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Studies of the Sodium Salts of Homologues of Alkyl Sulfates in Aqueous Solutions in Relation to the Water Structure

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The adiabatic compressibility (β) and the partial molar volume at an infinite dilution ($\bar{V}_0$) were obtained for aqueous solutions of the sodium alkylsulfates (SAS) of lower homologues. The sound velocity (U) and the density (ρ) were determined by the use of an ultrasonic interferometer and the float-balance method respectively. The results indicate that the slope at an infinite dilution $(d\beta/dC)_0$ of β *vs.* the concentration (C) diagram is in a linear relation with the carbon number (ϕ) of SAS. A similar relation was obtained between $\bar{V}_0$ and ϕ. We have derived these two relations by a statistical thermodynamical treatment based on the interstitial model of water, consisting of two species, one constituting the framework of an extended ice-1 structure with many cavities, and the other species, non-hydrogen-bonded water, occupying part of these cavities. The occupancy of the cavity with alkyl radical leads to a decrease in the structural compressibility, while the hydration of the ionic parts of the solute leads to a decrease in the compressibility due to the electrostriction. According to the calculations, the theoretical dependency of $(d\beta/dC)_0$ on ϕ is about three times larger than the experimental value. The theoretical dependency of $\bar{V}_0$ on ϕ is nearly in agreement with the experimental value, while the constant-addivite term is different.

It is known that sodium salts of sulfates of higher alkyl, such as *n*-tetradecyl, *n*-dodecyl, and *n*-octyl, are surface-active substances in aqueous solutions. The dissolved state and properties of these salts in an aqueous solution have been studied by various methods. The adiabatic compressibility is a very useful parameter in elucidating the dissolved state and properties of a solution. Shigehara[1-3] has studied the adiabatic com-

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[1] K. Shigehara, This Bulletin, **38**, 1700 (1965).
[2] K. Shigehara, *ibid.*, **39**, 2332 (1966).
[3] K. Shigehara, *ibid.*, **39**, 2643 (1966).

pressibility and density of these salts in aqueous solutions. He has found that the slope at an infinite dilution $(\mathrm{d}\beta/\mathrm{d}C)_0$ of the β *vs.* concentration (C) diagram is in a linear relation:

$$(-\mathrm{d}\beta/\mathrm{d}C)_0 = (0.776\phi+5.94) \times 10^{-12}\ (\mathrm{cm^2/dyn})/(\mathrm{mol}/l)$$

with the number of carbon atoms (ϕ) of alkyl chains. A similar relation, $\bar{V}_0=15.9\phi+46$ (cm³/mol), is obtained between the partial molar volume at an infinite dilution ($\bar{V}_0$) and the number of carbon atoms (ϕ) of sodium alkylsulfate (SAS). He discussed the dissolved state and properties of SAS in aqueous solutions.

In this investigation, we investigated the SAS of lower alkyl homologues (methyl (SMS), ethyl (SES), and butyl (SBS)) in aqueous solutions by means of an ultrasonic interferometer, and found that the systematic dependences of $(\mathrm{d}\beta/\mathrm{d}C)_0$ and $\bar{V}_0$ are obtained also for lower homologues, the relations in this case being:

$$(-\mathrm{d}\beta/\mathrm{d}C)_0 = (0.68\phi+5.85) \times 10^{-12}\ (\mathrm{cm^2/dyn})/(\mathrm{mol}/l)$$

$$\bar{V}_0 = 16\phi + 53\ (\mathrm{cm^3/mol})$$

Also, we derived these two relations by a statistical thermodynamical treatment based on the interstitial model[4,5] of the water structure.

Experimental

Materials. The alkylsulfates used are SMS, SES, and SBS. They were prepared from their corresponding alcohols by reactions with chlorosulfonic acid and by further neutralization with sodium hydroxide, and were then purified with alcohol by means of recrystallization. Sodium hydrogen sulfate (SHS) was also used for the purpose of comparison. It was prepared by dissolving an equimolar amount of pure sulfuric acid and sodium sulfate in water, and was obtained as a precipitate.

