Studies of the Aqueous Solution of a Surface Active Substance by Means of an Ultrasonic Interferometer.

I. Determinations of the Critical Concentration and Compressibility of Micelles of Several Alkyl Sulfates

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The dissolved state and the properties, especially the micelle formation and the solubilization, of surface active substances in an aqueous solution have been studied by various methods of measurements, such as light scattering, X-ray diffraction, diffusion, electrolytic conductance, osmometry and dialysis.[1] The hydration of the surface active substance in a solution has been studied by many authors, it also is important for the study of the properties of an aqueous solution of a surface active substance. Among such studies, Stigter, Williams and Mysels[2] have estimated the hydration of micelles to be monomolecular, a theory which is in accordance with the light scattering and micelle diffusion data. However, little is known about the hydration of the solute in the state of a single molecule, which is rather important in relation to the amphipathic nature of the substance in question and also in relation to the builder action of the inorganic salt usually added to enhance the surface activity. In this connection, ultrasonic interferometry offers another useful method, since the compressibility of a solution of a surface active substance, as calculated from the sound velocity, is closely related to the hydration of the solute in a solution, which is often difficult to measure by other methods. Thus, a number of studies have been reported on the hydration of inorganic and organic substances using an ultrasonic interferometer.[3,4] However, similar studies have not yet been reported of solutions of surface active substances. This is mainly due to the fact that the accuracy of the sound velocity of ±0.5 m./sec. attainable by an ordinary ultrasonic interferometer is still insufficient for a study which requires the measurement of such a small difference in sound velocity as that between pure water and dilute solution of the most surface active substance near CMC. The present investigation, therefore, used a differential ultrasonic interferometer with an accuracy of ±3 cm./sec. which had already been devised by Sasaki and Yasunaga.[5]

The present paper will describe the results of measurements of the sound velocity and compressibility of aqueous solutions of homologues of alkyl sulfates and sodium hydrogen sulfate. Further, the CMC's will be determined and the compressibility of micelles calculated from sound velocity data.

Experimental

Materials.—The alkyl sulfates used were sodium *n*-tetradecyl (STS), *n*-dodecyl (SDS), *n*-octyl (SOS) and methyl (SMS) sulfates. They were prepared from their corresponding alcohols and then purified, except for SMS, which was prepared from a commercial product by drying it over silica gel. Sodium hydrogen sulfate (SHS) was also used for the sake of comparison. Its aqueous solution was prepared by dissolving an equimolar amount of pure sulfuric acid and recrystallized sodium sulfate in water.

Apparatus and Procedure.—The apparatus used for the measurement of the sound velocity was the usual ultrasonic interferometer, somewhat modified so as to determine the change in the sound wavelength in the solution resulting from the change in the concentration of the solute by measuring the change in the length of a series of several hundred stationary sound waves. The main part of the cell (Fig. 1) consisted of a glass tube 34 cm. long and 1.8 cm. in diameter, to one end of which a guartz ultrasonic generator plate 2.5 cm. in diameter and with a frequency of $f=1.432$ Mc./sec. was attached, while to the opposite end there was connected a vertical glass tube so that a vertical glass reflector

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[1] M. E. McBain and E. Hutchinson, "Solubilization and Related Phenomena," Academic Press, New York (1955); A. M. Schwartz and J. W. Perry, "Surface Active Agents," Vol. I, Interscience Publishers, New York (1949), pp. 289—315; T. Yamamoto, S. Okazaki and T. Sasaki, *Kolloid-Z.*, **178**, 97 (1961).

[2] D. Stigter, R. J. Williams and K. J. Mysels, *J. Phys. Chem.*, **59**, 330 (1955).

[3] A. Passynski, *Acta Physicochimica USSR*, **8**, 385 (1938); T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 87, 89 and 336 (1951); K. Tamura and T. Sasaki, This Bulletin, **36**, 975 (1963).

[4] Y. Miyahara, This Bulletin, **26**, 390 (1953); H. Shiio, T. Ogawa and H. Yoshihashi, *J. Am. Chem. Soc.*, **77**, 4890 (1955); etc.

[5] T. Sasaki and T. Yasunaga, *Chem. & Chem. Ind.* (*Kagaku to Kogyo*), **7**, 138 (1954).

