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Studies of the Aqueous Solution of a Surface Active Substance by Means of an Ultrasonic Interferometer.
II. The Effects of Added Electrolytes on the Dissolved State of Sodium Alkyl Sulfate

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The sound velocity (U) and the density of aqueous solutions of sodium dodecyl (SDS) and octyl (SOS) sulfates with inorganic electrolyte have been measured by using a differential ultrasonic interferometer and a float balance respectively, and the compressibility (β) has then been calculated from these results. The CMC's of SDS solutions of various concentrations of sodium salts have been determined from U-vs.-SDS and β-vs.-SDS concentration (C_2) diagrams. The results show a linear relationship between the logarithm of CMC and the logarithm of the concentration of sodium ions. The values of $d\beta/dC_2$ below CMC are affected by the addition of electrolytes, while the values above CMC are almost not affected at all by the addition of electrolytes. The diagrams of $d\beta/dC_2$ of alkyl sulfate vs. the number of carbon atoms in alkyl sulfate molecules with varying concentrations of added electrolytes showed straight lines which all passed through the same point when extrapolated to a zero number of carbon atoms. These results have been explained by taking account of the dissolved state of a surface active substance under the builder action of added inorganic electrolytes, which action decreases not only the mutual repulsion of the ionized-head group of a surface active substance but also the nonionic hydration of the CH_2-chain of the surface active substance.

In previous papers,(1) it has been shown that differential ultrasonic interferometry is one of the most useful methods for the study of aqueous solutions of surface active substances. The sound velocity measurements by this method, together with the density measurements, has made possible the calculation of the compressibility and the critical micelle concentrations (CMC) of aqueous solutions of several alkyl sulfates, and from these data the compressibility, the molar volume, and the hydration number of the ionic micelle were determined. It was concluded therefrom that the hydrocarbon interior of an ionic micelle assumes a liquid-like structure rather than a solid-like one.

It has been well known that the addition of some inorganic salts, often called the "builders," enhances the surface activity. This effect can also be well studied by hydration measurements using differential ultrasonic interferometry. Hitherto little has been known experimentally, however, about the hydration of surface active substances in connection with the builder action. The present paper will describe the results of measurements of the sound velocity, the density, and the compressibility of aqueous solutions of sodium alkyl sulfates containing inorganic electrolytes. The CMC, the hydration, and the compressibility of single molecules and micelles of alkyl sulfates in the presence of the added electrolytes will also be discussed.

Experimental

Sodium *n*-dodecyl (SDS) and *n*-octyl (SOS) sulfate were prepared from the respective alcohols and purified as usual. The sodium chloride, sodium sulfate, and magnesium chloride used to study the builder action were purified from commercial products by recrystallization.

The method of measuring the small changes in the sound velocity (ΔU) due to the small changes in the concentrations (C_2) of the alkyl sulfates by the differential ultrasonic interferometer was the same as that reported in previous papers.(1) The concentration of the added inorganic electrolytes was kept constant during the measurements. The sound velocity of an aqueous solution containing the inorganic electrolyte alone was also measured. The measurements were carried out in a thermostat at 30.00±0.003°C. The frequency of the ultrasonic wave was 1.432 Mc./sec., and the error in the measurement of ΔU was ±3 cm./sec.

The density of the solution at 30°C was determined by the float-balance method.(2) As the standard,(3)

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1) T. Sasaki and K. Shigehara, IVth International Congress of Surface Activity, B/IV. 13, Brussels, Belgium (1964); K. Shigehara, This Bulletin, **38**, 1700 (1965).

2) T. W. Richards and J. W. Shipley, *J. Am. Chem. Soc.*, **34**, 599 (1912); T. W. Richards and G. W. Harris, ibid., **38**, 1000 (1916).

3) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York (1928), p. 51.

the aqueous solution of the inorganic electrolyte was used, and the change in density ($\Delta\rho$) caused by the addition of alkyl sulfates was measured. The thermostat used was controlled to ±0.001°C. The accuracy of the measurements was $\pm 10^{-6}$ g./cc.