Apparatus. The apparatus used for the measurement of the sound velocity was a differential ultrasonic interferometer of 1.432 MHz designed by Sasaki and Yasunaga,[6] with an accuracy of ±3 cm/sec. The measurements were carried out in a thermostat at 30.000±0.003°C. The density of the solution at 30.000°C, controlled to ±0.001°C, was determined by the float-balance method. The accuracy of the measurements was $\pm 10^{-6}$ (g/cm³).

The adiabatic compressibility of solutions was calculated from the sound velocity (U) and density (ρ) by the following relation:

$$\beta = 1/(\rho U^2).$$

Determination of Concentration. All the solutions used in the experiment were prepared at a constant temperature of 30°C. The volume of the liquid was measured by means of a measuring flask (250 cc) and a full transfer pipet previously maintained at 30°C. Distilled and degased water was used for the preparation of the solution and for further dilution. A known amount of the solute, measured by means of a chemical balance, was used to obtain a stock solution of 250 cc. When v_0 cc of the stock solution (density ρ_0) is added to v_w cc of water (density ρ_w), we obtain a diluted solution (density ρ) of the volume, V:

$$V = (v_0\rho_0+v_w\rho_w)/\rho.$$

Although V is nearly equal to v_0+v_w for the dilute solutions here investigated, we used the above-mentioned relation as the computed V value; the molarity of the concentration thus determined is better than 0.2%.

Results

Figure 1 shows the density difference ($\Delta\rho$) between the solution and solvent as a function of the concentration (C) for various solutes. The increment of the density difference is proportional to the concentration in all cases.

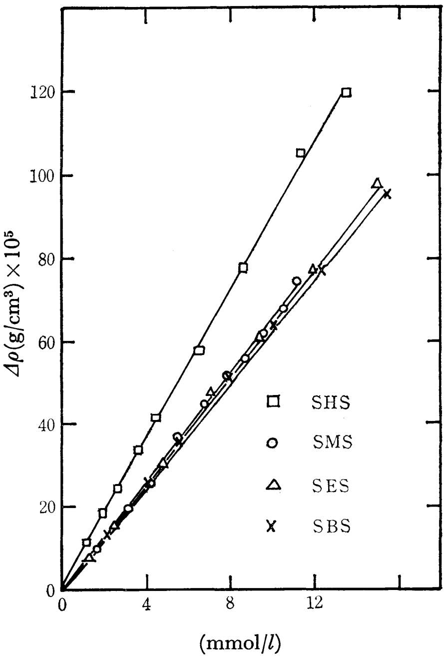

Fig. 1. The difference of density ($\Delta\rho$) between solution and solvent as function of concentration in aqueous solutions at 30°C.

Figure 2 shows the increments in the sound velocity (ΔU) against the concentration for aqueous solutions of SHS, SMS, SES, and SBS, where $\Delta U=U-U_0$ is the difference between the sound velocity for a solution and for the solvent respectively. The increment in sound velocity is proportional to the concentration, except for the case of SHS. The slope ($\partial\Delta U/\partial C$) of the sound velocity-against-concentration curves increases with an increase in the molecular weight for SAS.

Figure 3 shows the difference in adiabatic compressibility $\Delta\beta(=\beta-\beta_0)$ between a solution and the solvent as a function of the concentration for various salts. Except for the SHS solution, $\Delta\beta$ is proportional to the concentration, the ($|\partial\Delta\beta/\partial C|$) slope becoming larger with an increase in the molecular weight: −6.6, −7.1, and $-8.5\times(10^{-12})$ (cm²/dyn)/(mol/l) for SMS, SES, and SBS respectively.

By plotting the value of $(-\mathrm{d}\beta/\mathrm{d}C)_0$ against the number of carbon atoms (ϕ) for SMS, SES, and SBS, we obtain a linear relation (solid line in Fig. 4). It can be represented by the following empirical relation:

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[4] O. Nomoto and H. Endo, *ibid.*, **44**, 1519 (1971).