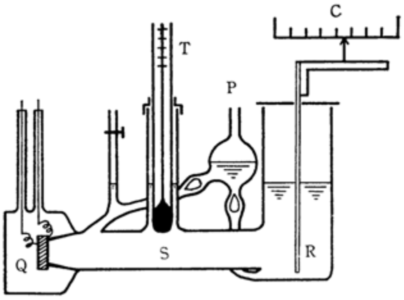

Fig. 1. Differential ultrasonic interferometer.
S Cell with solution
Q Quartz ultrasonic generator
R Reflector plate
C Comparator
P Circulation pump
T Thermometer

plate could move in the solution contained in the cell by means of a comparator with a ±0.002 mm. accuracy. The sample liquid in the cell was circulated during the measurement by means of an all-glass circulation pump. The cell was immersed in a thermostat of 30.00±0.003°C.

The principle of measurement is based on the fact that if we fix the reflector plate of the interferometer to the n'th node (counting from the quartz ultrasonic generator plate) of the stationary wave produced in the sample solution, as in the case of ordinary ultrasonic interferometry, and trace the change in the position (ΔL) of the same node due to the increase in the wavelength ($\Delta\lambda$) produced by the change in the concentration (C) of the solution, we can calculate $\Delta\lambda$ and the change in the sound velocity (ΔU) by:

$$\Delta\lambda=\Delta L/n \tag{1}$$

and

$$\Delta U=f\times\Delta\lambda \tag{2}$$

The actual position we follow shifts from the node by a constant amount equal to the phase difference of the sound wave at the reflector plate, but this dose not alter the above relation, since it is considered to be constant and does not affect ΔL.

To carry out the experiment, it is necessary to increase the concentration gradually, starting from pure water, and following carefully the shift of the specified node of the stationary sound wave produced in it. For this purpose, 250 cc. of distilled and degassed water was first introduced in the cell, and then the reflector plate was fixed to an appropriate node corresponding to the minimum of the interference current. Then a certain volume (10—50 cc.) of water in the cell was replaced by an equal volume of the sample solution of a known concentration, and the concentration of the solution in the cell was slightly changed. The reflector plate was then shifted in order to follow the resulting change in the position of the node to which the plate was initially fixed. The distance (ΔL) traveled by the plate was recorded. $\Delta\lambda$ was then calculated by means of Eq. 1. Here the n value was calculated from the distance between the quartz oscillator and the reflector divided by the exactly-measured wavelength of the stationary sound wave.* The value of n was a definite integer near 300. From the value of $\Delta\lambda$, we calculated change in the sound velocity by means of Eq. 2. From the measurements of a series of such successive increments ΔU corresponding to the successive values of concentration C, we obtain the relation:

$$\Delta U=F(C) \quad \text{or} \quad U_c=U_w+\Delta U=U_w+F(C)$$

where U_w and U_c denote the sound velocity in pure water and in the solution with the concentration C respectively, and $F(C)$, the measured concentration function of the sound velocity. The value of $U_w=1509.44$ m./sec. was used in the present experiment.[6] The error introduced in the measurement of ΔU was ±3 cm./sec. for $n=300$.

The density of the solution at 30°C was calculated from the measurement of its change from the value of pure water, which was taken as a standard,[7] by using an ordinary float balance[8] in a thermostat controlled to ±0.001°C (measurement being possible down to $\pm10^{-6}$ g./cc.), except for the measurement of concentrated solutions of SOS and SHS where a pycnometer was used at 30 ±0.01°C.

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

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

and was also expressed as a function of the solute concentration.

Results and Discussion

Figures 2 and 3 show the sound velocity vs. concentration diagrams, and Figs. 4 and 5, the compressibility vs. concentration diagrams for aqueous solutions of SHS, SMS, SOS, SDS and STS. It can be seen in these figures that the diagrams for SMS and SHS solutions consist of a single straight line, while in the cases of

TABLE I. VALUES OF CMC

Substance	CMC value (10^{-3} mol./l. unit)		
	Ultrasonic method	Conductivity method[a]	Surface tension[b]
SOS	130	130	130*
SDS	8.0	8.1	6.9—8.0
STS	2.2	—	2.0—2.2

* Measured by the present author using the drop weight method.

[a] F. D. Haffner, F. A. Piccione and C. Rosenblum, *J. Phys. Chem.*, **46**, 662 (1942).

[b] J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937); A. Lottermoser and F. Stoll, *Kolloid-Z.*, **63**, 49 (1933).

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* Calculated by the measurement of the total length of 10 successive waves produced in the solution.

[6] M. Greenspan and C. E. Tschiegg, *J. Research Natl. Bur. Standards*, **59**, 249 (1957).

[7] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York (1928), p. 25.

[8] 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).

