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The Micellar Properties of Disodium Monoalkyl Phosphates in Aqueous Solutions

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The disodium monoalkyl phosphate with *n*-dodecyl, *n*-tetradecyl and *n*-hexadecyl radical was synthesized, and pNa and light scattering studies were performed on the micellar properties of these surfactants in aqueous solutions. The critical micelle concentrations (CMC) of these salt solutions were confirmed to be considerably higher than those of ordinary 1–1 type ionic surfactants with the same alkyl chain length. The degree of dissociation of the micelle was, however, found to be not so different from that of corresponding sodium alkyl sulfate. The fact that these salts have comparatively large aggregation number reflects one of the characteristic features of alkyl phosphate anion which has two dissociable groups.

The detailed surface chemical studies of various ionic surfactant solutions have led to the realization that the micellar properties, such as critical micelle concentration, aggregation number and the degree of dissociation of the micelle, depend on the structure of constituent detergent molecule, *e. g.*, on the valency of counter ion and on the number of ionic groups at the end of the hydrocarbon chain.

The studies with the ionic surfactants which have two dissociable groups were performed by Shinoda,[1] who determined the CMC's of potassium alkyl malonates, $RCH(COOK)_2$, and confirmed that they are much higher than those of corresponding fatty acid soaps.

The elevation of the CMC is also anticipated to be the case with the monoalkyl phosphate detergents. However, in spite of their wide industrial applications, the available informations on the basic surface chemical properties of purified alkyl phosphate detergents are extremely scanty, since the purification procedures of the reaction mixture are rather complicated. So far as we know, the only available data were presented by Cooper,[2] who synthesized the mono- and disodium alkyl phosphates with various chain length and determined the CMC's of their aqueous solutions on the basis of surface tension measurements.

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[1] K. Shinoda, *J. Phys. Chem.*, **59**, 432 (1955).

[2] R. S. Cooper, *J. Am. Oil Chemists' Soc.*, **40**, 642 (1963).

It is, thus, desirable to investigate the micellar properties of alkyl phosphate detergents in order to make clear their characteristics which will in turn contribute to the general understanding of common features of ionic surfactants.

The present work concerns the preparation and the determination of CMC and other related micellar properties of disodium monoalkyl phosphates with alkyl chain length from n-C_{12} to n-C_{16}.

Experimental

Materials. The monoalkyl phosphoric acids {RH_2PO_4; here, R=dodecyl, tetradecyl and hexadecyl radical} were synthesized from the purified alkyl alcohols and pyrophosphoric acid by violent stirring in absolute benzene for 100 hr at 25°C.[3]

$$\begin{aligned} \text{R-OH} + H_4P_2O_7 &\rightarrow RH_2PO_4 + H_3PO_4 \\ &\rightarrow RH_3P_2O_7 + H_2O, \\ \text{R-OH} + RH_3P_2O_7 &\rightarrow R_2HPO_4 + H_3PO_4 \\ &\rightarrow R_2H_2P_2O_7 + H_2O, \textit{ etc.} \end{aligned}$$

The reaction mixture was dissolved in ether and washed twice with water to remove residual inorganic acids. The crude monoalkyl phosphoric acid in oil phase was then treated with an aqueous solution of sodium hydroxide (pH=12) to extract the water soluble disodium monoalkyl phosphate into aqueous phase. By the addition of hydrochloric acid to the aqueous phase obtained above until the pH of the solution was lowered to about 0.5, alkyl phosphoric acids were precipitated. Then the monoalkyl phosphoric acid was selectively extracted into ether at pH 0.5, since the solubility of alkyl phosphoric acids in ether is known to be in the decreasing order of mono-, di- and trialkyl substitute.[4] The purity of the monoalkyl phosphoric acid was improved by repeating above processes until a thin layer chromatographical test gave 1 spot of monoalkyl phosphoric acid.

The test plate used in the thin layer chromatography was made of silica gel mixed with 0.5N oxalic acid solution in the ratio of 7 to 10. For the purpose of activation, the plate was first heated for 1 hr at 80°C. The subsequent development was carried out by using the mixed solvent which contains five parts of benzene and one part of methanol. We used 5% ethanol solution of molybdatophosphoric acid for the detection. The value of R_f was found to be in the order of mono->di-> trialkyl substitute.

