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The Effects of Organic Additives on the Solubilities and CMC's of Potassium Alkyl Sulfates in Water. II. Effects of Some Nonhydroxy Compounds

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Solubilities and critical micelle concentrations (CMC) of potassium dodecyl sulfate (KDS) and hexadecyl sulfate (KHS) were measured in aqueous solutions to which dioxane, acetone, urea, or dimethyl sulfoxide had been added over the temperature range of 5—40°C. It was found that all additives mentioned above raised solubility and CMC with an exception for dioxane which showed a slight minimum on a CMC-additive concentration curve. Solvent effects on the alkyl and ionic groups of a surfactant molecule were separated by considering the difference of the standard free energy change for the solution process of KHS and that of KDS. It was deduced that a primary effect on the alkyl group is the one that a strongly cohesive solvent, water, is replaced by a less cohesive organic solvent and other mechamisms, such as an effect on the water structure, follow as the secondary. In terms of the above considerations, effects on the Krafft point were also referred to.

In Part I of this series, the solvent effects on potassium alkyl sulfates of such compounds as lower alcohols and glycols were reported.[1] The present paper will describe solvent effects, on the same surfactants, of dioxane, acetone, urea and dimethyl sulfoxide which are characterized by the name, nonhydroxy compounds. The effects on CMC caused by these additives have been reported by many authors,[2-6] but the nature of the effects has not been elucidated. We believe that the phenomena should be understood in terms of solvent effects on single-ion dispersion as well as on micelle dipersion, as these two are equilibriated with each other. Then it was attempted to measure solubilities and CMC's of KDS and KHS (solubility only) in various mixed solvents of aqueous organic compounds mentioned above. Dioxane was employed because of the diverse dielectric constants of its aqueous solution, and other three are interesting for their related chemical structures.

Experimental

Materials. Potassium alkyl sulfates are the same samples as used in the previous work.[1] Dioxane was refluxed on metallic sodium for hours and distilled. Acetone was purified by distillation, after treated with a small amount of potassium permanganate. Urea was recrystallized twice from ethanol-water (2 : 1 in volume) mixture and dried in vacuum. Dimethyl sulfoxide was shaken and distilled in the presence of alumina under reduced pressure.

Procedures. Solubility and CMC measurements were performed by the same methods as in Part I. Urea solutions were kept in refrigerator and used within 10 days so as to avoid any error that may come from the hydrolysis of urea.

Results and Discussion

Solubilities and CMC's of KDS are plotted against temperature in Figs. 1—4.*[1] It is evident from the figures that the increase in concentration of the additive results in increases both in solubility and in CMC except for the dioxane-water mixed solvent in which a slight CMC-decreasing effect was observed. These results are in contrast with the effects caused by hydroxy compounds,[1] where the solubility curve crosses that for pure water. Thus, the hydroxy additives caused increase in

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[1] K. Shirahama, M. Hayashi and R. Matuura, This Bulletin, **42**, 1206 (1969).

[2] K. Shirahama and R. Matuura, *ibid.*, **38**, 373 (1964).

[3] M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, **71**, 3320 (1967).

[4] J. M. Corkill, J. F. Goodman, S. P. Harrold and J. R. Tate, *Trans. Faraday Soc.*, **63**, 240 (1967).

[5] M. J. Schick, *J. Phys. Chem.*, **68**, 3585 (1964).

[6] P. Mukerjee and A. Ray, *ibid.*, **67**, 190 (1963).

*[1] In Figs. 2 and 4, the CMC curves were completed by extrapolating the CMC's in the lower additive concentrations to the ones in the higher additive concentrations, *i. e.*, 7.34% acetone and 27.9% dioxane.

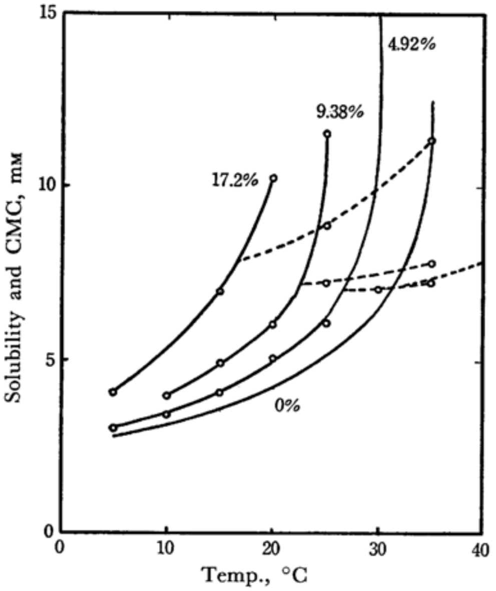

Fig. 1. Solubilities and CMC's of KDS in dioxane-water mixed solvents.
solid line: solubility curve
dotted line: CMC curve

