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Studies of the Aqueous Solution of a Surface Active Substance by Means of an Ultrasonic Interferometer.
III. Determinations of Ionic and Nonionic Hydrations of Sodium Alkyl Sulfate

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The amounts of water of ionic and nonionic hydration were calculated for sodium alkyl sulfate in the state of molecular dispersion from the data obtained by the author and under the assumptions usually adopted: (a) the solution, as a whole, consists of several volume elements of different compressibilities; (b) the ionic radical together with its hydration water is incompressible; (c) the compressibility of the water of nonionic hydration for the CH_2 group of the hydrocarbon chain is the same as that of ordinary ice; (d) the compressibility and the molar volume of the CH_2 radical in the state of molecular dispersion are the same as those in the micellar state. The water of hydration was calculated to be 2.1 mole per mole of the CH_2 radical, and 4.9 mole per mole of the ionic radical, the latter value being the same as that of the solute in the micellar state previously reported. The molar volume of the water of nonionic hydration is found to be slightly less than that of free water, in accordance with the prediction of others. The dehydration of sodium alkyl sulfate caused by the addition of inorganic electrolyte has also been observed.

In previous papers,[1,2] 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 measurement by this method, together with the density measurement, makes possible the calculation of the compressibility and the critical micelle concentrations (CMC) of aqueous solutions of several alkyl sulfates with or without the addition of inorganic electrolytes, and from these data the compressibility, the molar volume and the hydration number of ionic micelle were determined. It has been inferred therefrom that the hydrocarbon interior of the ionic micelle is liquid-like rather than solid-like; the nonionic hydration of CH_2-chain is also one of the most important factors responsible for the dissolution of the surface active substance, and the builder action of the inorganic electrolyte is due not only to the decrease in the mutual repulsion of the ionized head group of the surface active substance caused by the gegenion attachment to this group, but also to the decrease in the amount of nonionic hydration of the CH_2-chain of the surface active substance. However, no quantitative discussion of the nature and the amount of the nonionic hydration of the CH_2-chain of a surface active substance has yet been reported. The present paper will give an estimation of the nonionic hydration of the CH_2-chain of the surfactant molecule.

Calculation

A solution (total volume, V; compressibility, β) is assumed to consist of several volume elements, $v_1, v_2, \cdots$, of different compressibilities, $\beta_1, \beta_2, \cdots$, in such a manner as:[1]

$$V = v_1 + v_2 + \cdots \tag{1}$$

$$V\beta = v_1\beta_1 + v_2\beta_2 + \cdots \tag{2}$$

Then, for a solution of an alkyl sulfate below CMC, we have:

$$V = V_1(n_1 - nn_x - nn_yN) + V_2nn_yN + V_3nN + V_4n \tag{3}$$

$$V\beta = V\beta_1 + V_2nn_yN(\beta_2 - \beta_1) + V_3nN(\beta_3 - \beta_1) + V_4n(\beta_4 - \beta_1) \tag{4}$$

where n_1 and n denote the mole numbers of the solvent and the solute in the solution of the volume (V) respectively; n_x, the mole number of the water of ionic hydration per mole of the SO_4Na radical; n_y, the mole number of the water of nonionic hydration per mole of the CH_2 radical of the alkyl chain; N, the number of carbon atoms in a solute molecule; V_1 and V_2, the molar volume of free water and the water of nonionic hydration respectively; V_3, the molar volume of the CH_2 radical of the solute molecule; V_4, the molar volume of the SO_4Na radical together with its n_x moles of

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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] K. Shigehara, This Bulletin, **39**, 2332 (1966).

