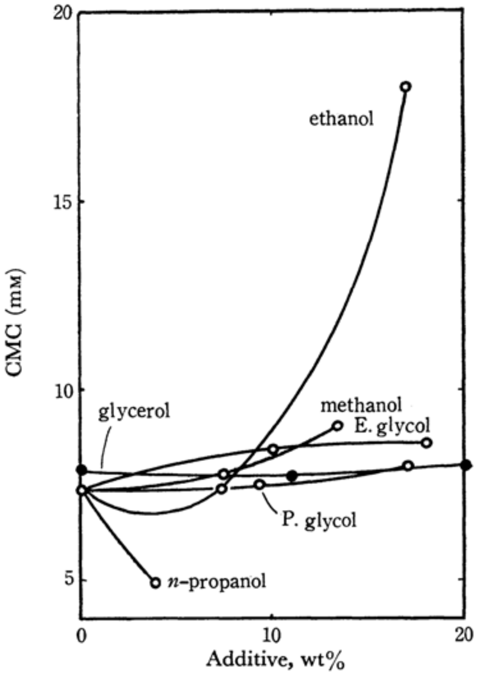

Fig. 7. CMC's of KDS in mixed solvents at 35°C (glycerol solvents at 40°C).
CMC's in ethanol-water mixtures ar extrapolated from lower temperatures to 35°C in Fig. 3.

Solvent Effects on Micelle Formation. The CMC's at 35°C are shown in Fig. 7, where the abscissa indicates the weight percentages of the organic additives. As for the effect of alcohols on the CMC, it has been known that there are both CMC-increasing and CMC-decreasing effects, depending on the chain lengths of the alcohols added.[1,3,5] The same is observed here: methanol shows a CMC-increasing effect, ethanol both, and propanol may have a CMC-decreasing effect, but the addition of much more propanol will have a CMC-increasing effect, too.[2]

In contrast, glycols have a CMC-increasing effect only. Glycerol brings about a very slight minimum in the CMC curve, but it is not clear whether or not this minimum is related to the action of sucrose, which lowers the CMC of sodium dodecyl sulfate. This is attributable to the dehydration of surfactant ions, caused by the strong hydrophile of the sucrose added.[7]

The CMC-decreasing effect found in alcohol solutions may be due to the solubilization of alcohol molecules into micelles, resulting in a decease in the free energy caused by both the entropy of mixing and the reduction of the charge density on the micelle surface.[8,9] Glycols and glycerol do not penetrate the micelle because they have fewer lipophile. Thus, solvent effects other than solubilization have to be sought in connection with

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[7] M. Nakagaki and S. Kawamura, *Yakugaku Zasshi* (*J. Pharm. Soc. Japan*), **84**, 246 (1964).

[8] Y. Ooshika, *J. Colloid Sci.*, **9**, 254 (1954).

[9] K. Shinoda, This Bulletin, **26**, 101 (1953).

these compounds.

As the CMC is the characteristic parameter of the micelle-single ion equilibrium, a solvent effect on single ions as well as on the micelle should be taken into account. For this purpose, the solubilities of the surfactants in the lower temperature range, where only single-ion dispersion is supposed, was examined.

Solvent Effects on Single Ions. It is evident from Figs. 2—6 that the addition of alcohols causes a comparatively small solubility change, but an observable increase in the temperature coefficient of the solubility. For example, the solubility of KDS in the 9.3 wt% methanol solution intersects at 16°C with that for pure water. Thus, the solubility of KDS in a methanolic solution is larger at 20°C, but becomes smaller at 10°C, than in pure water. These properties become exaggerated with increases of alcohol concentration and the chain length of alcohols.