[5] A. H. Narten, M. D. Danford, and H. A. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967).

[6] T. Sasaki and T. Yasunaga, *Kagaku to Kogyo*, **7**, 138 (1954).

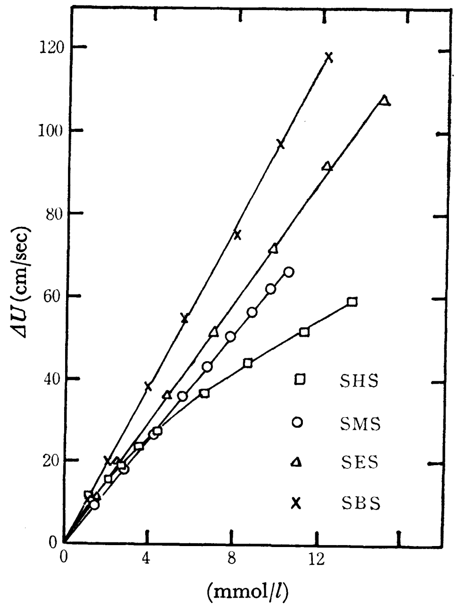

Fig. 2. The difference of sound velocity (ΔU) between solution and solvent as a function of concentration in aqueous solutions at 30°C.

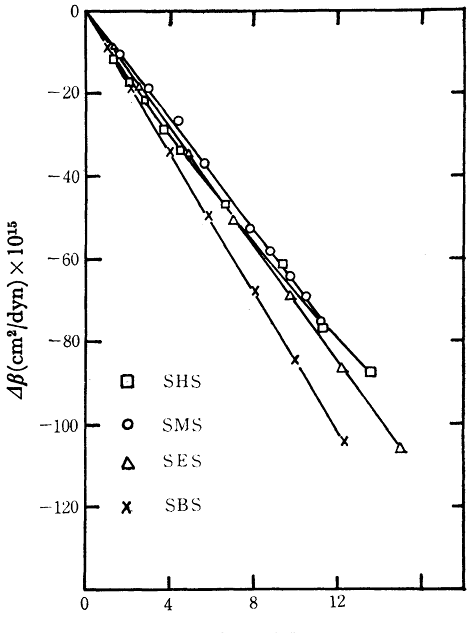

Fig. 3. The difference of adiabatic compressibility ($\Delta\beta$) between solution and solvent as a function of concentration in aqueous solutions at 30°C.

$$(-\mathrm{d}\beta/\mathrm{d}C)_0 = (0.68\phi+5.85)\times10^{-12}\ (\mathrm{cm^2/dyn})/(\mathrm{mol}/l) \quad (1)$$

It means that the contribution to $(-\mathrm{d}\beta/\mathrm{d}C)_0$ of each CH_2 (or CH_3) radical in the alkyl chain is constant, being 0.68×10^{-12} per unit of methylene (or methyl) radical. This may indicate that the effect of the destruction of the water structure with a CH_2 (or CH_3) radical, irrespective of the position in the molecule, is always the same.

The values of the partial molar volume ($\bar{V}_0$) at an infinite dilution of the sulfate, obtained from the density of the solution, are plotted as a solid line in Fig. 5.

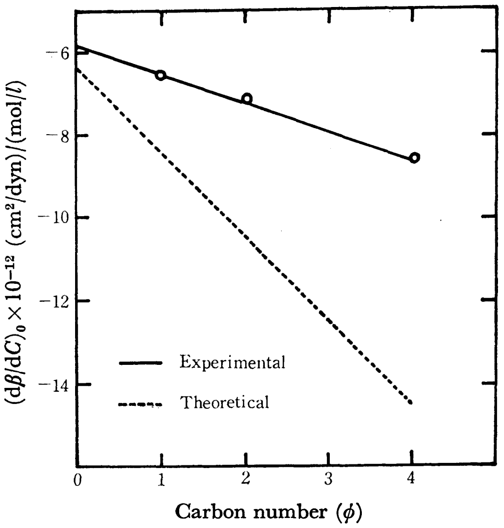

Fig. 4. The slope at infinite dilution $(\mathrm{d}\beta/\mathrm{d}C)_0$ of β against concentration (C) *vs.* carbon number (ϕ) of SAS.