The evaporation of the ether solution *in vacuo* yielded white waxy solid of monoalkyl phosphoric acid. It was then recrystallized several times from hot n-hexane until the white crystalline monoalkyl ester could be obtained. The purity of the product was confirmed by elementary analysis, mp measurement and pH titration with sodium hydroxide.

The disodium monoalkyl phosphate was easily obtained by the neutralization to pH 12 with NaOH solution and the subsequent dehydration process by the successive extraction with acetone. In order to remove surface active impurities, the sodium salts were extracted with ether for 50 hr, and then dried *in vacuo* over phosphorus pentoxide. The final products are white crystalline compounds which have hygroscopicity. It was, however, confirmed by means of thermogravimetric and elementary analysis that these salts have no water of crystallization.

Apparatus and Method. The method used in the present experiment for measuring the counter ion activity in the solution was exactly the same as the technique previously used to study the solutions of sodium alkyl sulfates.[5] That is, we used a Horiba pNa meter model N-5 with the sodium sensitive glass electrode, making a cell as follows:

Na glass electrode | Detergent solution | N NH_4NO_3 |
3.33N KCl agar bridge | Calomel electrode

We used the mean activity of sodium chloride presented by Janz and Gordon[6] for calibrating the apparatus. The experimental reproducibility of the sodium ion activity was found to be within ±0.005 pNa unit. The measurements were conducted at 35 and 45°C for C_{12} and C_{14} salts, and at 45°C for C_{16} salt, in order to prevent the formation of the precipitation of ammonium alkyl phosphate at the liquid junction.

The conductivity measurements were performed by using Yanagimoto conductivity outfit model MY-7 at the same temperature as above.

A Shimadzu photoelectric light scattering photometer model PG-21 was used for estimating the micellar molecular weights of the detergents in solution. The measurements were carried out at 436 mμ with a semi-octagonal cell. The concentration dependence of the refractive indices was estimated by a Shimadzu differential refractometer at the same wavelength. The temperature of the cell was controlled at about 48°C.

Results and Discussion

Figure 1 shows the typical plots of the logarithm of sodium ion activity *vs.* the logarithm of the molar concentration of disodium dodecyl phosphate at 35 and 45°C, and of hexadecyl phosphate at 45°C, respectively. As is clearly shown in this figure, a sharp break occurs at the CMC of each detergent. The values of CMC determined from the break points in Fig. 1 are given in Table 1, together with those obtained from the specific conductivity (κ) *vs.* concentration plots. The differences between them are found to be within an experimental error. The observed values of CMC for disodium monoalkyl phosphates are considerably higher than those of 1–1 type ionic surfactants with the same alkyl

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[3] K. Nelson and A. D. F. Toy, *Inorg. Chem.*, **2**, 775 (1963).

[4] N. L. Gershfeld, *J. Phys. Chem.*, **66**, 1923 (1962).

[5] I. Satake, T. Tahara and R. Matuura, This Bulletin, **42**, 319 (1969).

[6] G. J. Janz and A. R. Gordon, *J. Am. Chem. Soc.*, **65**, 218 (1943).

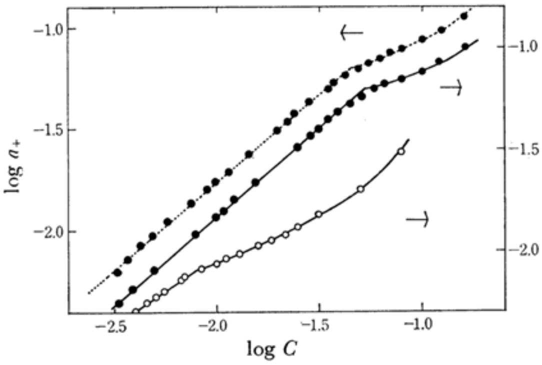

Fig. 1. The plots of log a_+ *vs.* log C for C_{12} and C_{16} salts.
●: C_{12} salt, ○: C_{16} salt, —: at 45°C, ⋯: at 35°C