On the other hand, in glycerol mixtures KDS is less soluble than in pure water at all temperatures lower than the Krafft point. Glycols are intermediate between glycerol and mono-alcohols, in that their solubility curves intersect at higher temperatures. In order to observe these effects more quantitatively, a standard free-energy change for the solution process, ΔF°, will now be introduced:

$$\Delta E^\circ = -2RT\ln X_s \tag{1}$$

where X_s is a solubility in the mole fraction scale which should be replaced by an activity, but the experimental concentrations are so low (less than 5 mM) that the mole fraction can be used with a minimum loss of accuracy. The other notations have the usual meanings. The temperature coefficient of the solubility and thermodynamics also give:

$$\Delta H^\circ = -R\frac{\partial \ln X_s}{\partial\left(\frac{1}{T}\right)} \tag{2}$$

and:

$$\Delta S^\circ = \frac{\Delta H^\circ - F\Delta^\circ}{T} \tag{3}$$

where ΔH° and ΔS° are the standard enthalpy and entropy changes for the solution process respectively. In Fig. 8, ΔH°'s and $T\Delta S^\circ$'s are shown as functions of the weight percentages of the organic additives. It is evident that the longer the alkyl group in an alcohol molecule, the more temperature-dependent the solubility becomes, while the hydroxy group in additives surpresses the temperature dependence of the solubility. The higher hydroxy density in ethylene glycol and glycerol solutions supports the idea of a net-work structure formation which resists the thermal breaking of the structure much more than in alcohol solutions. The net-work structure also refuses to share space with dissolved solutes, *i. e.*, with surfactant molecules. This might be closely related to the smaller solvent effect seen in glycols and, above all, in glycerol solutions. On the other hand, the alkyl group in alcohol solutions interferes with the net-work formation and favors the thermal agitation. Thus, at higher temperatures, the alkyl group in a mixed solvent loosens the structure and affords space for surfactant molecules. At lower temperatures, the structure in the solvent becomes more rigid due both to hydrogen bonding and to iceberg formation about the alkyl group in the sense of Némethy-Scheraga.[10] In connection with the structure formation between the hydroxy compound and water, it may be noted that the micelle formation was found in a 34.5% ethanol solution at a lower temperature than 10°C, as may be seen in Fig. 3. As a micelle is an aggregation of "refugees" of surfactant molecules from a highly cohesive solvent, *i. e.*, water, a concentrated ethanol solution which is free from micelle formation at higher temperatures would cohesive enough to be disliked by the surfactant molecules at sufficiently low temperatures. It is also clear from Fig. 8

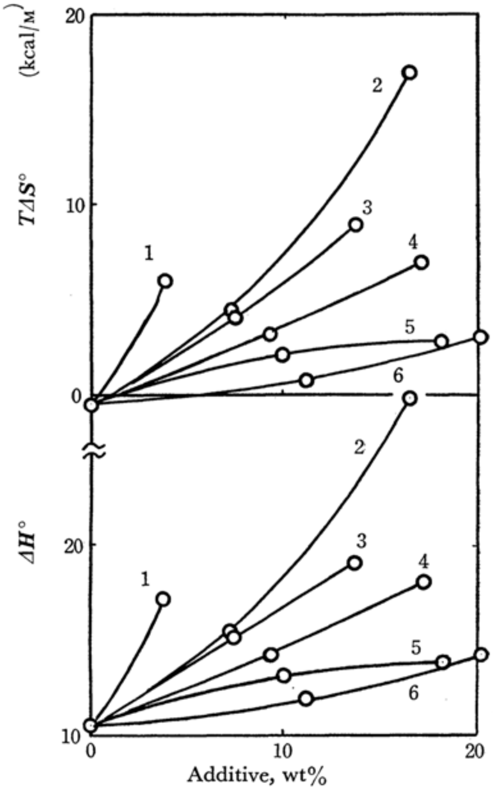

Fig. 8. ΔH's and $T\Delta S$'s of KDS in mixed solvents. 1: 1-propanol, 2: ethanol, 3: methanol, 4: propylene glycol, 5: ethylene glycol, and 6: glycerol.

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[10] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

that propylene glycol lies between glycerol and alcohols in that it has both glycol and methyl groups in a molecule. The iceberg around the hydrocarbon entity of a surfactant molecule might be attacked by the additives, because $T\Delta S^\circ$ increases from negative value to a positive one with the additive concentration, as may be seen in Fig. 8.