hydration water; and β, β_1, β_2, β_3 and β_4, the compressibility of the solution as a whole and of the parts which have the molar volumes of V_1, V_2, V_3 and V_4 in the solution respectively. Thus, the terms of the right hand side of Eq. 3 indicate the volumes of free water, the water of hydration of the hydrocarbon chain, the hydrocarbon chain, and the hydrated ionic head respectively in that order. From Eqs. 3 and 4, we obtain:

$$\overline{V} = (-n_yV_1 + n_yV_2 + V_3)N + V_4 - n_xV_1 \quad (5)$$

$$\mathrm{d}\beta/\mathrm{d}C = [V_2(\beta_2 - \beta_1) + V_3(\beta_3 - \beta_1)]N + V_4(\beta_4 - \beta_1) \quad (6)$$

where $\overline{V}$ denotes the partial molar volume of alkyl sulfate, and C, the molarity of the solute ($C=n/V$).

It is assumed that such ionic radicals as HSO_4^- and $-SO_4^-$ (alkyl sulfate), and its hydration water, are incompressible, as has been accepted by many authors,3) that V_3 and β_3 are equal to the molar volume (V_m) of CH_2 in the micelle and the compressibility (β_m) of the hydrocarbon parts in the micelle respectively, and that β_2 is equal to the compressibility (β_{ice}) of ordinary ice, as was accepted by Sasaki and Yasunaga4) and by Shiio et al.5) The last assumption is also in accordance with the view that the water molecule is oriented towards the CH_2 radical and that they form an ice-like structure by means of H-bonds between them, thus producing a microscopic "iceberg" around dissolved molecules of hydrocarbon.6,7) The following equations can then be obtained for the solution of alkyl sulfates below CMC:

$$\overline{V} = (-n_yV_1 + n_yV_2 + V_m)N + V_4 - n_xV_1 \quad (7)$$

$$\mathrm{d}\beta/\mathrm{d}C = [V_2(\beta_{\mathrm{ice}} - \beta_1) + V_m(\beta_m - \beta_1)]N - V_4\beta_1 \quad (8)$$

where the values of β_1, β_{ice}, β_m, V_1 and V_m are 44.082,1) 11.1,8) $70._1$1) (all in 10^{-12} cm^2/dyn.), 18.0949) and 17.11) (both in cc./mol.) respectively.

In his previous papers,1) the author has reported empirical equations* corresponding to those of Eqs. 7 and 8:

$$\overline{V} = 15.9N + 46 \quad (9)$$

$$\mathrm{d}\beta/\mathrm{d}C = -0.776\times10^{-12}\times N - 5.94\times10^{-12} \quad (10)$$

where $\overline{V}$ and $\mathrm{d}\beta/\mathrm{d}C$ are expressed in cc./mol. and (cm^2/dyn.)/(mol./l.) respectively.

By comparing Eq. 7 with Eq. 9, and Eq. 8 with Eq. 10, with due consideration of the difference in units, the n_x, n_y, V_2 and V_4 values are calculated to be as shown in Table I.

TABLE I

Radical	Amount of hydration water of (mol./mol.)	Molar volume of hydrated (cc./mol.)	Molar volume of hydration water of (cc./mol.)
SO_4Na	4.9	135	—
CH_2	2.1	—	17.5

The mole number of the water of ionic hydration per mole of the SO_4Na radical, $n_x=4.9$, and the molar volume of the hydrated SO_4Na radical, $V_4=135$ (cc./mol.), are consistent with those of the solute in the micellar state, determined independently in previous papers.1) The mole number of the water of nonionic hydration per mole of the CH_2 radical, $n_y=2.1$, agrees with Butler's assumption,6) which he adopted to calculate the heat of hydration of a homologous series of alcohols. There he considered that two hydrogen atoms of the CH_2 radical give rise to two H-bonds around it. The molar volume of the water of nonionic hydration, $V_2=17.5$ cc./mol., is slightly less than that of free water. This fact agrees with those reported by other authors.7) All these facts lead us to the conclusion that the assumptions used in the calculation are permissible.