The compressibility (β) of the solution was calculated from the sound velocity (U) and the density (ρ) by using the Laplace equation:

$$\beta=1/U^2\rho$$

Results and Discussion

In Figs. 1 and 2, the change in sound velocity (ΔU) is plotted against the concentration of alkyl sulfates (C_2), while in Figs. 3 and 4, the change in compressibility ($\Delta\beta$) is plotted against the concentration of aqueous solutions of SOS and SDS, with and without the addition of inorganic electrolytes. As may be seen in Figs. 2 and 4, the diagrams for SDS solutions consist of two linear portions with a sharp break point between them; this break point may reasonably be ascribed to the CMC of SDS, as will be mentioned later. The change in density ($\Delta\rho$)-vs.-SDS concentration diagrams show similar break points corresponding to CMC, but they are not shown in this paper.

The change in the value of CMC with the concentration of sodium chloride and sulfate is shown in Fig. 5. As may be seen in Fig. 5, the logarithm of CMC changes linearly with the logarithm of the concentration of sodium ions; a similar linear relationship has been reported by Corrin and

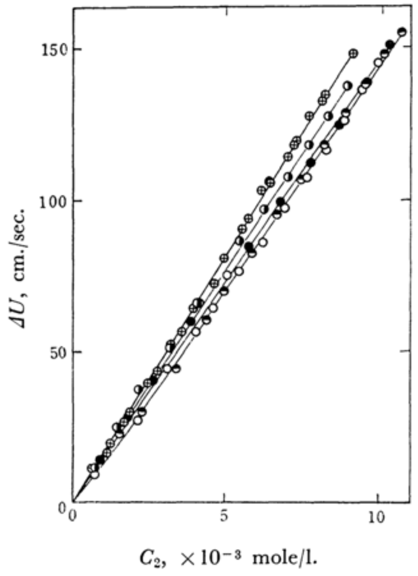

Fig. 1. ΔU vs. C_2 diagram for SOS solution.

⊕ without electrolyte ◑ 0.05 N NaCl
○ 0.1 N NaCl ◓ 0.5 N NaCl ● 0.05 N Na_2SO_4

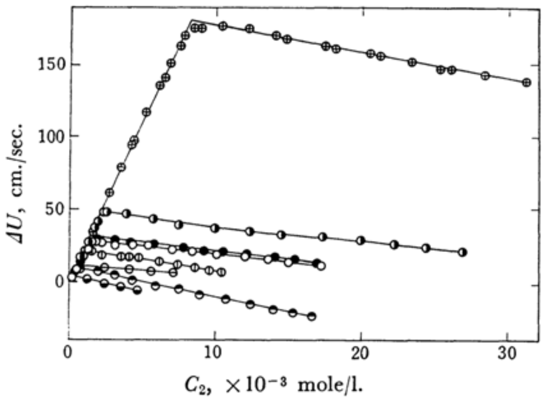

Fig. 2. ΔU vs. C_2 diagram for SDS solution.

⊕ without electrolyte ◑ 0.05 N NaCl
○ 0.1 N NaCl ◓ 0.5 N NaCl ◒ 1 N NaCl
● 0.1 N Na_2SO_4 ⦶ 0.05 N $MgCl_2$
⊖ 0.1 N $MgCl_2$

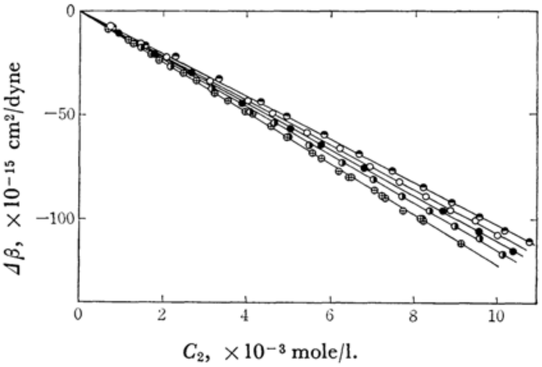

Fig. 3. $\Delta\beta$ vs. C_2 diagram for SOS solution.