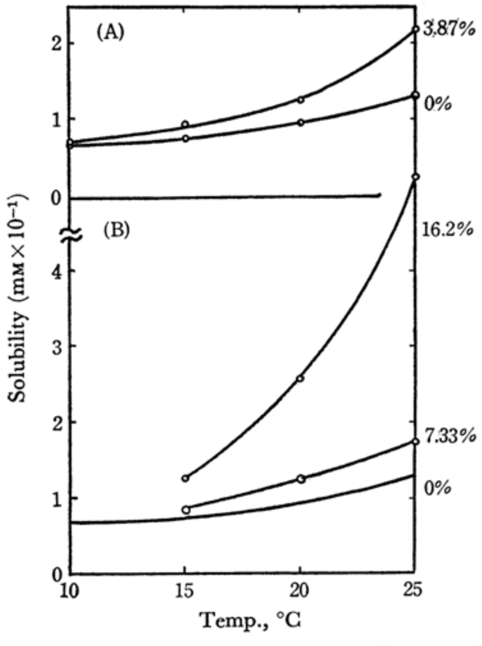

Fig. 9. Solubilities of KHS in propanol-water mixtures (A), and in ethanol-water mixtures (B).

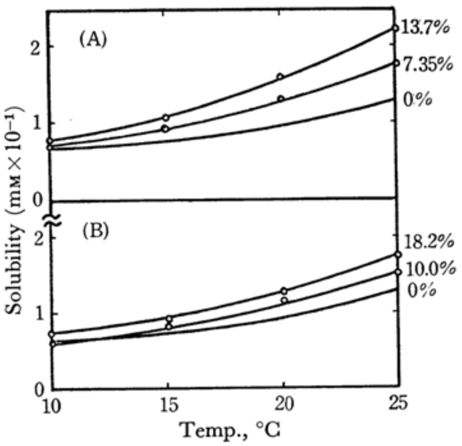

Fig. 10. Solubilities of KHS in methanol-water mixtures (A), and in ethylene glycol-water mixtures (B).

TABLE 1. SOLUBILITIES OF KHS IN MIXED SOLVENTS AT 15°C (10^{-1} mM)

Propylene glycol Add. wt%	 Soly.	Glycerol Add. wt%	 Soly.
9.29	0.828	11.2	0.754
17.2	0.780	20.2	0.749

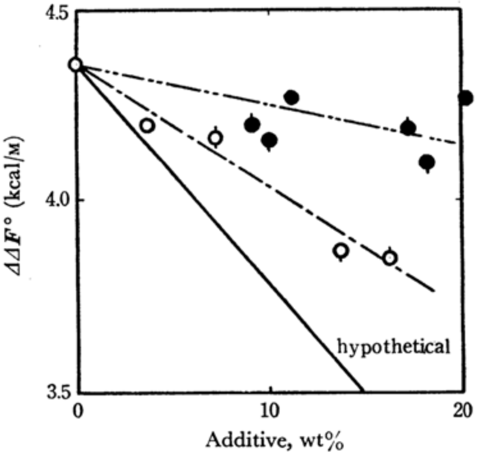

Fig. 11. Solvent effect on nonpolar group.
○: propanol, ○: ethanol, ○: methanol,
●: glycerol, ●: propylene glycol,
●: ethylene glycol

Separation of Solvent Effects. The solvent effects can be divided into two groups: the solvent effect on a nonpolar group and that on an ionic group of a surfactant molecule. On the assumption that these two effects are additive, the separation can be experimentally made by measuring the solubility of, for example, KHS in each solvent and by applying the following equation:

$$\Delta\Delta F^\circ = \Delta F^\circ_{\mathrm{KHS}} - \Delta F^\circ_{\mathrm{KDS}} = -2RT\ln\frac{C_{\mathrm{KHS}}}{C_{\mathrm{KDS}}} \qquad (4)$$