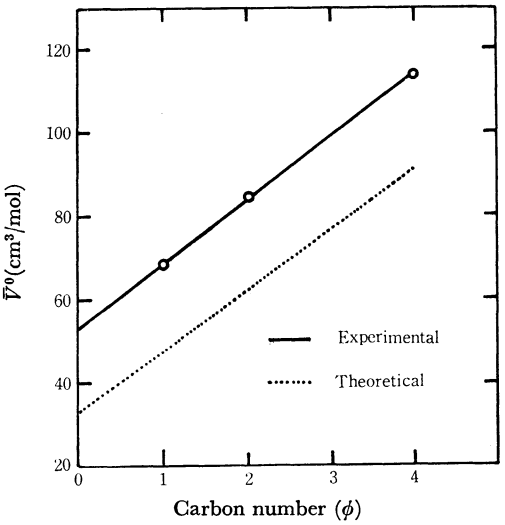

Fig. 5. The partial molar volume at intinite dilution $(\bar{V})_0$ *vs.* carbon number of SAS.

The relation between the partial molar volume and the carbon number in the alkyl chain is also linear and is expressed by the following equation:

$$\bar{V}_0 = 16\phi + 53\ (\mathrm{cm^3/mol}) \quad (2)$$

Theoretical

From their X-ray diffraction studies of liquid water, Narten *et al.*[5] proposed an interstitial model of liquid water, a kind of mixture model. This model consists of two species of water molecules, one constituting the framework of an extended ice-1 structure with many cavities, and the other species, non-hydrogen-bonded water, occupying part of these cavities.

Acoustic pressure in water accompanies two sorts of compression: a) the compression of the intermolecular distance, and b) the breakdown of the intermolecular bonds, accompanied by the destruction of the open structure. The former is represented by the instantaneous compressibility, β_∞, while the latter is the origin of the structural compressibility, β_{st}.

In the case of an aqueous solution, we may expect some changes in the adiabatic compressibility corresponding to changes in water structure under the influence of the solutes. In estimating these changes, we make the following assumptions:

(I) We treat the partial molar volume and the partial molar compressibility extrapolated to "infinite dilution," so that the solute-solvent interaction alone needs to be considered.

(II) When SAS is dissolved in water, we have alkylsulfate anions and sodium cations, almost entirely dissociated. In estimating the influence of the alkylsulfate anion on the partial molar volume and the adiabatic compressibility, we postulate the effect to be composed of two parts, one due to the alkyl chain, $C_\phi H_{2\phi+1}$, and the other, due to OSO_3^-. This is presumably admissible, at least for an infinite dilution.

(III) As regards the effect of the ionic parts (OSO_3^- and Na^+ ions) on $(d\beta/dC)_0$ and $\bar{V}_0$, we use empirical quantities in place of making theoretical treatments. The hydration of the ionic parts of the solute results in a decrease in the volume and compressibility due to the destruction of the water structure by the electrostriction.

(IV) The framework water makes cavities which are large enough to accommodate moderate-sized molecules and various radicals (*cf.* Narten *et al.*,[5,7,8] *etc.*[9-12]); therefore, the solute occupies sites in it as in a quasiclathrate. Since the alkyl chain of the anion is considered to be easily located in the cavity, the carbon-water interaction is very weak, and we assume the framework structure of ice-1 not to be deformed or dilated by the occupation of alkyl radicals.

(V) The occupancy of the cavity by a methyl, ethyl, or butyl radical leads to a decease in the structural compressibility, this decrease becoming larger with an increase in the carbon number. When the ethylene radicals successively occupy the cavities, we do not take the C–C bond angle of the alkyl radical into consideration in order to avoid complicated calculations.