⊕ without electrolyte ◑ 0.05 N NaCl
○ 0.1 N NaCl ◓ 0.5 N NaCl ● 0.05 N Na_2SO_4

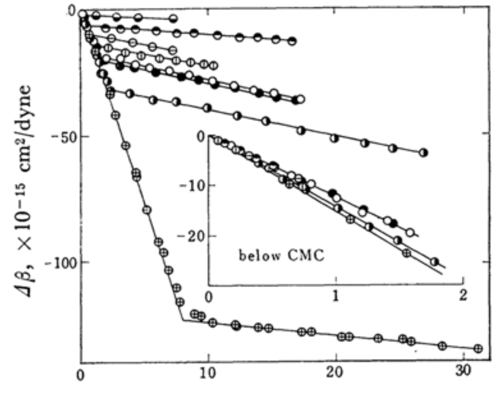

Fig. 4. $\Delta\beta$ vs. C_2 diagram for SDS solution.

⊕ without electrolyte ◑ 0.05 N NaCl
○ 0.1 N NaCl ◓ 0.5 N NaCl ◒ 1 N NaCl
● 0.1 N Na_2SO_4 ⦶ 0.05 N $MgCl_2$
⊖ 0.1 N $MgCl_2$

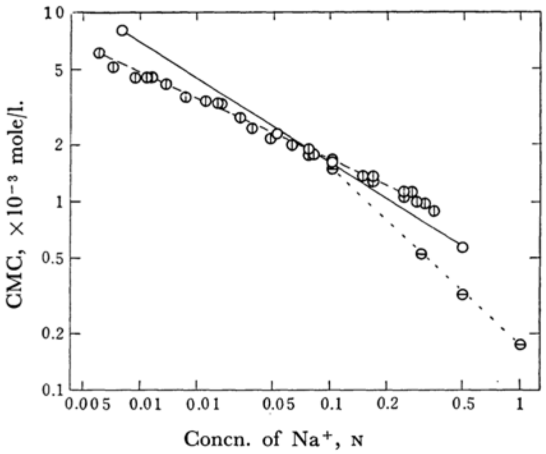

Fig. 5. CMC vs. concentration of Na^+.
○ and solid line, the present author
⦶ and broken line, Corrin and Harkins, by dye solubilization method
⊖ and dotted line, Matuura et al., by surface tension method

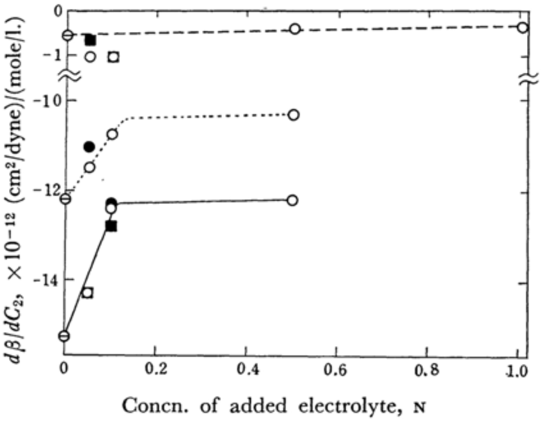

Fig. 6. dβ/dC_2 vs. concentration of added electrolyte.
solid line, SDS solution below CMC
dotted line, SOS solution below CMC
broken line, SDS solution above CMC
⊖ without electrolyte
○ presence of sodium chloride
● presence of sodium sulfate
■ presence of magnesium chloride

Harkins[4] and by Matuura et al.[5]

In the diagrams of $\Delta\rho$ vs. C_2, the slopes were not affected by the addition of inorganic electrolytes. This shows that the molar volume of alkyl sulfate in the dissolved state is not affected by the addition of inorganic electrolytes. This fact is consistent with the findings of Hutchinson and Mosher[6] on the partial molal volume of sodium decyl sulfate above CMC.