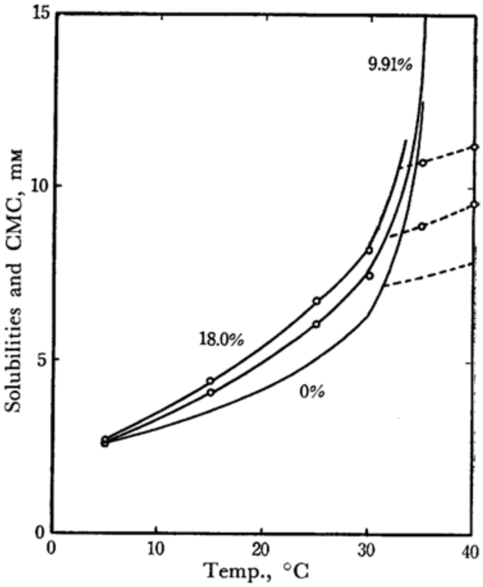

Fig. 3. Solubilities and CMC's of KDS in dimethyl sulfoxide - water mixed solvents.

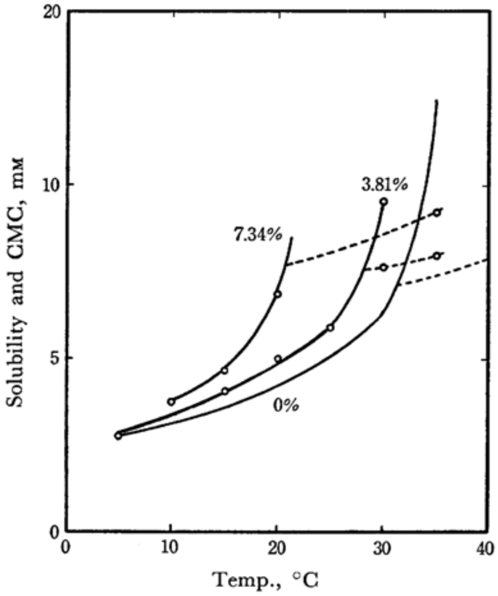

Fig. 2. Solubilities and CMC's of KDS in acetone-water mixed solvents.

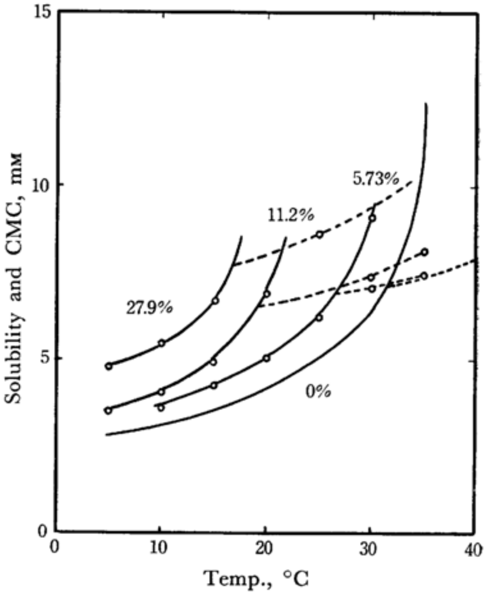

Fig. 4. Solubilities and CMC's of KDS in urea-water mixed solvents.

solubility at higher temperature ranges, but at lower temperature ranges they caused decrease in solubility, as compared with solubilities in pure water. On the other hand, the additives used in the present work enhance solubilities at all experimental temperatures, although for acetone-, and dimethyl sulfoxide - water systems, the solubility curves crossed at the lowest experimental temperature (near 5°C), and for dioxane- and urea-water mixed solvents, it may be expected that solubility curves will intersect each other at temperatures lower than 0°C. This enhanced solubility is a marked difference from the solubility of a simple electrolyte, for which electrostatic theory predicts reduced solubility in most organic solvent-water mixtures.[7] The organic additives in the

