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Surfactants in Solution

(2)

Edited by

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Table I. Micellar Diffusivities for CTACl + NaCl, with [t-AmOH]=2% (wt.).

[NaCl]	[CTACl]	D	D X 1.10 [*]
0.01 M	0.01 M	14.3 X 10 ⁻⁷ cm ² /s	15.8 X 10 ⁻⁷ cm ² /s
	0.02	18.5	20.3
	0.03	21.5	23.6
	0.04	22.6	24.9
	0.05	24.2	26.6
0.02	0.01	10.8	11.9
	0.02	13.0	14.3
	0.03	14.4	15.8
	0.04	----	----
	0.05	17.4	19.1
0.04	0.01	9.5	10.5
	0.02	10.1	11.1
	0.03	10.8	11.9
	0.04	11.6	12.8
	0.05	12.4	13.6
0.1	0.01	8.8	9.7
	0.02	9.3	10.2
	0.03	9.8	10.8
	0.04	10.2	11.2
	0.05	10.8	11.9

alcohol assumed ~ fully in solvent -- D corrected for viscosity of pure water at 25°C.

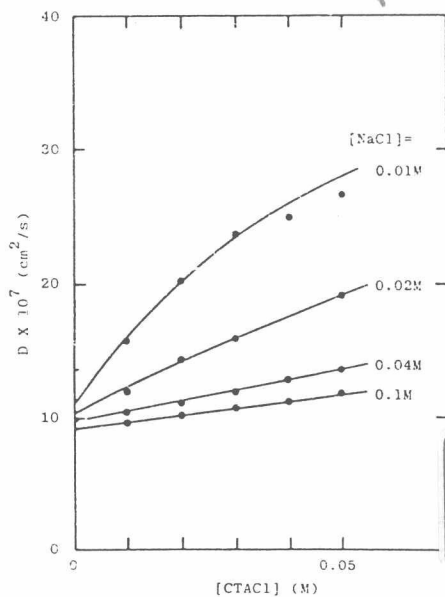


Figure 6. Micellar diffusivity D vs [CTACl] (0.01-0.05M) for [NaCl]=0.01-0.1M at 25°C; [t-AmOH]=2% (wt.), assuming ~ 100% in solvent.

The resulting viscosity-corrected diffusivities are plotted in Figure 6. The solid curves represent the best theoretical fits, discussed below.

The measured diffusivities for $[t\text{-AmOH}] = 4\%$ are listed in Table II, together with two sets of corrected values. The first set assumes that half the $t\text{-AmOH}$ remains in the solvent, while the other assumes that virtually all the alcohol stays outside the micelles. While these trial assumptions are arbitrary, they nevertheless represent reasonable limits on the actual situation. The corresponding plots are shown in Figure 7 (100% of the $t\text{-AmOH}$ in the solvent) and Figure 8 (50% in the solvent). Finally, the measured D values for $[t\text{-AmOH}] = 6\%$ are listed in Table III, with corrected values assuming that either half, or all, of the $t\text{-AmOH}$ remains in the solvent. The corresponding plots are shown in Figure 9 (100% of the $t\text{-AmOH}$ in the solvent) and Figure 10 (50%).

Figures 6-10 share a common trait: for a given $[t\text{-AmOH}]$ the extrapolated mean micellar diffusivity, D_o , differs for each $[\text{NaCl}]$, decreasing with increasing $[\text{NaCl}]$. The D_o values (referred to pure water as solvent), together with the corresponding micellar radii R_h (from Equation 1), are listed in Table IV. As was the case for the CTABr ternary system (with $[t\text{-AmOH}] \gtrsim 2\%$) addition of $t\text{-AmOH}$ shrinks the micelles: i.e. for a given $[\text{NaCl}]$ R_h decreases with increasing $[t\text{-AmOH}]$. The extent of shrinkage of CTACl micelles due to incorporation of $t\text{-AmOH}$ is particularly impressive for $[t\text{-AmOH}] = 6\%$ -- for $[\text{NaCl}] = 0.01\text{M}$, $R_h \approx 11 \text{ \AA}$, assuming (i.e. for

Table II. Micellar Diffusivities for CTACl + NaCl, with $[t\text{-AmOH}] = 4\%$ (wt.).

$[\text{NaCl}]$	$[\text{CTACl}]$	D	$D \times 1.10^*$	$D \times 1.21^\dagger$
0.01 M	0.005 M	$13.9 \times 10^{-7} \text{ cm}^2/\text{s}$	$15.3 \times 10^{-7} \text{ cm}^2/\text{s}$	$16.8 \times 10^{-7} \text{ cm}^2/\text{s}$
	0.01	17.3	19.0	20.8
	0.02	20.9	23.0	25.3
	0.03	22.8	25.1	27.6
	0.04	24.7	27.2	29.9
	0.05	25.8	28.4	31.2
0.02	0.005	11.3	12.4	13.6
	0.01	12.5	13.7	15.1
	0.02	15.6	17.2	18.9
	0.03	17.8	19.6	21.5
	0.04	18.6	20.5	22.5
	0.05	19.7	21.7	23.8
0.04	0.01	10.5	11.5	12.6
	0.02	11.4	12.5	13.8
	0.03	12.5	13.7	15.1
	0.04	13.7	15.1	16.6
	0.05	14.6	16.1	17.7
0.1	0.01	9.2	10.1	11.1
	0.02	9.6	10.6	11.6
	0.03	10.2	11.2	12.3
	0.04	10.7	11.8	12.9
	0.05	11.0	12.1	13.3

* alcohol assumed 50% in solvent, \dagger alcohol assumed $\sim 100\%$ in solvent;
 D values corrected in each case for viscosity of pure water at 25°C .