(VI) Both the alkyl chain in the cavity sites and the water molecules in the cavity sites have no effective volume. This means that the dimentions of the framework remain the same, whether the cavity is vacant or not. Therefore, the volume of the solution is assumed to be proportional to the number of framework sites.[9] When the cavities are crushed by acoustic pressure, the cavity occupied by the alkyl radical or water molecules leads to a smaller decrease in the cavity volume than does the unoccupied one.

(VII) Each methylene (or methyl) radical occupies one cavity.

(VIII) It is known that the heat of dissolution[13-17] in water of the alkyl homologues series is nearly of a constant increment for each CH_2 group of the alkyl chain. Such a relation may be applicable for SAS. Also, in the SAS aqueous solution, there is a linear relation[18] between ΔC_p (the change in heat capacity at a constant pressure) and the carbon number in SAS molecules.

In considering the molar free energy (G_H) of SAS in an aqueous solution, it is convenient to define the hypothetical state including the term of enthalpy change due to the water-solute interaction at an infinite dilution as the standard state of the Gibbs free energy ($G^0{}_H$) of SAS in water. This is the free energy for the hypothetical state in which SAS is imbedded in the cavity at the state of infinite dilution in water, but of the unit mole fraction. Therefore, $G^0{}_H$ is the standard molar free energy of SAS in the quasiclathrate solution. When the solute (the part of hydrocarbon) is allowed to occupy the cavities to form a quasiclathrate solution, it becomes a "regular solution," *i.e.*, with an ideal entropy of mixing. Accordingly, we can discuss this system by means of the entropy term alone. Also, Frank and Franks[19] have made their treatments of the water-urea-hydrocarbon system based on the entropy terms only.

Now we will derive Eqs. (1) and (2) on the basis of the above assumptions. Let us consider one mole of water containing N molecules (N=Avogadro's number), of which the w fraction is in the network position, while the $(1-w)$ fraction is the non-hydrogen-bonded water situated in the cavities. If z is the number of cavity sites per network site, then the number of total cavity sites becomes Nwz. If f_2 is the occupancy of cavity sites by water molecules, we have:

$$f_2 = \frac{(1-w)}{wz} \tag{3}$$

Here we assume that the cavity sites are independent of each other, whether occupied or not, and, further, that all the sites are occupied with equal probability by non-hydrogen-bonded water. The number of ways in which the non-hydrogen-bonded water can be distributed among the sites are:

$$\Omega_1 = \frac{Nwz!}{(f_2 Nwz)!\{(1-f_2)Nwz\}!} \tag{4}$$

Next we have to distribute the alkyl chain $C_\phi H_{2\phi+1}$ in the remaining cavities. Here, ϕ is the number of carbon atoms constituting the alkyl chain. We will denote the total number of solute molecules by N_H. Then, the ratio of the number of solute molecules to the number of cavity sites is:

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[7] A. H. Narten and S. Lindenbaum, *J. Chem. Phys.*, **51**, 1108 (1969).

[8] A. H. Narten, *J. Phys. Chem.*, **74**, 765 (1970).

[9] H. S. Frank and A. S. Quist, *J. Chem. Phys.*, **34**, 604 (1961).

[10] D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc. Ser., A*, **211**, 254 (1952).

[11] A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, **15**, 161 (1953).

[12] F. Franks and D. J. G. Ives, *Quart. Rev.*, **20**, 1 (1966).

[13] J. M. Corkill, J. F. Goodman, and J. R. Tate, *Trans. Faraday Soc.*, **63**, 773 (1967).

[14] J. A. V. Butler, *ibid.*, **33**, 229 (1937).

[15] R. Aveyard and R. W. Mitchell, *ibid.*, **64**, 1757 (1968).

[16] J. M. Corkill, J. F. Goodman, and J. R. Tate, *ibid.*, **65**, 1742 (1969).

[17] F. Franks and B. Watson, *ibid.*, **65**, 2339 (1969).

[18] K. Tamaki, Y. Isomura, and Y. Ohara, Preprints for the 26th Meeting of the Chemical Society of Japan, (April 1972), paper 1G19, (p. 508).