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7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publ. Corp., New York (1958), p. 81.

present work, *i. e.,* nonhydroxy compounds would form hydrogen bond with water just as hydroxy compounds do and strengthen the net-work structure which limits the dissolution of hydrophobic solutes. But this effect is well compensated by the fact that the structuredness of liquid water, or clusters, are "molten" by the presence of the additives, just as by the thermal agitation, and bulky closed space is liberated for the dissolved solute.[8]

To be more quantitative, the standard free energy change for the solution process, and the corresponding enthalpy and entropy changes defined as

$$\Delta F^\circ = -2\boldsymbol{R}T\ln X_s, \tag{1}$$

$$\Delta H^\circ = \frac{\partial \Delta F^\circ}{\partial(1/T)} \tag{2}$$

and

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

may be considered. Here X_s is a solubility in mole fraction, and other notations are usual ones. The values of ΔH° and $T\Delta S^\circ$ are shown as a function of weight percentage of the additives in Fig. 5, where the values in ethanol-water mixed solvents are also added for comparison. Both enthalpy and entropy changes are rather small as compared with those in alcohols-water mixed solvents. It is especially noted that the effect by urea is very small. This fact might suggest some different mechanism with this compound which is well-known for its protein denaturating ability, often discussed in connection with the structure of liquid water.[9] Another example of this difference would be seen in Fig. 6, where ΔH°'s are plotted against $T\Delta S^{\circ}$'s for the mixed solvents studied in both Parts I and II. Figure 6 represents that effects of hydroxy, nonhydroxy and urea fall on different lines, respectively. This fact may suggest that these additives would have some diverse roles in the solution process.

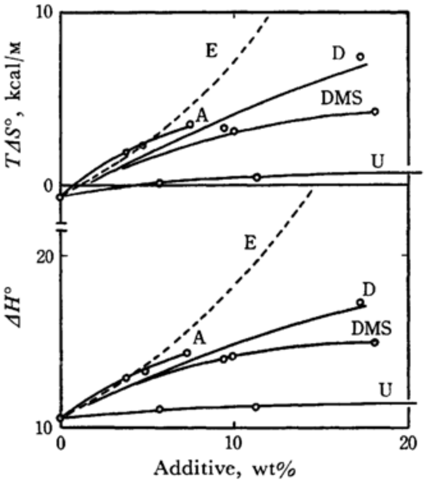

Fig. 5. The values of ΔH°'s and $T\Delta S^{\circ}$'s in mixed solvents.
E: ethanol, A: acetoxane, D: dioxane, DMS: dimethyl sulfoxide, U: urea

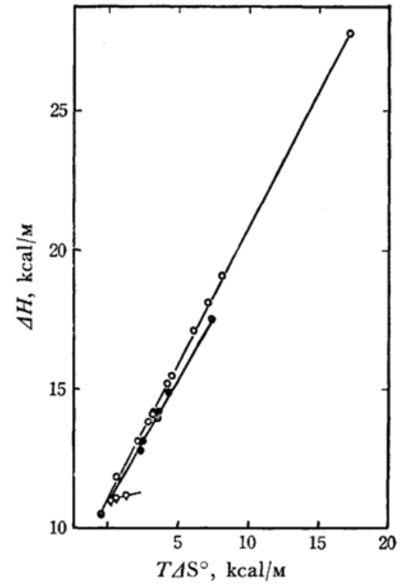

Fig. 6. ΔH°'s *vs.* $T\Delta S^{\circ}$'s plot.
○: hydroxy compound, ●: nonhydroxy compound, ϙ: urea, ⊙: water

At the same enthalpy change, the entropy change is in order of urea, nonhydroxy and hydroxy compounds. These differences may arise from the difference in the net-work structure formation effect and the space-releasing effect of these compounds. It was reported by Nakanishi[10] that an effect on the partial molar volume of water by the addition of the compounds can be classified by the two categories of hydroxy and nonhydroxy compounds.

Solvent Effect on CMC. In view of the above explanations, the changes in CMC's given in Fig. 7 are understood: in a monomer-micelle equilibrium, if monomer becomes more stable but micelle does not by an additive, the equilibrium should displace to the monomer side, thus CMC is raised. This is clearly seen in Fig. 8, where a relative solubility (r_s) is plotted against a relative CMC (r_m). The relative solubility here means a ratio of a solubility of single-ion dispersion extrapolated to 35°C in a mixed solvent to that in pure water. The extrapolated values obtained by the logarithm of solubility *vs.* the reciprocal of temperature plot, and the ones by the graphical extrapolation tracing the smooth curve agreed each other. The relative CMC also has a similar meaning. An approximate

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8) F. Franks and D. G. Ives, *Quart. Rev. (London),* **20**, 1 (1966).