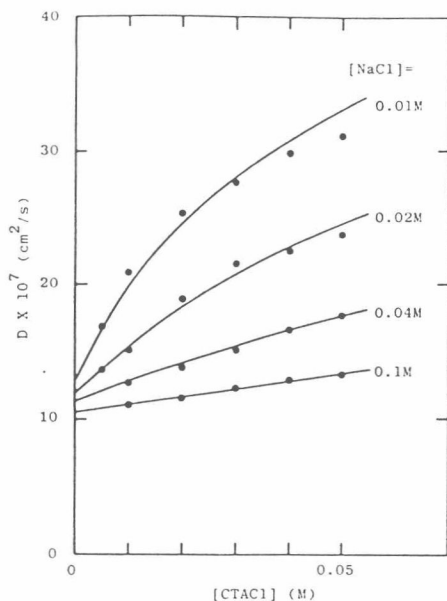


Figure 7. Same as Figure 6, but $[t\text{-AmOH}] = 4\%$ (wt), assuming 100% in solvent.

11 $[CTACl]$) that nearly 100% of the $t\text{-AmOH}$ is in the solvent. For a given $[t\text{-AmOH}]$, R_h decreases (i.e. D_0 increases) markedly with decreasing $[Cl]$. That is, the extent of micellar shrinkage due to addition of $t\text{-AmOH}$ is relatively small in high salt, $[NaCl] = 0.1M$, but very pronounced in lowest salt, $0.01M$. Therefore, as has been observed for many "normal"

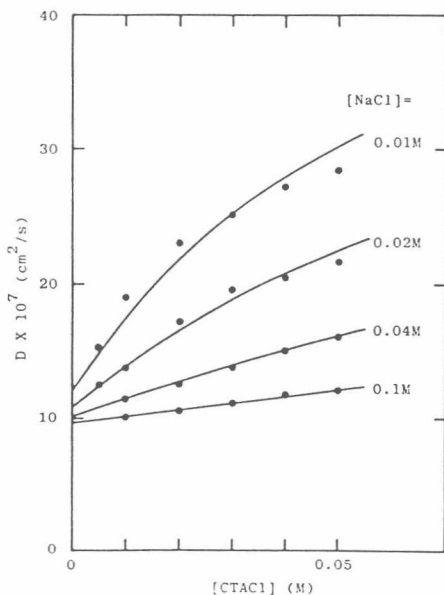


Figure 8. Same as Figure 6, but $[t\text{-AmOH}] = 4\%$ (wt), assuming 50% in solvent.

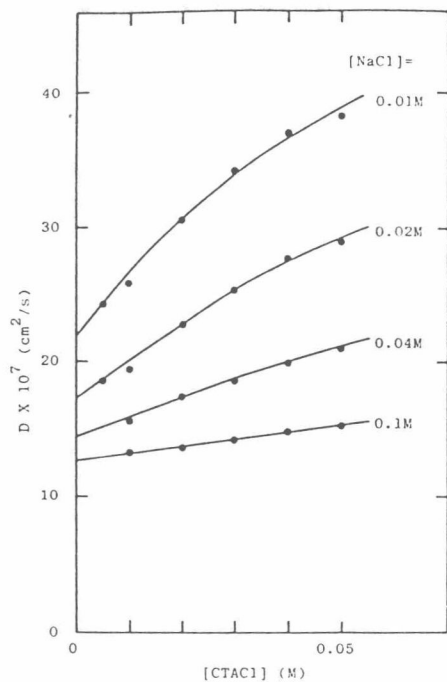


Figure 9. Same as Figure 6, but [t-AmOH]=6% (wt), assuming 100% in solvent.

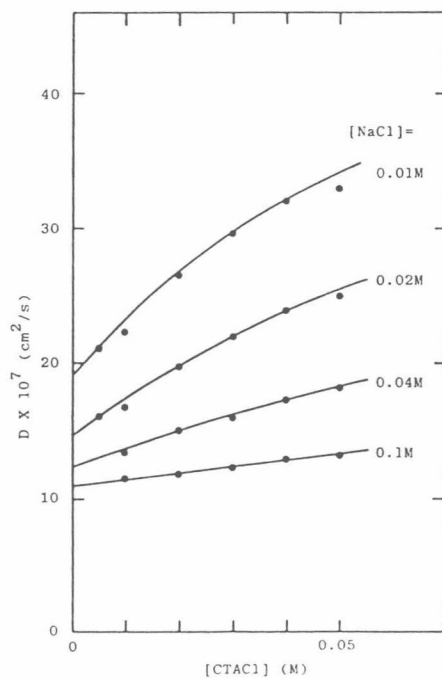


Figure 10. Same as Figure 6, but [t-AmOH]=6% (wt), assuming 50% in solvent.

II. Micellar Diffusivities for CTACl + NaCl, with [t-AmOH]=6% (wt.).

[CTACl]	D	D X 1.15*	D X 1.33†
0.005 M	$8.3 \times 10^{-7} \text{ cm}^2/\text{s}$	$21.1 \times 10^{-7} \text{ cm}^2/\text{s}$	$24.3 \times 10^{-7} \text{ cm}^2/\text{s}$
0.01	19.4	22.4	25.8
0.02	23	26.5	30.6
0.03	25.7	29.6	34.2
0.04	27.8	32	37
0.05	28.7	33	38.2
0.005	14.0	16.1	18.6
0.01	14.6	16.8	19.5
0.02	17.1	19.7	22.8
0.03	19.1	22	25.4
0.04	20.8	23.9	27.7
0.05	21.8	25.0	28.9
0.01	11.7	13.4	15.6
0.02	13.1	15.1	17.4
0.03	13.9	16.0	18.6
0.04	15.0	17.3	20
0.05	15.8	18.2	21
0.01	10.0	11.5	13.3
0.02	10.3	11.8	13.7
0.03	10.7	12.3	14.2
0.04	11.2	12.9	14.9
0.05	11.5	13.2	15.3

* alcohol assumed 50% in solvent, † alcohol assumed ~ 100% in solvent;
 values corrected in each case for viscosity of pure water at 25°C.

lar systems, such as SDS + NaCl^{26,27}, addition of salt tends to
 the micelles, which in this case are abnormally small to begin with
 alcohol incorporation. This behavior suggests that NaCl "protects"
 micelles from dissolution by the organic solvent, with increased elec-
 tric interactions between Cl⁻ and the quaternary ammonium (CTA⁺) head
 allowing the micelles to retain a radius close to that of CTACl
 micelles in water.