TABLE 1. THE pNa DATA OBTAINED FOR DISODIUM MONOALKYL PHOSPHATES

Deter-gent	Temp. (°C)	CMC (mol/*l*)		α	γ_+
		pNa	κ		
C_{12}	35	4.46×10^{-2}	4.43×10^{-2}	0.33	0.68
	45	5.12×10^{-2}	4.92×10^{-2}	0.35	0.52
C_{14}	35	1.65×10^{-2}	1.59×10^{-2}	0.29	0.62
	45	1.84×10^{-2}	1.84×10^{-2}	0.30	0.53
C_{16}	45	7.59×10^{-3}	7.00×10^{-3}	0.28	0.54

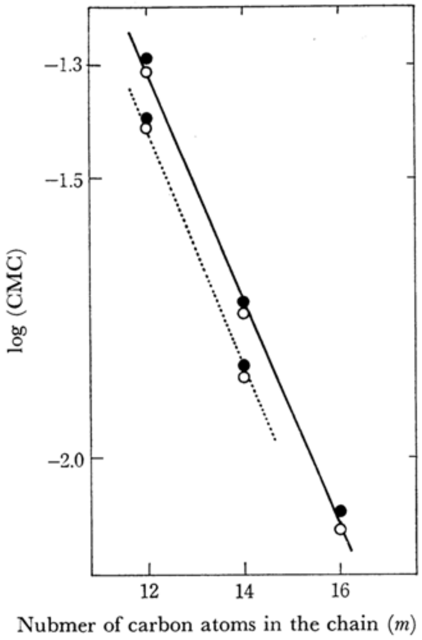

Fig. 2. The relation between log CMC and m.
●: determined from pNa data, ○: determined from conductivity data, ⋯: at 35°C, —: at 45°C.

chain length, suggesting the significant contribution of increased electrical repulsion between bivalent head groups to the micelle formation. The value of CMC obtained for C_{16} salt is in good agreement with that reported by Cooper.[2] A comparison of the values for C_{12} and C_{14} salts is, however, rather difficult since no exact values for these salts are given in his paper. As would be expected, the CMC's of disodium monoalkyl phosphates are nearly identical with those of potassium alkyl malonates.[1]

As is the case with ordinary 1–1 type ionic surfactants, there is a linear relationship between log CMC and the number of carbon atoms (m) in the alkyl chain. Figure 2 shows the relation between log CMC and m in the disodium monoalkyl phosphates. The slope of the straight line is determined as −0.21 at 45°C, which is considerably large compared with the value of −0.29—−0.30 observed for various types of 1–1 type surfactants.[7]

According to the theory of micelle formation of ionic surfactants,[7] the slope of the log CMC *vs.* m plot may be given as

$$d\log \mathrm{CMC}/dm = -\omega/2.303\boldsymbol{k}T(1+iK). \qquad (1)$$

Here, i is the number of ionic groups in the alkyl chain, ω the cohesive energy change transferring one methylene group from a hydrocarbon environment to an aqueous medium and K the experimental canstant for the particular surface active agent which has a meaning similar to the degree of dissociation of the micelle (α). It is thus anticipated from Eq. (1), that the values of K (or α) for the present detergents are not so different from those of 1–1 type surfactants, *e. g.*, of sodium alkyl sulfates.

The degree of dissociation of the micelle may be evaluated from the concentration dependence of the counter ion activity by using the convenient method derived by Botré *et al.*[8] and applied for various systems by subsequent authors.[9]

If we assume that the concentration of singly dispersed detergent anion is constant (C_0) over the concentration range above CMC, the sodium ion activity can be written as

$$a_+ = 2\gamma_{\mathrm{app}}C = 2\gamma_+\{C_0+\alpha(C-C_0)\} \qquad (2)$$

or

$$\gamma_{\mathrm{app}} = \alpha\gamma_+ + \gamma_+(1-\alpha)C_0/C, \qquad (3)$$

where, C is the total analytical concentration of the detergent in mol/*l*, γ_{app} the apparent ionic

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[7] K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants," Chap. 1, Academic Press, New York, N.Y. (1963).

[8] C. Botré, V. L. Crescenzi and A. Mele, *J. Phys. Chem.*, **63**, 650 (1959).

[9] L. Shedlovsky, C. W. Jakob and M. B. Epstein, *ibid.*, **67**, 2075 (1963); M. E. Feinstein and H. L. Rosano, *J. Colloid and Interface Sci.*, **24**, 73 (1967); P. Stenius and P. Ekwall, *Acta Chem. Scand.*, **21**, 1643 (1967).