9) For example: G. C. Kresheck and L. Benjamin, *J. Phys. Chem.,* **68**, 2476 (1964).

10) K. Nakanishi, This Bulletin, **33**, 793 (1960).

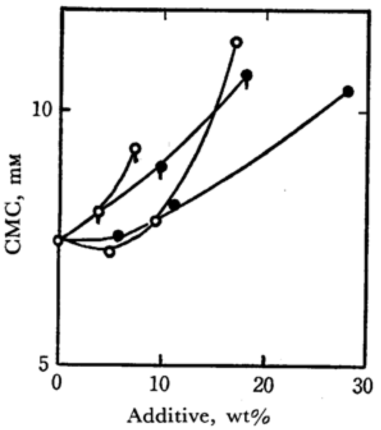

Fig. 7. CMC's of KDS in mixed solvents at 35°C.
○: dioxane, ○̩: acetone, ●: urea, ●̩: dimetyl sulfoxide

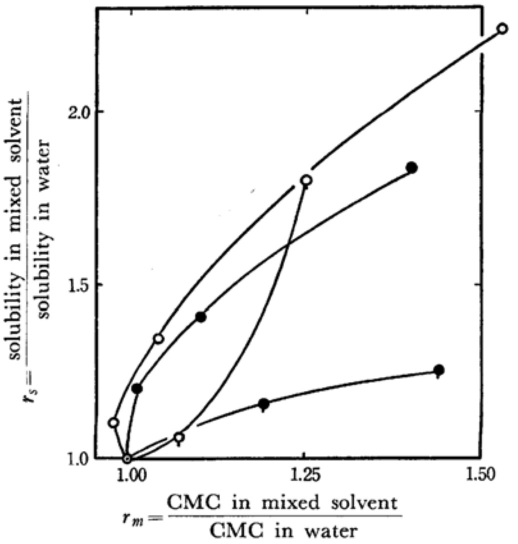

Fig. 8. Relative CMC (r_m) *vs.* relative solubility (r_s) plot.
⊙: water, ○: dioxane, ●: urea, ○̩: acetone, ●̩: dimethyl sulfoxide.

pararellism between the two ratios supports this idea. A less or non CMC-decreasing ability of dimethyl sulfoxide might be attributed to its highly hydrophilic nature as compared with others. The CMC-decreasing power of dioxane is, although slight, explicit in Fig. 7. Urea is also believed to be effective in breaking micelles because of high dielectric constant of its aqueous solutions.³⁾ The CMC-decreasing power of acetone might not be negligible, judging from its both hydrophilic and hydrophobic nature, but it would be overcome by a marked CMC-increasing effect. A shallow minimum of the CMC *vs.* additive concentration curve in dioxane-water mixed solvent was found for sodium dodecyl sulfates too,²⁾ and explained in term of solubilization of dioxane molecules into micelles just as seen in the cases of alcohols-water mixtures.¹¹,¹²⁾

Separation of Solvent Effects. As was done in Part I, solvent effects can be divided into two portions: a solvent effect on the nonpolar group and one on the ionic group of a surfactant molecule. In order to do so, solubilities of KHS in respective mixed solvents were measured (shown

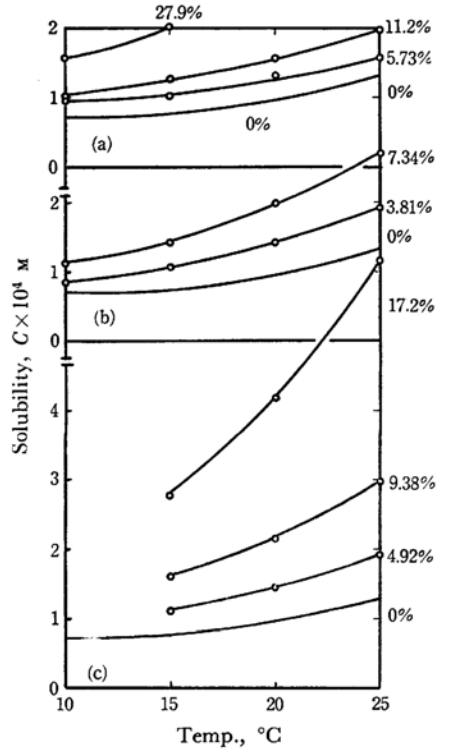

Fig. 9. Solubilities of KHS in mixed solvents. (a) urea, (b) acetone, (c) dioxane