The solid curves in Figures 6-10 represent fits to the data using
 interaction theory.¹⁰⁻¹⁴ For a given [NaCl] and D₀, the slope of
 [CTACl] is determined by the micellar charge, Q. (Here, we assume
 negligible attractive interactions, consistent with earlier fitting results
 for normal CTACl micelles.¹¹) A more meaningful parameter, however, is
 micellar fractional ionization, α, which is related to Q by the mi-
 micellar aggregation number, N: Q = αN. In our previous analyses of the
 diffusivities of normal micelles, we found that the theoretical fits yield
 values for α which, fortunately, are relatively insensitive to the choice

The reason for this is that the interaction coefficient, K, in the
 equation $D = D_0(1 + K\phi)$, turns out to be approximately linear in N over
 a very large range of N. The micellar volume fraction ϕ is inversely
 proportional to N, according to $\phi = (4/3)\pi R_m^3([surfactant]/N)(6 \times 10^{20})$
 (assuming, of course, a monodisperse distribution of micelles). Hence, to
 first order there is no N dependence in K ϕ , and the diffusivity fits are
 relatively insensitive to the choice of N.

Table IV. Summary of D_o and R_h for the CTACl Ternary System.

[t-AmOH]	% in Solvent	[NaCl]	D_o	R_h
2 %	100	0.01 M	$11 \times 10^{-7} \text{ cm}^2/\text{s}$	22.3 Å
		0.02	9.9	24.7
		0.04	9.7	25.2
		0.1	9.2	26.6
4	100	0.01	13.0	18.8
		0.02	12.0	20.4
		0.04	11.3	21.7
		0.1	10.5	23.3
	50	0.01	11.6	21.1
		0.02	10.7	22.9
		0.04	10.1	24.2
		0.1	9.6	25.5
6	100	0.01	22.1	11.1
		0.02	17.0	14.4
		0.04	14.4	17.0
		0.1	12.6	19.4
	50	0.01	19.1	12.8
		0.02	14.7	16.7
		0.04	12.4	19.7
		0.1	10.9	22.5

Note: for [t-AmOH]=0, $D_o = 8.5 \times 10^{-7} \text{ cm}^2/\text{s}$ and $R_h = 29 \text{ Å}$.

However, when the micelles shrink due to significant incorporation of alcohol, our ability to estimate α accurately using this fitting procedure suffers from the ambiguity in N . No longer is the volume fraction of surfactant/alcohol "droplets" given by the expression on the previous page, with N simply equal to the number of surfactant monomers in the droplet. Similarly, Q and α can no longer be used interchangeably in the theory because of the uncertainty in N . Nevertheless, we can demonstrate approximately the influence of t-AmOH on α by reporting representative values of α obtained from the fits shown in Figures 7 and 8, for [t-AmOH]=4%. In obtaining these fits, we made the naive assumption that N simply scales with the micellar surface area, given by $4\pi R_h^2$ (using $N=100$ and $R_h=29 \text{ Å}$ for normal CTACl micelles¹¹). Needless to say, the assumed values for N will be increasingly too large the greater the extent of alcohol incorporation; the average area per surfactant head group will undoubtedly grow as the micelle soaks up alcohol and shrinks.

Hence, for [t-AmOH]=4%, assuming that nearly all the alcohol remains in the solvent (Figure 7), we adopted values for N equal to 43, 50, 57 and 65 for [NaCl] = 0.01, 0.02, 0.04 and 0.1M, respectively. The resulting values of α obtained from the fits shown in Figure 7 are 0.28, 0.32, 0.30 and 0.34, respectively. While each of these values exceeds the fraction found for normal CTACl micelles, 0.27, the argument that addition of t-AmOH causes α to increase is hardly convincing. However, it is useful to realize that the fitting procedure in reality determines the micellar charge, Q , which for the above four values of [NaCl] becomes 12, 16, 17 and 22, respectively. Hence, to obtain more realistic values of α from

fits we should divide these Q values by reduced values of N, reflecting incorporation of alcohol into the micelles. The result, of course, is an increase in each of the above values of α .

Interestingly, similar quantitative "under estimates" of α are obtained assuming that only half of the 4% added t-AmOH remains in the solution (Figure 8). Here, the starting N values are 54, 63, 71 and 78 for $[t-AmOH] = 0.01, 0.02, 0.04$ and $0.1M$, respectively. The resulting α values are 0.27, 0.32, 0.31 and 0.32, with Q values of 15, 20, 22 and 25, respectively. Again, however, the actual N values will be substantially lower than those assumed above, resulting in correspondingly higher values of α . Similar trends are observed for the other [t-AmOH].

Our tentative finding that α increases due to incorporation of t-AmOH into CTACl micelles in the presence of NaCl are supported by a number of electrochemical estimations of the increase of α by addition of moderately hydrophobic alcohols to solutions of CTABr and CTACl.³¹⁻³⁴ n-Butyl and 1-octanol have very similar effects upon α for $0.1M$ CTABr. We are aware of electrochemical determinations of the effect of t-AmOH upon α for CTACl, but 3.7 wt% n-butyl alcohol increases α by approximately 0.25, and 0.1 units for $[CTACl] = 0.01, 0.07$ and $0.2M$, respectively, in the absence of added salt, and t-AmOH should behave similarly. Clearly, a more accurate determination of the effects of alcohols on α using the dynamic light scattering technique and theoretical fitting procedure outlined here requires that we better establish the partitioning of the alcohol between the solvent and micellar phases as well as the micellar aggregation number.