[19] H. S. Frank and F. Franks, *J. Chem. Phys.*, **48**, 4746 (1968).

$$f_{\mathrm{H}} = \frac{N_{\mathrm{H}}}{Nwz} \tag{5}$$

According to our seventh assumption, each CH_2 (or CH_3) of the alkyl chain occupies one cavity site. Therefore, the number of ways of occupation is difrent according to the length of the chain.

First, we will consider the case of the methyl radical, *i.e.*, $\phi=1$. In this case, the number of states is:

$$\Omega_{\mathrm{CH_3}} = \frac{\{(1-f_2)Nwz\}!}{(f_{\mathrm{H}}Nwz)!\{(1-f_2-f_{\mathrm{H}})Nwz\}!} \tag{6}$$

In the case of the ethyl radical ($\phi=2$), the CH_2-adjacent to CH_3 must, naturally, occupy the neighboring cavity site. Therefoe, we have, as the number of ways to distribute the second carbon atom (CH_2) in the remaining cavities:

$$\{(\zeta-1)(1-f_2-2f_{\mathrm{H}})\}^{f_{\mathrm{H}}Nwz} \tag{7}$$

Here, ζ is the cavity-site-nearest-neighbors and $(1-f_2-2f_{\mathrm{H}})$ is the probability that this is vacant. Similarly, we have, as the number of states for distributing the 3rd carbon atom (CH_2) of the propyl radical:

$$\{(\zeta-1)(1-f_2-3f_{\mathrm{H}})\}^{f_{\mathrm{H}}Nwz} \tag{8}$$

and as the number of states for distributing the ϕth carbon atom (CH_2) of the $C_{\phi}H_{2\phi+1}$ radical:

$$\{(\zeta-1)(1-f_2-\phi f_{\mathrm{H}})\}^{f_{\mathrm{H}}Nwz} \tag{9}$$

Thus, the number of all possible configurations of the alkyl chain in the cavity sites becomes:

$$\Omega_2 = \frac{\{(1-f_2)Nwz\}!}{(f_{\mathrm{H}}Nwz)!\{(1-f_2-f_{\mathrm{H}})Nwz\}!}[\{(\zeta-1)(1-f_2-2f_{\mathrm{H}})\}\{(\zeta-1)(1-f_2-3f_{\mathrm{H}})\}\cdots\{(\zeta-1)(1-f_2-\phi f_{\mathrm{H}})\}]^{f_{\mathrm{H}}Nwz} \tag{10}$$

The total number of possible configurations for the system containing N_{H} solute molecules (of $C_{\phi}H_{2\phi+1}$) and N water molecules, of which the f_2 fraction is in the cavity, is given by $\Omega=\Omega_1\cdot\Omega_2$ or by:

$$\Omega = \frac{(Nwz)!}{(f_2Nwz)!(f_{\mathrm{H}}Nwz)!\{(1-f_2-f_{\mathrm{H}})Nwz\}!} \times[\{(\zeta-1)(1-f_2-2f_{\mathrm{H}})\}\{(\zeta-1)(1-f_2-3f_{\mathrm{H}})\}\cdots\{(\zeta-1)(1-f_2-\phi f_{\mathrm{H}})\}]^{f_{\mathrm{H}}Nwz} \tag{11}$$

By employing the approximations of Stirling's formula: $N!\cong\sqrt{2\pi N}\ (N/e)^N\cong(N/e)^N$ and the Boltzmann relationship $S^M=k\ \ln\Omega$. We obtain S^M the entropy of mixing per mole of water. Here $k=\boldsymbol{R}/N$ is the Boltzman constant, and $\boldsymbol{R}$ is the universal gas constant.