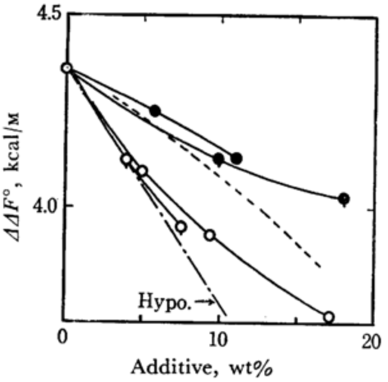

Fig. 10. Solvent effect on nonpolar group of a surfactant molecule.
○: dioxane, ○̩: acetone, ●: urea, ●̩: dimethyl sulfoxide
dotted line: ethanol
chain line: the hypothetical effect as reported in Part I.

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11) K. Shinoda, This Bulletin, **26**, 101 (1953).
12) Y. Ooshika, *J. Colloid Sci.*, **9**, 254 (1954).

in Fig. 9, and for aqueous dimethyl sulfoxide, 0.110, 0.129 mM in 9.91 and 18.0 DMS wt% respectively, at 15°C only) and then the solvent effect on the nonpolar group $\Delta\Delta F^\circ$ was calculated by applying the following equation,

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

where subscripts refer to the respective surfactants, C's are solubilities of surfactant in a solvent, and other notations are usual ones. The values of $\Delta\Delta F^\circ$ are presented as a function of weight percentage of additives in Fig. 10, where a hypothetical solvent effect is drawn as before.1) The hypothetical solvent effect is simply expressed as

$$\Delta\Delta F^\circ_{\mathrm{hypo}} = \Delta F^\circ_{\mathrm{w}}(1-\phi_{\mathrm{H}}), \quad (5)$$

where $\Delta F^\circ_{\mathrm{w}}$ is the standard free energy change of the nonpolar group for the solution process in pure water, *i. e.*, a solvent effect of water, ϕ_{H} is a volume fraction of hexane which was taken as a hypothetical additive. Here is again a positive deviation from the hypothetical behavior. This deviation is relatively small for acetone and dioxane which enhance the solubilities of the surfactants, probably due to their space-releasing effect. Another useful indication is a $\Delta\Delta F^\circ$ *vs.* CED plot in Fig. 11, where CED's (cohesive energy density) are calculated from the pressure-temperature, and density data from various sources of the corresponding binary systems.13)

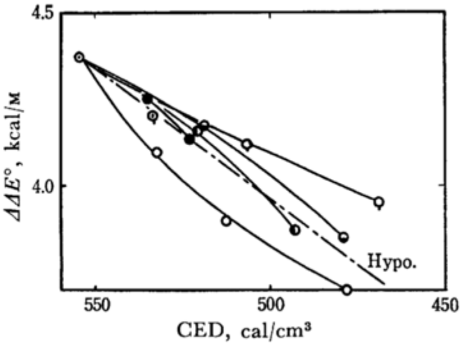

Fig. 11. $\Delta\Delta F^\circ$ *vs.* CED plot.
⊙: water, ○: dioxane, ○̩: acetone, ●: urea, ●̩: DMS, ◐: methanol, ◒: ethanol, ⊙̩: 1-propanol.

The CED of the hypothetical mixture was calculated by the equation,14)

$$(\mathrm{CED})_{\mathrm{hypo}} = (\phi_{\mathrm{w}}\delta_{\mathrm{w}} + \phi_{\mathrm{H}}\delta_{\mathrm{H}})^2, \quad (6)$$

where subscripts W and H refer to water and a hypothetical solvent, respectively, and ϕ's and δ's are volume fractions and solubility parameters, respectively. Here hexane was taken as a hypothetical additive, for which the density and the solubility parameter are available. In Fig. 11, points are scattered around the hypothetical effect. This may indicate a primary solvent effect that the strongly cohesive liquid, water, becomes energetically loosened by adding any less cohesive compound. Both the net-work formation and the space-releasing effect would follow this primary effect and work against, or sometimes, for it. Urea which is solid and therefore the most cohesive shows a remarkable solvent effect and thus should hold a special position in affecting the structure of liquid water.