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REFERENCES

- V.K. Bansal and D.O. Shah in "Microemulsions: Theory and Practice", L.M. Prince, Editor, p. 149, Academic Press, New York, 1974.
J.H. Schulman, W. Stoeckenius and L.M. Prince, J. Phys. Chem. 63, 1677 (1959).
R.A. Mackay, Adv. Colloid Interface Sci. 15, 131 (1981).
A.M. Bellocq, J. Baïas, P. Bothorel, B. Clin, G. Fourche, P. Lalanne, B. Lemaire, B. Lemanceau and D. Roux, Adv. Colloid Interface Sci. 20, 167 (1984).
F. de Buzzaccarini, "Structure and Reactivity in Microemulsions", PhD thesis, University of California at Santa Barbara, Dept. of Chemistry, 1981.
R. Zana, J. Lang and P. Lianos in "Surfactants in Solution", K.L. Mittal and B. Lindman, Editors, Vol. 3, p. 1627, Plenum, New York, 1984.
R. Zana, S. Yiv, C. Strazielle and P. Lianos, J. Colloid Interface Sci. 80, 208 (1981).
D. Hall, P. Jobling, J.E. Rassing and E. Wyn-Jones, J. Chem. Soc. Faraday Trans. II 73, 1582 (1977).
A.M. Bellocq, J. Baïas, B. Clin, P. Lalanne and B. Lemanceau, J. Colloid Interface Sci. 70, 524 (1979).
R.B. Dorshow, J. Briggs, C.A. Bunton and D.F. Nicoli, J. Phys. Chem. 86, 2388 (1982).
R.B. Dorshow, C.A. Bunton and D.F. Nicoli, J. Phys. Chem. 87, 1409 (1983).
D.F. Nicoli, R.B. Dorshow and C.A. Bunton, in "Surfactants in Solution",

- K.L. Mittal and B. Lindman, Editors, Vol. 1, p. 455, Plenum, New York, 1984.
13. R.B. Dorshow, "A Study of Micelles and Microemulsions by Laser Light Scattering", PhD thesis, University of California at Santa Barbara, Dept. of Physics, 1983.
 14. M. Corti and V. Degiorgio, *J. Phys. Chem.* 85, 711 (1981).
 15. B. Chu, "Laser Light Scattering", Academic Press, New York, 1974.
 16. B.J. Berne and R. Pecora, "Dynamic Light Scattering", Wiley, New York, 1976.
 17. T.L. Hill, "An Introduction to Statistical Thermodynamics", Addison-Wesley, Reading, MA, 1980.
 18. B.U. Felderhof, *J. Phys. A: Math. Gen.* 11, 929 (1978).
 19. G.K. Batchelor, *J. Fluid Mech.* 74, 1 (1976).
 20. E.J.W. Verwey and J.Th.G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier, New York, 1948.
 21. P.C. Hiemenz, "Principles of Colloid and Surface Chemistry", Marcel Dekker, New York, 1977.
 22. D.F. Nicoli, V. Athanassakis, J.R. Moffat, C.A. Bunton, R.B. Dorshow and G. Savelli, these Proceedings.
 23. V. Athanassakis, J.R. Moffat, C.A. Bunton, R.B. Dorshow, G. Savelli and D.F. Nicoli, *Chem. Phys. Lett.* 115, 467 (1985).
 24. C.A. Bunton, L.S. Romsted and C.J. Thamavit, *J. Am. Chem. Soc.* 102, 3900 (1980).
 25. V. Athanassakis, "A Study of Micelles and Microemulsions by Reaction Kinetics and Light Scattering", M.S. thesis, University of California at Santa Barbara, Dept. of Chemistry, 1984.
 26. N.A. Mazer, M.C. Carey and G.B. Benedek, in "Micellization, Solubilization and Microemulsions", K.L. Mittal, Editor, Vol. 1, p. 359, Plenum, New York, 1977.
 27. P.J. Missel, N.A. Mazer, G.B. Benedek and C.Y. Young, *J. Phys. Chem.* 84, 1044 (1980).
 28. H. Hoffmann, G. Platz, H. Rehage and W. Schorr, *Ber. Bunsenges. Phys. Chem.* 85, 877 (1981); also, private communication.
 29. J. Geltins, D. Hall, P.L. Jobling, J.E. Rassing and E. Wyn-Jones, *J. Chem. Soc. Faraday Trans. II* 74, 1957 (1978).
 30. V. Athanassakis, C.A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.* 86, 5002 (1982).
 31. J.W. Larsen and L.B. Tepley, *J. Colloid Interface Sci.* 49, 113 (1974).
 32. R. Zana, *J. Colloid Interface Sci.* 78, 330 (1980).
 33. P. Lianos and R. Zana, *J. Colloid Interface Sci.* 84, 100 (1981).
 34. C.A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.* 86, 5010 (1982).

ANIONIC SURFACTANTS WITH DIVALENT GEGENIONS OF DIFFUSE OR SEPARATE ELECTRIC
CHARGE: SOLUBILITY AND MICELLE FORMATION

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In order to clarify the relationships among solubility, micelle formation, and Krafft point, anionic surfactants with three types of divalent gegenions were prepared and their micelle formation and solubility examined. The first gegenion type was characterized by localized charge (divalent metal ion), the second by diffuse charge (1,1'-dimethyl-[4,4'] bipyridinium ion or methylviologen ion), and the last by separate charge (1,1'-alkanediyl-bis-pyridinium ion). The effects of the unlocalized gegenions were compared with those of the localized gegenions, and the following conclusions could be drawn from the experimental results: (i) the crystalline state with gegenion of diffuse or separate charge is less stable energetically and has higher solubility, and (ii) the difference in cmc value among the three types of surfactants is relatively small when the charge separation is small, but a large charge separation gives rise to marked decrease in cmc value suggesting that the alkylchain of separate gegenion folds and penetrates the inner hydrophobic part of the micelle. Also we observed that surfactants with more water of crystallization are easier to dissolve with a smaller enthalpy change of dissolution. Krafft point is also discussed together with solubility and cmc, and the micelle temperature range (MTR) or Krafft range is proposed instead of the Krafft point.