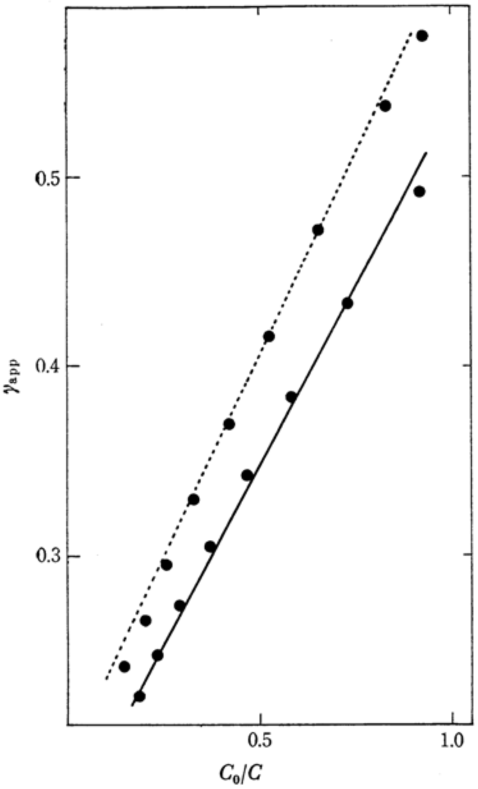

Fig. 3. The plots of γ_{app} *vs.* C_0/C for C_{14} salt at 35 (------) and 45°C (——).

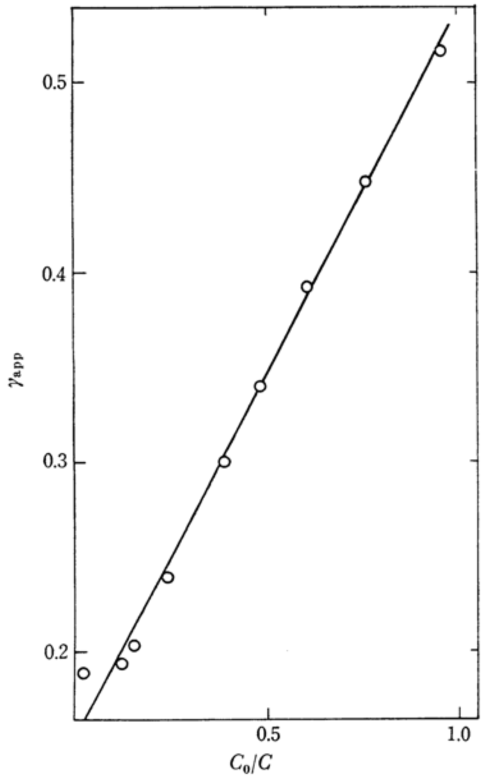

Fig. 4. The plot of γ_{app} *vs.* C_0/C for C_{16} salt at 45°C.

activity coefficient of sodium ion defined by $a_+/2C$, γ_+ the ionic activity coefficient of the sodium ion and α the degree of the dissociation of the micelle. A theoretical consideration on Eq. (3) based on lamellar micelle model was given in our previous work.[5] Equation (3) suggests that γ_{app} will vary linearly with C_0/C throughout the concentration range in which both γ_+ and α are assumed to be constant. This is the case for present experimental results. As is shown in Figs. 3 and 4, γ_{app} *vs.* C_0/C plots give straight lines over whole concentration range studied. The values of α and γ_+ estimated from the intercept and slope of γ_{app} *vs.* C_0/C plots are summarized in Table 1. In the previous pNa study with the sodium alkyl sulfates,[5] the degree of dissociation of the micelle was determined to be 0.28 for sodium dodecyl sulfate and 0.24 for sodium tetradecyl sulfate, both at 35°C. Although the values of α obtained for disodium monoalkyl phosphates are slightly larger than those of sodium alkyl sulfates it, seems reasonable to consider that the degree of dissociation of the micelle is almost unaffected by the number of ionizable groups so far as the other structural constitutions are the same.