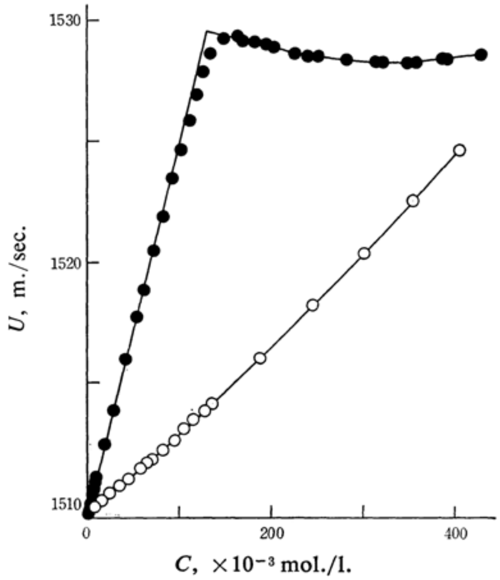

Fig. 2. Sound velocity vs. concentration.
○ SHS ● SOS

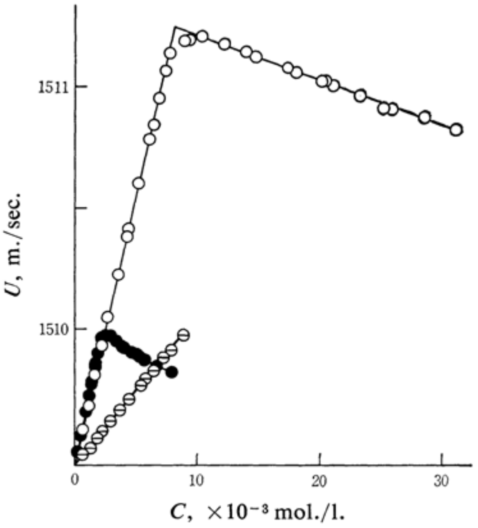

Fig. 3. Sound velocity vs. concentration
⊖ SMS ○ SDS ● STS

STS, SDS and SOS solutions each of the diagrams, especially that for compressibility, consists of two linear portions with a break point between them. This break point coincided with the CMC of the respective solute, as is shown in Table I. This proves the differential ultrasonic interferometry to be a useful method for the measurement of the CMC.

Figure 6 further shows that the inclination of the β vs. concentration diagram ($d\beta/dC$) above and below CMC is in a linear relation with the number of carbon atoms (N) in the solute molecule, and that when extrapolated the two straight lines to $N=0$ coincide with each other and with the $d\beta/dC$ value for sodium hydrogen sulfate of a moderate concentration of about 0.1 mol./l., where it is considered to behave as a uni-univalent electrolyte composed of HSO_4^- and Na^+.⁹⁾ These relations are expressed by the following equations:

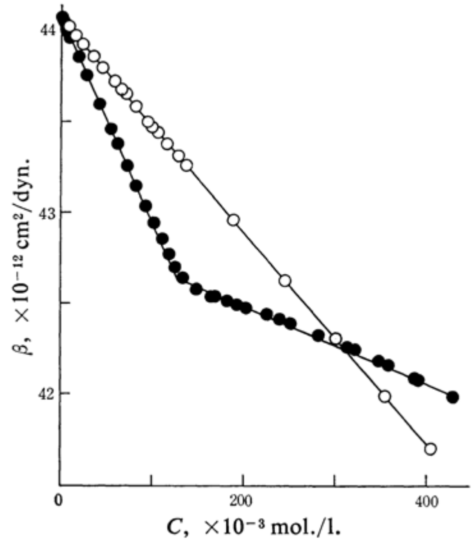

Fig. 4. Compressibility vs. concentration.
○ SHS ● SOS

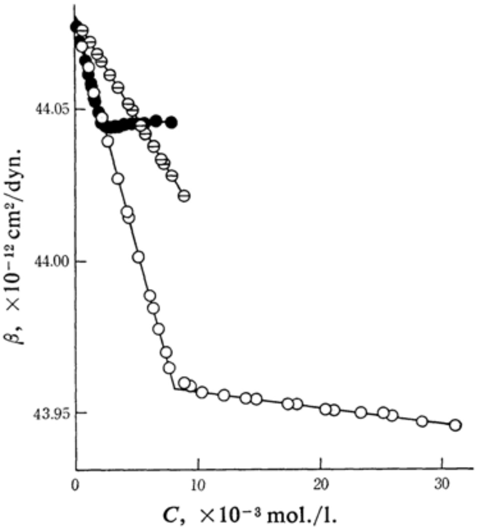

Fig. 5. Compressibility vs. concentration.
⊖ SMS ○ SDS ● STS

$$d\beta/dC = -5.94\times10^{-12} + 0.445\times10^{-12}\times N \quad (3)$$

for solutions above CMC, and:

$$d\beta/dC = -5.94\times10^{-12} - 0.776\times10^{-12}\times N \quad (4)$$

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9) I. M. Klotz and C. F. Eckert, *J. Am. Chem. Soc.*, **64**, 1878 (1942); P. L. Khare, *Trans. Faraday Soc.*, **58**, 359 (1962).