INTRODUCTION

As is well known, surfactant molecules aggregate above a certain concentration leading to an abrupt change in solution properties.^{1,2} The properties of aggregates or micelles of ionic surfactants are strongly influenced by the kind of surfactant ion and gegenion. Gegenions of conventional anionic surfactants so far investigated have been alkali or alkaline earth metal ion, their electrical charge being localized within a very small volume. The electrical potential of such ions seems to be

energetically stabilized by Coulombic interaction. This leads to smaller aqueous solubility of the surfactants, resulting in higher Krafft point.^{3,4} On the other hand, anionic surfactants with nonmetallic cationic gegenions of unlocalized, diffuse or separate charge are expected to have physico-chemical properties much different from those of conventional surfactants.⁶

The present study concerns itself with the crystalline state, solubility, and micelle formation of surfactants with three types of divalent gegenions: the first with localized charge (divalent metal ions), the second with diffuse charge (1,1'-dimethyl-[4,4']bipyridinium ion or methylviologen ion) and the last with separate charge (1,1'-alkanediyl-bispyridinium ion). The effects of the charge unlocalized gegenions are compared with those of localized charge. The Krafft point or Krafft range is also discussed together with solubility and cmc because they are all closely related.

RELATIONSHIP AMONG SOLUBILITY, CMC, AND KRAFFT POINT

The solubility, cmc, and Krafft point of an ionic surfactant are often discussed independently, in spite of the fact that they are closely related. Therefore, consideration of experimental results from the

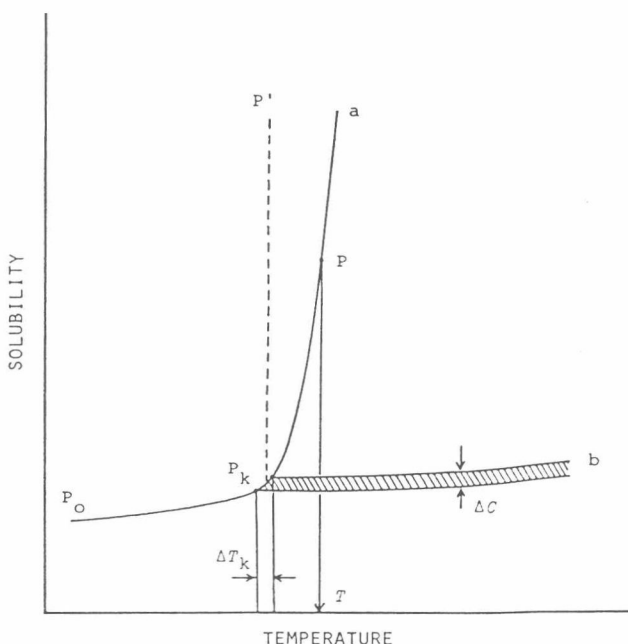


Figure 1. Changes in solubility and cmc with temperature; (a) solubility curve; (b) cmc curve; ΔC narrow concentration range of cmc; ΔT_K Krafft temperature range.

viewpoint of only one of the above three could lead to a wrong conclusion. The relation between the solubility and cmc of an ionic surfactant with change in temperature is shown schematically in Figure 1. The Krafft point is defined as the temperature at which the solubility curve intersects the cmc curve. The important point of the figure is that there exist innumerable temperatures above the Krafft point, temperature T for example, at constant pressure on the solubility curve for which two phases (surfactant solid phase and micellar solution phase) are in equilibrium. This fact rules out the phase separation model of micelles.² According to the phase rule, a system composed of two components (water and surfactant) and three phases (solid surfactant, surfactant solution and a micellar phase) has one degree of freedom. If the pressure is fixed, the temperature becomes invariant. In the case where the micellar aggregation number is infinite the phase separation would take place and the solubility would approach the path $P_O \rightarrow P_K \rightarrow P'$ with increasing temperature contrary to the observed behavior in Figure 1. The cmc has been defined as the surfactant concentration corresponding to the maximum change in gradient in an ideal property-concentration relationship⁷. This definition has been accepted and adopted in most cases. According to it, the cmc depends upon the property of the solution examined and, therefore, should be defined as the narrow concentration range,¹ which incorporates the various maxima. Thus, it becomes impossible to define the Krafft point as a single point at the intersection between solubility and cmc changes with temperature. In this sense, it seems correct that the Krafft point is not a single point but a diffuse region which might be called the Krafft range. It is concluded from the above discussion that micelles must be regarded as a chemical species and that the mass action model must be used for micellization.²

We now make a few remarks about how to shift Krafft point to lower temperatures, because it really is of practical importance for ionic surfactants. It is essentially correct to define the Krafft point or Krafft range as the temperature at which the solubility vs temperature curve intersects the cmc vs temperature curve. This definition can be

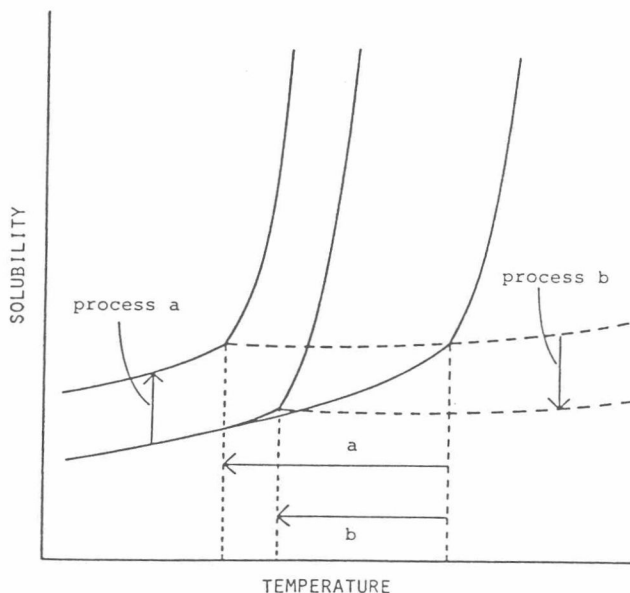


Figure 2. Schematic diagram to decrease the Krafft point: process a increase of monomer solubility; process b decrease of cmc value.