where $\Delta\Delta F^\circ$ means the solvent effect on the nonpolar group (exactly on the tetramethylene group) and where the subscripts KHS and KDS refer to the surfactants used. The C's are the solubilities of the surfactants. The solubilities of KHS are shown in Figs. 9—10 except for those in propylene glycol-, and glycerol-water mixed solvents, for which measurements were made at 15°C only; the results are shown in Table 1. In Fig. 11, the $\Delta\Delta F^\circ$'s are plotted against the weight percentages of the additives at 15°. Although the points are scattered, it is observed that all alcohols show the same inclination and that glycols and glycerol show a smaller solvent effect, as was also noted in the enthalpy change for the solution process. For comparison, a hypothetical solvent effect, defined below, may be tentatively introduced:

$$\Delta\Delta F^\circ_{\mathrm{hypo}} = \phi_{\mathrm{w}}\Delta F^\circ_{\mathrm{w}} + \phi_{\mathrm{H}}\Delta F^\circ_{\mathrm{H}} \qquad (5)$$

where ϕ_{W} and ϕ_{H} are, respectively, the volume fractions of water and some hypothetical solvent such as "hexane" in a hypothetical mixed solvent where the two components are supposed to be freely miscible without any overall change in the water structure, and where ΔF°_W and ΔF°_H are the standard free-energy changes for the nonpolar group when it is dissolved into water and into "hexane" respectively. Furthermore, $\Delta F^\circ_W > \Delta F^\circ_H \doteqdot 0$, because, when, for example, butane is dissolved into hexane, its free-energy change is negligibly small; therefore, Eq. (5) reduces to:

$$\Delta\Delta F^\circ_{\text{hypo}} = \Delta F^\circ_{\text{w}}\,(1-\phi_{\text{H}}) \qquad (6)$$

Equation (6) proves that a strongly cohesive solvent, such as water, becomes energetically void and liable to accept a hydrocarbon entity when mixed with "hexane." A formula similar to Eq. (6) can be derived from the Flory-Huggins' equation for three component system on the assumptions that: (1) the molar volumes are all alike, (2) the solution is very dilute with respect to solute, and (3) all the interaction energies except that between solute and water molecules are zero.[11] The hypothetical solvent effect is shown as a solid line in Fig. 11. A positive deviation from the hypothetical line would be due to the structure formation in alcohols-, in glycols-, and, above all, in glycerol-water mixed solvents.

The solvent effect on the ionic group can be calculated by the following equation:

$$\Delta F^\circ_{\text{ion}} = \Delta F^\circ_{\text{KDS}} - \Delta\Delta F^\circ \times 3 \qquad (7)$$

Since $\Delta\Delta F^\circ$ is a contribution from a tetramethylene group, the factor of three is introduced to obtain the contribution from a dodecyl group. The values of $\Delta F^\circ_{\text{ion}}$'s are plotted against the reciprocal of the dielectric constant[*1] of the mixed solvents in Fig. 12. The straight line was drawn by the least-square method; the slope gives a "Born radius" of 0.3 Å. This value is smaller than the probable one (around 5 Å) deduced by the electric conductivity method for sodium dodecyl sulfate.[12] However, it may not be unacceptable taking into account the facts that the solvation energy cannot be explained by the Born mechanism alone and that, in addition, the experimental points are scattered. As a first approximation, the solvent effect on the ionic group is explained by the electrostatic theory; further mechanisms, such as selective solvation and the effect of a large hydrocarbon

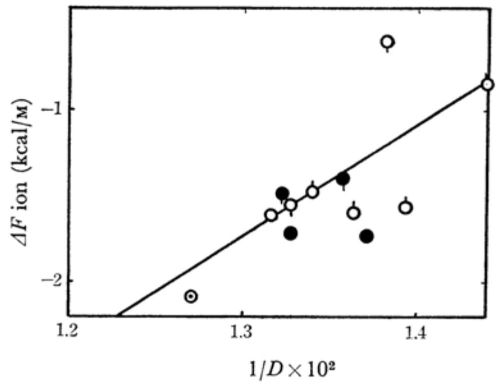

Fig. 12. Solvent effect on ionic group.
⊙: water, other indications are the same as in Fig. 11.