In a preceding paper,2) the present author has reported that the $\overline{V}$ value of alkyl sulfate is not affected by the addition of inorganic electrolyte, that $\mathrm{d}\beta/\mathrm{d}C$ below CMC increases with the concentration of the added electrolyte, and that the extrapolated value of $\mathrm{d}\beta/\mathrm{d}C$ to $N=0$ shows the same value independently of the presence of the added electrolyte (Fig. 1). From these results and from Eqs. 7 and 8, the n_x, n_y, V_2 and V_4 values in the presence of inorganic electrolytes are obtained by a calculation similar to that mentioned above. It was confirmed that the values of n_x, V_2 and V_4 thus obtained were not affected by the addition of inorganic electrolytes. On the other hand, as is shown in Fig. 2, the mole number of the water of nonionic hydration per mole of the CH_2 radical, n_y, decreases with the increase in the concentration of inorganic electrolytes until it reaches a minimum value which is about 80% of the n_y value in the absence of electrolytes. This

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9) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York (1928), p. 26.

3) A. Passynski, *Acta Physicochimica USSR*, **8**, 385 (1938); Y. Wada, S. Shimobo, M. Oda and J. Nagumo, *Applied Phys. (Oyo Buturi)*, **17**, 257 (1948); T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zassi)*, **72**, 87, 89 and 366 (1951); T. Sasaki and T. Yasunaga, This Bulletin, **28**, 269 (1955); K. Tamura and T. Sasaki, ibid., **36**, 975 (1963).

4) T. Sasaki and T. Yasunaga, This Bulletin, **26**, 175 (1953).

5) H. Shiio, T. Ogawa and H. Yoshihashi, *J. Am. Chem. Soc.*, **77**, 4980 (1955).

6) J. A. V. Butler, *Trans. Faraday Soc.*, **33**, 229 (1937).

7) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945); W. F. Claussen and M. F. Polglase, *J. Am. Chem. Soc.*, **74**, 4817 (1952); F. Franks and D. J. G. Ives, *J. Chem. Soc.*, **1960**, 741; J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York and London (1961), pp. 18 and 163.

8) F. Joha and P. Scherrer, *Helv. Phys. Acta*, **25**, 35 (1952).

* The measurements at 30°C.

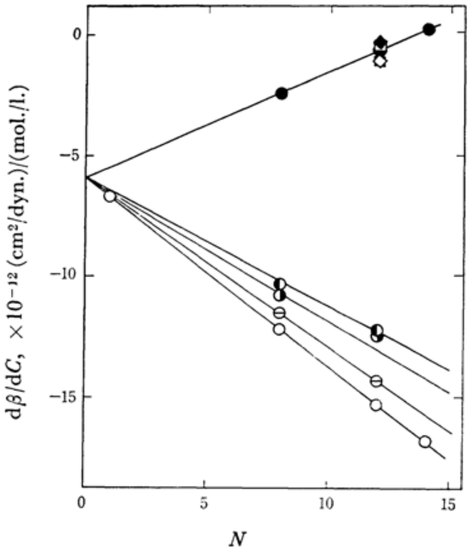

Fig. 1. $d\beta/dC$ vs. N.

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

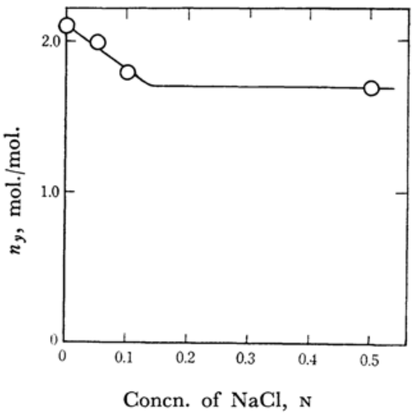

Fig. 2. n_y vs. concentration of NaCl.

confirms the view inferred in the former report[2] that the addition of inorganic electrolytes not only serves to increase the gegenion attachment, as is generally believed, but may also remove water of hydration from the hydrophobic chain of surface active substances. Both of these factors may be considered to decrease the CMC of the surface active substance.

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