stated in another way: the Krafft range is the temperature at which the solubility of surfactants in monomer state becomes high enough for the monomers to start aggregating or micellizing notably. It can be easily understood from the above definition that there are two ways to decrease the Krafft range one is to increase the monomer solubility (process a in Figure 2) and the other is to decrease the cmc value of surfactants (process b in the figure).² Process a based on solubility increase is closely related to the crystalline state of the surfactant. The less energetically stable the solid surfactant is, the higher its solubility becomes. A decrease in stability could be brought about by dispersion of the electrical charge of the gegenion, a volume increase of the gegenion, an increase of water of crystallization, the introduction of a branched chain into the hydrophobic surfactant chain, and so on. On the other hand, process b due to cmc decrease can be expected from a decrease in dissociation of the gegenion from micelle, an increase in hydrophobicity of the gegenion and surfactant ion, and so on. Taking into account the above considerations, we started the present project mainly to study the effects of the diffusion and separation of electrical charge and the hydrophobicity of the gegenion on the relation among solubility, cmc, and Krafft point of anionic surfactants.

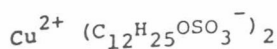
EXPERIMENTAL

Materials. Copper(II) dodecyl sulfate ($\text{Cu}(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2$ or $\text{Cu}(\text{DS})_2$) and sulfonate ($\text{Cu}(\text{C}_{12}\text{H}_{25}\text{SO}_3)_2$ or $\text{Cu}(\text{DSO})_2$) were prepared from respective sodium salts and purified by the standard procedure.⁵ 1,1'-dimethyl-[4,4']-bipyridinium(II)(methylviologen) dodecyl sulfate ($\text{MV}(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2$ or $\text{MV}(\text{DS})_2$) and sulfonate ($\text{MV}(\text{C}_{12}\text{H}_{25}\text{SO}_3)_2$ or $\text{MV}(\text{DSO})_2$) were synthesized as follows. Sodium dodecyl sulfate and sulfonate were converted to corresponding silver salts by double decomposition with AgNO_3 in aqueous suspension. Silver ions were then exchanged with methylviologen ions by introducing excess methylviologen dichloride, and the precipitated AgCl was removed by centrifugation. $\text{MV}(\text{DS})_2$ and $\text{MV}(\text{DSO})_2$ thus prepared were purified by recrystallization twice from the aqueous solution with excess MV^{2+} and twice from water. 1,1'-ethanediyl-bis-pyridinium(II) dodecyl sulfate ($\text{C}_2\text{BP}(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2$ or $\text{C}_2\text{BP}(\text{DS})_2$) and sulfonate ($\text{C}_2\text{BP}(\text{C}_{12}\text{H}_{25}\text{SO}_3)_2$ or $\text{C}_2\text{BP}(\text{DSO})_2$) were synthesized by the same method for the corresponding viologen compounds. 1,1'-hexanediyl-bis-pyridinium(II) dodecyl sulfate ($\text{C}_6\text{BP}(\text{C}_{12}\text{H}_{25}\text{SO}_3)_2$ or $\text{C}_6\text{BP}(\text{DSO})_2$) and 1,1'-decanediyl-bis-pyridinium(II) dodecyl sulfonate ($\text{C}_{10}\text{BP}(\text{C}_{12}\text{H}_{25}\text{SO}_3)_2$ or $\text{C}_{10}\text{BP}(\text{DSO})_2$) whose Krafft points are less than 0°C , are not obtainable directly from the corresponding aqueous solutions by cooling. They were obtained by evaporation of water from their aqueous solutions under vacuum and purified by three recrystallizations from acetone. 1,1'-alkanediyl-bis-pyridinium bromides used for the present synthesis were gifts from Prof. Kuwamura of Gunma University. Purities of these surfactants were checked by elemental analyses; observed and theoretical values were in satisfactory agreement. From the elemental analysis three of them were found to have water of crystallization as: $\text{Cu}(\text{DS})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{DSO})_2 \cdot 2\text{H}_2\text{O}$, and $\text{MV}(\text{DSO})_2 \cdot 2\text{H}_2\text{O}$. $\text{MV}(\text{DS})_2$ has no water of crystallization at 35°C . 1,1'-alkanediyl-bis-pyridinium compounds were very hygroscopic, but the absorbed water could be removed easily at room temperature under reduced pressure. The structural formulae of the surfactants used are shown in Figure 3.

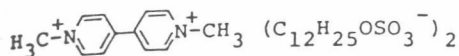
Solubility measurement. A suspension of recrystallized surfactant solids obtained by cooling the aqueous solutions below the Krafft point was used *in situ* for the solubility measurement except $\text{C}_6\text{BP}(\text{DSO})_2$ and $\text{C}_{10}\text{BP}(\text{DSO})_2$. The apparatus and the method employed were the same as those described in the previous papers.^{8,9,10} Mechanical agitation was maintained for more than one hour to permit the system to reach a complete equilibrium.

Dodecylsulfates

(Abbreviation)



$\text{Cu}(\text{DS})_2$



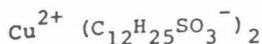
$\text{MV}(\text{DS})_2$



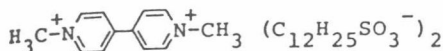
$\text{C}_2\text{BP}(\text{DS})_2$

Dodecylsulfonates

(Abbreviation)



$\text{Cu}(\text{DSO})_2$



$\text{MV}(\text{DSO})_2$



$\text{C}_2\text{BP}(\text{DSO})_2$



$\text{C}_6\text{BP}(\text{DSO})_2$



$\text{C}_{10}\text{BP}(\text{DSO})_2$

Figure 3. Structural formulae and abbreviations of synthesized surfactants.