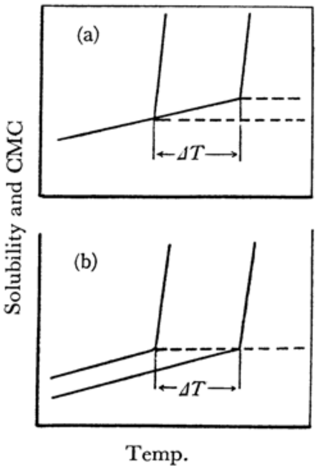

Fig. 13. Schema of the Krafft point changes.

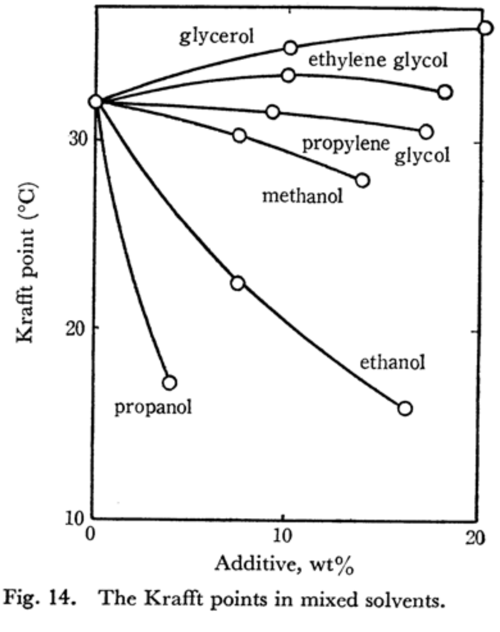

Fig. 14. The Krafft points in mixed solvents.

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[11] P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New Yrok (1953), p. 548.

[*1] The dielectric constants of the mixed solvents are quoted from H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publ. Corp., N. Y. (1958), p. 161, except for that for aqueous propylene glycol, which was calculated by weighing the volume fractions on the dielectric constants of each component.

[12] G. D. Parfitt and A. L. Smith, *Trans. Faraday Soc.*, **61**, 2736 (1965).

group adjacent to the charged center, would be important and more precise experiments and theory would be required before they could be established.

Solvent Effect on the Krafft Point. In order to clarify the solvent effects on the Krafft point, detailed knowledge of the CMC and the single-ion dispersion, and of their temperature dependence is necessary. However, for the sake of simplicity, we consider in Fig. 13 two extreme cases in which: (a) the solubility curve is unchanged, but the CMC curve is increased or decreased, and (b) the CMC curve is unchanged, but the solubility curve is altered by the addition of organic compounds. The Krafft points are shown in Fig. 14 as functions of the weight percentages of the additives. If, from (a), CMC decreases, the Krafft point also decreases. This corresponds to the effect of propanol, which lowers the CMC, as has been pointed out above. An extreme example of this type of effect has been reported by Shinoda and Nakayama, who studied the very sensitive Krafft point-decreasing power of some higher alcohols (C_6–C_8).[13] As for the (b) case, the effect of glycerol may be pointed out. The solubility-decreasing effect and the small effect on the CMC of glycerol cause an increase in the Krafft point; such an increase is rare except as an effect of added electrolytes.[14] The medium decrease in the Krafft point affected by methanol can be understood on the assumption that the mechanism (b) slightly exceeds the (a), as there is also a CMC-increasing effect, which would otherwise raise the Krafft point. The effect of ethanol is indicative of the mechanism (a), which results from the large temperature dependence of CMC. For glycols, the two mechanisms compensate each other; hence, relatively small changes in the Krafft point are observed. Propylene glycol's greater inclination to decrease may well represent the effect of the methyl group, which ethylene glycol lacks.

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13) H. Nakayama and K. Shinoda, *J. Phys. Chem.*, **70**, 3502 (1965).

14) H. Nakayama and K. Shinoda, This Bulletin, **40**, 1797 (1966).