In a crude picture of micellar solution, the activity coefficient of sodium ion may be expected to be characterized by the ionic strength of the solution. It is, therefore interesting to note that the constant

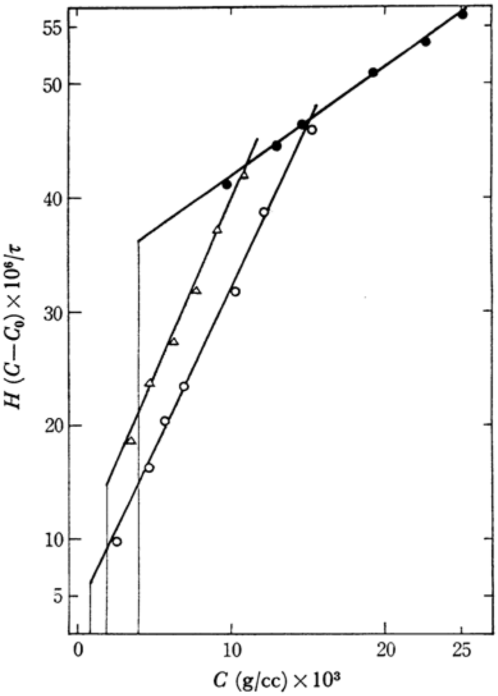

Fig. 5. $H(C-C_0)/\tau$ *vs.* C curves for disodium monoalkyl phosphates in NaCl solution at 48°C.
●: C_{12} salt, △: C_{14} salt, ○: C_{16} salt

value of γ_+ obtained for C_{14} salt at 35°C is considerably small as compared with the value of 0.83 for sodium dodecyl sulfate having the similar CMC at the same temperature. Since no difference is found between the values of α, this depression must be ascribed to the existence of more highly charged polyions in disodium tetradecyl phosphate solution than in sodium dodecyl sulfate solution. This means that the micellar aggregation number of the tetradecyl phosphate micelle is much larger than that of sodium dodecyl sulfate.

In Fig. 5 are given the scattering data for disodium monoalkyl phosphates in sodium chloride solution. The values of CMC in salt solutions were determined from turbidity curves. The micellar molecular weights estimated from the intercept at CMC are summarized in Table 2.

TABLE 2. THE MICELLAR MOLECULAR WEIGHTS OF DISODIUM MONOALKYL PHOSPHATES DETERMINED FROM LIGHT SCATTERING EXPERIMENT

Detergent	Solvent	CMC (mol/l)	MMW	AN
C_{12}	0.5N NaCl	1.25×10^{-2}	27800	90
C_{14}	0.2N NaCl	4.2×10^{-3}	70400	207
C_{16}	0.08N NaCl	1.73×10^{-3}	156200	426

MMW: Micellar molecular weight
AN: Aggregation number

In accordance with the consideration on the sodium ion activity coefficients above CMC, the aggregation number of 207 obtained for C_{14} salt is about twice as large as that of 101 for sodium dodecyl sulfate,[10] both in 0.2N NaCl solution. This result indicates an interesting feature of disodium monoalkyl phosphates that their micellar aggregation number is considerably large compared with that of 1-1 type surfactant which has the comparable order of CMC. It is, however, rather difficult to compare the obtained aggregation number for the present detergents with that of 1-1 type surfactants which have the same chain length, since they are found to increase with increasing concentration of added salt.[10,11]

In view of the acidic character of the phosphate radical, these detergents may be considered to be hydrolyzed in water, giving rise to the minimum in surface tension *vs.* concentration curve. It was, in fact, observed in the present experiment that the surface tension *vs.* concentration curves for these salt solutions showed a pronounced minimum. However, the fact that the minimum could be reduced with the addition of sodium chloride, explains well the hydrolyzing nature of these salts in solutions. From the pH measurements on these salt solutions, the degree of hydrolysis was estimated to be 0.12% in 0.1 mol/l, 0.14% in 5×10^{-2} mol/l and 0.55% in 1.1×10^{-2} mol/l for C_{12} salt, and 0.37% in 0.1 mol/l and 0.60% in 1.5×10^{-2} mol/l for C_{16} salt, both at 45°C, respectively. Since the values of the degree of hydrolysis of the alkyl phosphate anion are negligibly small, the effect of hydrolysis products on the bulk properties is not taken into account in this paper.

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[10] K. J. Mysels and L. H. Princen, *J. Phys. Chem.*, **63**, 1696 (1959).

[11] D. Stigter and K. J. Mysels, *ibid.*, **59**, 45 (1955).