The temperature was controlled within $\pm 0.02^\circ\text{C}$. Methylviologen ion and 1,1'-ethanediyl-bis-pyridinium ion have maximum absorption bands at 255 and 59nm, respectively. The bands were used for the determination of surfactant concentration, where the concentrations for absorption measurements were brought below the cmc. Solubilities of cupric surfactants were measured by the conductometric method.

Cmc determination. The critical micelle concentration (cmc) was determined by the usual conductivity method as the concentration at an intersection of two lines obtained by plotting the specific conductance against concentration.

RESULTS AND DISCUSSION

Plots of specific conductance against concentration at 25°C are shown in Figure 4 for the four surfactants whose Krafft points are less than 25°C . It should be noted that the cmc of $\text{MV}(\text{DS})_2$ is less than half the cmc's of others. From the slope of the conductance plot above cmc, it is seen that the degree of MV^{2+} dissociation is less from $\text{MV}(\text{DS})_2$ than from $\text{MV}(\text{DSO})_2$ micelle, which might lead to smaller cmc value of $\text{MV}(\text{DS})_2$. In addition, two gegenions, diffuse (MV^{2+}) and separate (C_2BP^{2+}), act similarly as regards micellization of dodecylsulfonate in view of their close cmc values, although they are slightly lower than the cmc of $\text{Cu}(\text{DSO})_2$ with gegenion of localized charge, Cu^{2+} . This suggests that the charge

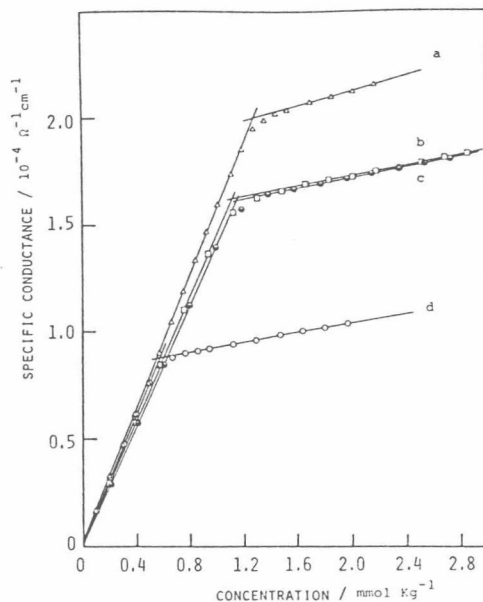


Figure 4. Specific conductance vs concentration at 25°C: (a) $\text{MV}(\text{DSO})_2 \cdot 2\text{H}_2\text{O}$; (b) $\text{C}_2\text{BP}(\text{DSO})_2$; (c) $\text{Cu}(\text{DS})_2 \cdot 4\text{H}_2\text{O}$; (d) $\text{MV}(\text{DS})_2$.

effects on micellization of localized, diffuse, and separate gegenions are similar when the diffusion and separation of gegenion charge are relatively small. This will be discussed more extensively later.

The solubility and cmc changes with temperature of dodecylsulfates are plotted in Figure 5. From the figure we see that

$\text{C}_2\text{BP}(\text{DS})_2 < \text{MV}(\text{DS})_2 < \text{Cu}(\text{DS})_2 \cdot 4\text{H}_2\text{O}$ for solubility
and $\text{MV}(\text{DS})_2 \leq \text{Cu}(\text{DS})_2 \cdot 4\text{H}_2\text{O} < \text{C}_2\text{BP}(\text{DS})_2$ for the Krafft point,

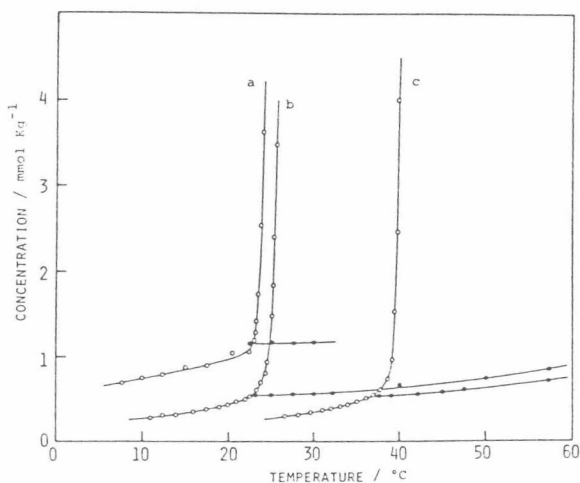


Figure 5. Solubility(o) and cmc(●) changes with temperature for dodecylsulfates: (a) $\text{Cu}(\text{DS})_2 \cdot 4\text{H}_2\text{O}$; (b) $\text{MV}(\text{DS})_2$; (c) $\text{C}_2\text{BP}(\text{DS})_2$.

the cmc's also show the same order as the solubilities. The cmc changes less temperature-dependent as compared with monovalent metal ion salts. The differences between the cmc's of $C_2BP(DS)_2$ and $MV(DS)_2$ is 11, and their cmc's are less than half the cmc of $Cu(DS)_2$. The former is also true, but the latter is not, for dodecylsulfonate micelles. The hydrophobicity of C_2BP^{2+} and MV^{2+} might be reflected more effectively in dodecylsulfate micelles than in dodecylsulfonate micelles. As for the solubility measurement the system is divariant from the phase rule,² and temperature can absolutely specify the system at atmospheric pressure only below the Krafft point but also above it. The Krafft points determined from the temperature at which the two temperature-dependent curves intersect are given in Table I. As is clear from Figure 5, the Krafft point of $Cu(DS)_2 \cdot 4H_2O$ is due to its relatively high solubility in terms of its high cmc value. The high solubility comes evidently from the molecules of water of crystallization. On the other hand, the Krafft point of $C_2BP(DS)_2$ is relatively high, a high temperature being required for its solubility to reach the cmc value.