The solvent effect in the ionic group $\Delta F^\circ_{\mathrm{ion}}$ was calculated from the equation,

$$\Delta F^\circ_{\mathrm{ion}} = \Delta F^\circ_{\mathrm{KDS}} - \Delta\Delta F^\circ \times 3. \quad (7)$$

In Fig. 12, $\Delta F^\circ_{\mathrm{ion}}$'s are plotted against the reciprocals of dielectric constants of the mixed solvents. A line was determined by the least square method. The slope gives the Born radius 0.5 Å.

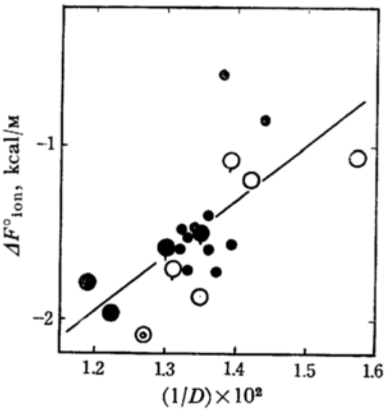

Fig. 12. Solvent effect on ionic group of a surfactant molecule.
⊙: water, ○: dioxane, ○̩: acetone, ●̩: DMS, ●: urea, small full circles are for hydroxy compounds as repoted in Part I.

Solvent Effects on the Krafft Point. The Krafft point is defined as the intersection of solubility curve and CMC curve. Thus detailed knowledge on the two curves might be required to predict the solvent effect on the Krafft point, but here, as in Part I, two simplified extremes are considered: (a) CMC curve changes (increase or decrease) with solubility curve fixed, (b) solubility curve changes with CMC curve fixed. These two extreme cases are schematically shown in Fig. 13. In Fig. 14, the observed Krafft points are plotted against the weight percentage of additives. It is noted that dimethyl sulfoxide affects only a little on the Krafft point probably due to a cancellation of the (a) and (b) effects.

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13) a) For acetone and alcohols, "International Critical Tables," Vol. III, pp. 111, 292 (1928). b) For dioxane, F. Hovorka, R. A. Schaeffer and D. Dreisbach, *J. Am. Chem. Soc.*, **58**, 2264 (1936). c) For urea, G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3016 (1938); H. M. Chadwell and F. W. Politi, *ibid.*, **60**, 1291 (1938).

14) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold, New York (1950), p. 198.

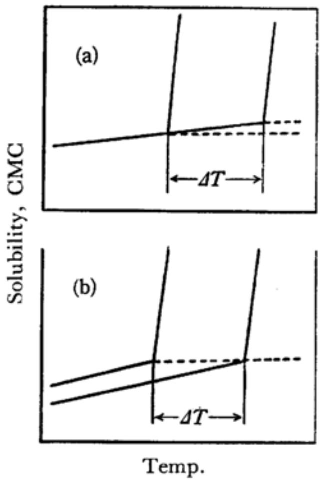

Fig. 13. The two extreme cases of the effects on the Krafft point.
solid line: solubility curve
dotted line: CMC curve
ΔT: change in the Krafft point.

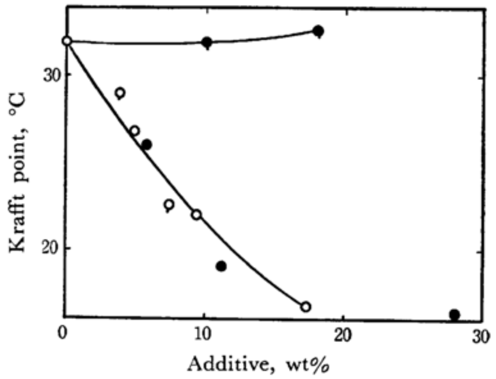

Fig. 14. Solvent effect on the Krafft point. ○: dioxane, ○: acetone, ●: urea, ●: dimethyl sulfoxide.

On the other hand, dioxane, acetone and urea show the effects of the same magnitude. The lowering of the Krafft point might be brought about by the (b) mechanism exceeding the (a). This is also clear from Fig. 8 which shows a marked increase in solubility as compared with the CMC increase.