for solutions below CMC, where $d\beta/dC$ is expressed as (cm^2/dyn.)/(mol./l.). This suggests that the dissolved state of the SO_4Na radical of alkyl sulfates in an aqueous solution is the same as that of HSO_4Na, whether they are in the state single ions or micelles, and that the contribution to $d\beta/dC$ of each CH_2-chain in the solute molecule is constant, which is different in signs according to their dissolved states. Since the value of -5.94×10^{-12} in Eq. 4 expresses the compressibility decrease due to the introduction of one mole of Na^+ and HSO_4^- in water, the portion of the ordinate of the lower line below the dotted horizontal line in Fig. 6 expresses the 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, and the portion of the ordinate between the dotted horizontal line and the upper straight line expresses a similar increase in compressibility due to the introduction of one mole of alkyl chains in a micellar state in water. Both of these values may, therefore, be considered to be proportional to the carbon number in the solute molecule, and Eqs. 3 and 4 may be expected to intersect at the zero point of the carbon number in the solute molecule.

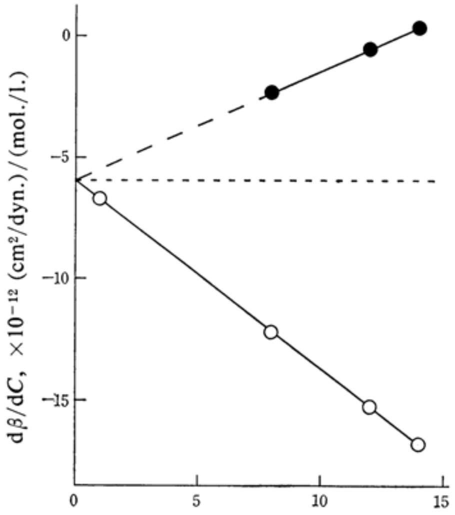

Fig. 6. $d\beta/dC$ vs. N.
○ $d\beta/dC$ below CMC
● $d\beta/dC$ above CMC
Dotted line: $d\beta/dC$ for SHS

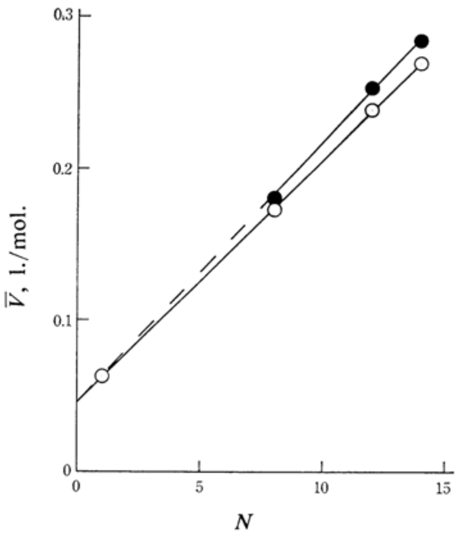

Fig. 7. $\bar{V}$ vs. N.
○ $\bar{V}$ below CMC
● $\bar{V}$ above CMC

Similar results are obtained for the partial molar volume ($\bar{V}$) of alkyl sulfate by the measurement of the density for the solution. Figure 7 shows the results. Here the diagram of $\bar{V}$ vs. the carbon number (N) in the solute molecule consists of two straight lines, above and below CMC, which coincide with each other at $N=0$. These ralations are expressed by the following equations:

$$\bar{V}=0.0171\,N+0.046 \tag{5}$$

for solutions above CMC, and:

$$\bar{V}=0.0159\,N+0.046 \tag{6}$$

for solutions below CMC, where $\bar{V}$ is expressed in l./mol.