The solubility changes of the dodecyl sulfonates with temperature are shown in Figure 6 together with their cmc changes. The following order is observed:

$Cu(DSO)_2 \cdot 2H_2O < C_2BP(DSO)_2 < MV(DSO)_2 \cdot 2H_2O$ for solubility
 $MV(DSO)_2 \cdot 2H_2O < C_2BP(DSO)_2 < Cu(DSO)_2 \cdot 2H_2O$ for the Krafft point.

The striking difference in solubility between sulfonates and sulfates is that the Cu^{2+} sulfonate is the least soluble among the three, whereas the other two sulfonates are much more soluble than corresponding sulfates. Especially for $MV(DSO)_2 \cdot 2H_2O$ two moles of water of crystallization could be removed under vacuum over P_2O_5 , which indicates not only a strong interaction of $MV(DSO)_2$ with water but also that the two moles of water are in a crystalline state. As for the cmc it is notable that the differences are rather small for three sulfonates compared with those of the corresponding sulfates. This suggests a similar charge effect on micellization for the three kinds of gegenions: localized, diffuse, and separate gegenions. In other words, these gegenions are free to move about the cellular charged surface just carrying the same divalent charge, and their

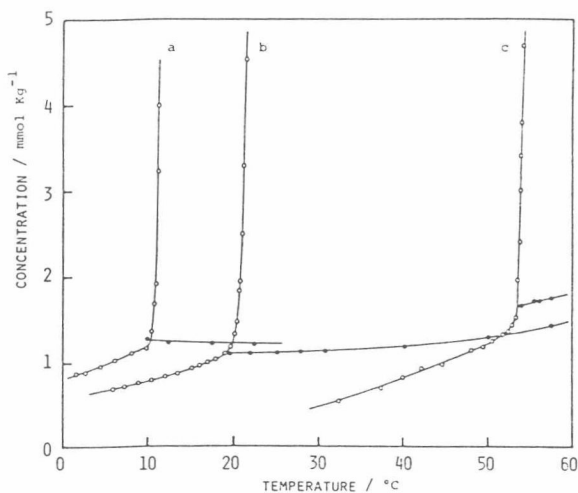


Figure 6. Solubility(o) and cmc(●) changes with temperature for dodecylsulfonates: (a) $MV(DSO)_2 \cdot 2H_2O$; (b) $C_2BP(DSO)_2$; (c) $Cu(DSO)_2 \cdot 2H_2O$.

differences cannot influence micellization. This is consistent with the higher dissociation of MV^{2+} from alkylsulfonate micelles and a higher cmc value. However, the extent of separation of divalent charge must have an effect of micellization and solubility. In Figure 7 are shown the cmc's and solubilities of 1,1'-alkanediyl-bis-pyridinium with different charge separation, $C_2BP(DSO)_2$, $C_6BP(DSO)_2$, and $C_{10}BP(DSO)_2$. Two remarkable findings are (i) Krafft points of the latter two are below $0^\circ C$, and (ii) there is almost no difference between the cmc's of the former two. From these facts the following inferences can be drawn: (i) the charge separation up to six CH_2 groups does not make any difference in cmc, (ii) an extreme decrease in cmc due to gegenion changing from C_6BP^{2+} to $C_{10}BP^{2+}$ is brought about by increasing hydrophobicity of the latter ion, (iii) decrease in Krafft point for $C_6BP(DSO)_2$ and $C_{10}BP(DSO)_2$ is due to their increased solubility which results from enhanced instability of crystalline state caused by an introduction of bulky gegenions. In particular, the fact that the cmc's of $C_2BP(DSO)_2$ and $C_6BP(DSO)_2$ are almost the same irrespective of the differences in gegenions by four CH_2 groups is quite contrary to our expectation. This fact also indicates the free motion of the gegenions about micellar surface. In addition, it can easily be imagined from inference (ii) that the alkylchain of the $C_{10}BP^{2+}$ ion can fold and penetrate the hydrocarbon core of the micelle, leading to its smaller cmc value. These inferences are based upon rather meager experimental evidence. Therefore, more systematic measurements of the cmc and solubility as the alkylchains of both gegen and surfactant ions are changed in a stepwise manner are required before definite conclusion can be reached.¹²

Finally, we may make a few remarks about what can be derived from solubility changes with temperature. In order to calculate the enthalpy change of dissolution, values of $\ln(\text{solubility})$ are plotted against reciprocal of the absolute temperature (Figure 8). From the slope of the plots below the Krafft point the enthalpy change (Δh^0) of dissolution can be evaluated from the following equation¹³:

$$\Delta h^0 = -3R[d \ln S / d(1/T)]_p$$

where R is the gas constant, S is the solubility, T is the absolute

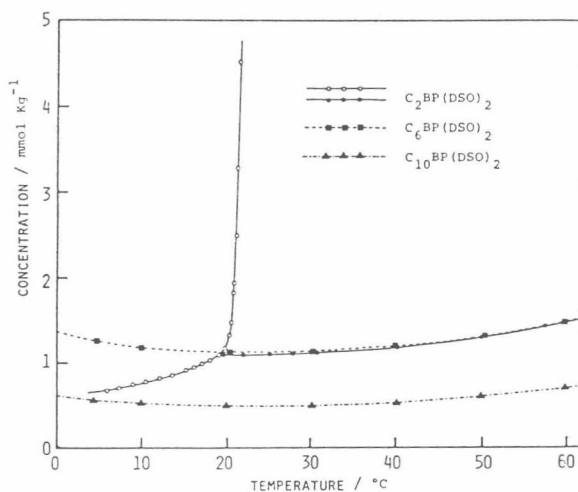


Figure 7. Solubility(o) and cmc(●,■,▲) changes with temperature for $C_nBP(DSO)_2$.