The increase in $\Delta\beta$ with C_2 (d$\Delta\beta$/dC_2 or dβ/dC_2) for solutions of SOS and SDS is plotted against the concentration of the added electrolyte in Fig. 6. In this figure, the dβ/dC_2 increases with the concentration of the electrolyte up to CMC. This result may be ascribed to the dehydration of SOS and SDS by the added electrolytes. After the CMC, the value of dβ/dC_2 is almost independent of the concentration of inorganic electrolytes.

Figure 7 shows the plots of dβ/dC_2 vs. the number of carbon atoms (N) in the solute molecule. As may be seen in Fig. 7, the values of dβ/dC_2 change linearly with N when sodium chloride is added to the solution. The values without the addition of sodium chloride reported in previous papers[1] also fall on straight lines. From this figure, the values of dβ/dC_2 for the solutions of various NaCl contents at the zero carbon number were estimated by extrapolation below and above CMC. These values all fall at the same point. This suggests that the hydration characteristics of the SO_4Na radical of alkyl sulfates are independent of the carbon number as well as of the presence of the builder and of the micellization. The contribution of each CH_2-chain in the solute molecule to the value of dβ/dC_2 is independent of the total number of

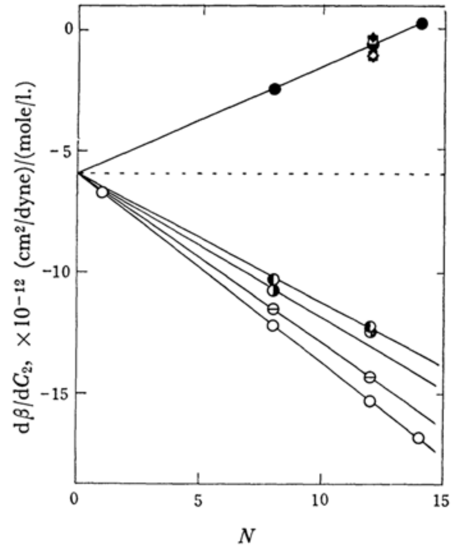

Fig. 7. dβ/dC_2 vs. N.

below CMC:	above CMC:
○ without electrolyte	● without electrolyte
⊖ 0.05 N NaCl	■ 0.05 N NaCl
◑ 0.1 N NaCl	◇ 0.1 N NaCl
◐ 0.5 N NaCl	□ 0.5 N NaCl
	◆ 1 N NaCl

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[4] M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

[5] R. Matuura, H. Kimizuka, A. Matsubara, K. Matsunobu and T. Matsuda, This Bulletin, **35**, 552 (1962).

[6] E. Hutchinson and C. S. Mosher, *J. Colloid Sci.*, **11**, 352 (1956).

carbon atoms in its molecule, but it is changed by the addition of electrolytes. As has been pointed out in the previous papers,[1] the value of $d\beta/dC_2$ obtained by the extrapolation to $N=0$ shows a compressibility decrease due to the introduction of one mole of Na^+ and $-SO_4^-$ each in water. The decrease in this value with respect to N for the solution below CMC, namely, the vertical difference between the dotted horizonatal line and the straight line for the solution below CMC in Fig. 7, shows an additional decrease in compressibility due to the dissolution of one mole of alkyl chains of the respective carbon numbers in a molecule in the state of molecular dispersion in water; the increase for the solutions above CMC, namely, the vertical difference between the dotted horizontal line and the upper straight line, shows a similar increase in compressibility due to the introduction of one mole of alkyl chains in micelles. Therefore, the fact that the $d\beta/dC_2$ value above CMC was almost unchanged by the addition of the electrolyte indicates that the compressibility of micelles is presumably not affected by the addition of an inorganic electrolyte.

It may be inferred from these results that the non-ionic hydration of the CH_2-chain, together with ionic hydration, is one of the important factors in the dissolution of surface active substance into water, and that the builder action of inorganic electrolytes is due not only to the decrease in the mutual repulsion of the ionized head group of the surface active substance by the gegen-ion attachment, as may be understood from Fig. 5, but also to the decrease in the non-ionic hydration of the CH_2-chain of the surface active substance.

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