To derive theoretically the equations corresponding to those of Eqs. 3 and 4, the solution of the volume (V) and compressibility (β) as a whole is assumed to consist of several volume elements (V_1, V_2, $\cdots$) of different compressibilities (β_1, β_2, $\cdots$). Therefore, we have:

$$V=V_1+V_2+\cdots \tag{7}$$

$$V\beta=V_1\beta_1+V_2\beta_2\cdots \tag{8}$$

From these equations and with an additional assumption, usually accepted,3) that such an ionic radical as HSO_4^- or $-SO_4^-$ of alkyl sulfate, together with its water of hydration, is incompressible and is independent of the micellization of the solute, as may reasonably be understood from Fig. 6, the following equations are derived for solutions above CMC:

$$d\beta/dC=V_mN\ (\beta_m-\beta_1)-V_s\beta_1 \tag{9}$$

$$\bar{V}=V_mN+V_s-n_xV_1 \tag{10}$$

where $\bar{V}$ denotes the partial molar volume of alkyl sulfate; V_1 and V_m, the molar volume of free water and of CH_2 in micelle respectively; β_1 and β_m, the compressibility of free water and the hydrocarbon part of the micelle

TABLE II

Substance Hydrocarbon or alkyl sulfate	State of aggregation	Compressibility (10^{-12} cm^2/dyne) of hydrocarbon: Solid or liquid	Compressibility of hydrocarbon: Micelle	Molar vol. (cc./mol.) of CH_2 in: Solid or liquid[17]	Molar vol. of CH_2 in: Micelle	Amount of hydration of SO_4Na (mol./mol.)	Molar vol. (cc./mol.) of hydrated SO_4Na
n-C_8	Liquid	109.0[a]		20.57			
n-C_{10}	Liquid	93.50[b]		19.66			
n-C_{12}	Liquid	84.68[b]	$70._1$	19.11	17.1	4.9	135
n-C_{14}	Liquid	—		18.70			
n-C_{16}	Liquid	74.5[c]		18.45			
Paraffin	Solid	—		15.5		5.7	
		26*				for aq.	
Polyethylene	Solid	25.2**		15.2		$NaHSO_4$	

* Calculated by the present author.

** Value at 20°C, Ref. 18.

a B. B. Freyer, J. C. Hubbard and D. H. Andrews, *J. Am. Chem. Soc.*, **51**, 759 (1929).

b A. Weissler and V. A. Del Grosso, *J. Am. Chem. Soc.*, **72**, 4209 (1950).

c F. Danusso and E. Fadigati, *Rendiconti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. e Natur.*, **14**, 81 (1953).

d "International Critical Tables," Vol. II, p. 314 (1927) and Vol. III, pp. 27 (1928), McGraw-Hill Book Co., New York, etc.

e P. Heydemann, *Acustica*, **9**, 446 (1959).

respectively; n_x, the mole number of hydration water per mole of SO_4Na, and V_s, the molar volume of the SO_4Na radical, together with the volume of n_x moles of hydration water.

By comparing Eq. 9 with Eq. 3, and Eq. 10 with Eq. 5, the V_s, V_m, n_x and β_m values are calculated to be as shown in Table II.

It may be seen in this table that the compressibility of the micelle and the mole volume of the CH_2 radical in the micellar state are constant, independent of the number of the carbon atoms of the alkyl sulfate molecule, and that they are nearer to the value for liquid rather than solid hydrocarbon. These facts are additional evidence for the view that the hydrocarbon interior of the ionic micelle is liquid-like rather than solid-like.[10] The amount of hydration, $n_x=4.9$, for the SO_4Na radical is comparable with the corresponding value of 5.7 for $NaHSO_4$ near a 0.1 molar solution, where the solution as a whole is considered to contain HSO_4^- and Na^+ ions,[9] although we can cite other data which is somewhat different.[11]

Summary

The sound velocity and the density of aqueous solutions of sodium hydrogen (SHS), methyl (SMS), octyl (SOS), dodecyl (SDS) and tetradecyl (STS) sulfates have been measured by using, respectively, a differential ultrasonic interferometer and a float balance, and the compressibility (β) has then been calculated from these results. Each of these three quantities, when plotted against the concentration (C), has shown a nearly straight line for SHS and SMS, while it consists of two nearly straight lines, with a break point between them at CMC, in the cases of SOS, SDS and STS. The values of $d\beta/dC$ below and above CMC, when plotted against the number of carbon atoms in the alkyl chain of the solute molecule, again showed two straight lines which intersected with each other at the zero number of carbon atoms. This value of $d\beta/dC$ is equal to that of SHS at a moderate concentration. These results have been explained by taking account of the dissolved state of these solutes. The compressibility of the micelle (β_m), the molar volume of the CH_2 radical in the micellar state (V_m), and the ionic hydration number of solute have been calculated; the values of β_m and V_m show evidence for the view that the hydrocarbon interior of the ionic micelle is liquid-like rather than solid-like.

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10) G. S. Hartley, "Aqueous Solutions of Paraffin Chain Salts," Hermann et Cie, Paris (1936); K. Shinoda and T. Soda, *J. Phys. Chem.*, **67**, 2072 (1963); etc.

11) T. F. Young and L. A. Blatz, *Chem. Revs.*, **44**, 93 (1949).