$$\begin{aligned}S^{\mathrm{M}} = \boldsymbol{R}wz[&-f_2\ln f_2-f_{\mathrm{H}}\ln f_{\mathrm{H}}-(1-f_2-f_{\mathrm{H}})\ln(1-f_2-f_{\mathrm{H}})\\&+f_{\mathrm{H}}\{(\phi-1)\ln(\zeta-1)+\ln(1-f_2-2f_{\mathrm{H}})\\&+\ln(1-f_2-3f_{\mathrm{H}})+\cdots+\ln(1-f_2-\phi f_{\mathrm{H}})\}]\end{aligned} \tag{12}$$

Therefore, we obtain as the molar Gibbs free energy (G):

$$G = wG^0_{\mathrm{N}} + (1-w)G^0_{\mathrm{I}} + mG^0_{\mathrm{H}} - TS^{\mathrm{M}} \tag{13}$$

or:

$$G = G^0_{\mathrm{I}} + w\Delta G^0_{\mathrm{I}} + mG^0_{\mathrm{H}} - TS^{\mathrm{M}} \tag{14}$$

Here, G^0_{N}, G^0_{I}, and G^0_{H} are the hypothetical standard molar free energies of network molecules, cavity molecules, and SAS molecules respectively. $\Delta G^0_{\mathrm{I}}=G^0_{\mathrm{N}}-G^0_{\mathrm{I}}$, and T and m are the absolute temperature and the N_{H}/N mole ratio. By differentiating Eq. (14) with respect to w and setting $(\partial G/\partial w)_{P,T,m}=0$, we obtain:

$$\Delta G^0_{\mathrm{I}} = T\frac{\mathrm{d}S^{\mathrm{M}}}{\mathrm{d}w} \tag{15}$$

while from Eq. (12) we get:

$$\begin{aligned}\frac{\mathrm{d}S^{\mathrm{M}}}{\mathrm{d}w} = \boldsymbol{R}\Big[&\ln f_2-(1+z)\ln(1-f_2-f_{\mathrm{H}})\\&+\frac{m}{w^2z}\left\{\frac{1}{(1-f_2-2f_{\mathrm{H}})}+\frac{1}{(1-f_2-3f_{\mathrm{H}})}+\cdots\right.\\&\left.+\frac{1}{(1-f_2-\phi f_{\mathrm{H}})}\right\}+\frac{m^2}{w^2z}\left\{\frac{2}{(1-f_2-2f_{\mathrm{H}})}\right.\\&\left.+\frac{3}{(1-f_2-3f_{\mathrm{H}})}+\cdots+\frac{\phi}{(1-f_2-\phi f_{\mathrm{H}})}\right\}\Big]\end{aligned} \tag{16}$$

By substituting Eq. (16) into Eq. (15) and by assuming $f_{\mathrm{H}}\ll1$, we obtain approximately:

$$\begin{aligned}\Delta G^0_{\mathrm{I}} = \boldsymbol{R}T\Big[&\ln f_2-(1+z)\ln(1-f_2)+\frac{m(1+z)}{wz(1-f_2-f_{\mathrm{H}})}\\&+\frac{m(\phi-1)}{w^2z(1-f_2-\phi f_{\mathrm{H}}/2)}+\frac{m^2(\phi-1)(\phi+2)}{2w^2z(1-f_2-\phi f_{\mathrm{H}}/2)}\Big]\end{aligned} \tag{17}$$

Now, we can use the relation $(\partial\Delta G^0_{\mathrm{I}}/\partial p)=V_{\mathrm{fr}}-V_{\mathrm{I}}$ to obtain $(\partial w/\partial p)$ from Eq. (17). Here, V_{fr} and V_{I} mean the molar volumes of the framework water and the cavity water respectively, and we obtain $V_{\mathrm{I}}=0$ using the sixth assumption. Therefore, we obtain from Eq. (17), by differentiating both sides with respect to pressure (p), and after rearrangements the following relation:

$$\begin{aligned}-\frac{1}{(\partial w/\partial p)} = \frac{\boldsymbol{R}T}{V_{\mathrm{fr}}}\Big[&\frac{1}{w(1-w)}+\frac{z+1}{w\{w(z+1)-1\}}\\&+\frac{m(m+1)(z+1)}{w^3z^2(1-f_2-f_{\mathrm{H}})^2}+\frac{m(z+1)}{w^2z(1-f_2-f_{\mathrm{H}})}\\&+\frac{2m(\phi-1)(m\phi+2)}{w^4z^2(2-2f_2-\phi f_{\mathrm{H}})^2}+\frac{4m(\phi-1)}{w^3z(2-2f_2-\phi f_{\mathrm{H}})}\\&+\frac{m^2(\phi-1)(\phi+2)(m\phi+2)}{w^4z^2(2-2f_2-\phi f_{\mathrm{H}})^2}+\frac{2m^2(\phi-1)(\phi+2)}{w^3z(2-2f_2-\phi f_{\mathrm{H}})}\Big]\end{aligned} \tag{18}$$

From the sixth assumption, the molar volume of the solution, V, is given by the following relation:

$$V = wV_{\mathrm{fr}} + mV_{\mathrm{ion}}, \tag{19}$$

since the interstitial alkyl chain radical has no effective volume. Therefore, the effective volume of the solution consists of two parts, one the volume of framework water and the other, the molar volume of the ionic parts.

The adiabatic compressibility is thermodynamically given by the following equation: $\beta=-1/V\cdot(\partial V/\partial p)_s$. When we treat the compressibility of aqueous solutions at low concentrations, we assume that the adiabatic compressibility of solutions is nearly equal to the isothermal one, since the ratio of specific heat in water is nearly 1. Therefore, we calculate the compressibility of solutions at the isothermal condition. As the ionic parts have no structural compressibility, we have from Eq. (19) $\beta_{\mathrm{st}}=V_{\mathrm{fr}}/V\cdot(-\partial w/\partial p)$, where $(-\partial w/\partial p)$ and V are given by Eqs. (18) and (19) respectively. Here, the constant terms of derivatives are omitted for the simplicity of description. We write Eq. (19) as $-1/(\partial w/\partial p)=(\boldsymbol{R}T/V_{\mathrm{fr}})\cdot A$; therefore, we have:

$$\beta_{\mathrm{st}} = \frac{V_{\mathrm{fr}}}{V}\cdot\left(-\frac{\partial w}{\partial p}\right) = \frac{(V_{\mathrm{fr}})^2}{\boldsymbol{R}T}\cdot\frac{1}{VA} \tag{20}$$

We intend to calculate the dependency of β_{st} on the mole ratio, m. We obtain from Eq. (20), by taking logarithm $\log\beta_{\mathrm{st}}=\log\{(V_{\mathrm{fr}})^2/\boldsymbol{R}T\}-\log V-\log A$:

$$\frac{1}{\beta_{\mathrm{st}}}\cdot\frac{\mathrm{d}\beta_{\mathrm{st}}}{\mathrm{d}m} = -\left\{\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}m}+\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}m}\right\} \tag{21}$$

Here, the first term in the parentheses from Eq. (19) as:

$$\frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}m}\right) = \frac{V_{\mathrm{fr}}}{V}\cdot\left(\frac{\mathrm{d}w}{\mathrm{d}m}\right) + \frac{\bar{V}_{\mathrm{ion}}}{V} \tag{22}$$

By employing Eq. (17), we obtaine $(\mathrm{d}w/\mathrm{d}m)$ from the equilibrium conditions at the concentration m:

$$(\mathrm{d}\Delta G_{\mathrm{I}}^{\circ}/\mathrm{d}m)=(\partial\Delta G_{\mathrm{I}}^{\circ}/\partial w)(\mathrm{d}w/\mathrm{d}m)+(\partial\Delta G_{\mathrm{I}}^{\circ}/\partial m)=0$$

Now, $(\mathrm{d}w/\mathrm{d}m)$ becomes, at the limit of low concentrations, $\lim_{m\to 0}(\mathrm{d}w/\mathrm{d}m)=(\mathrm{d}w/dm)_0$, and, after some calculations, we attain the result:

$$\left(\frac{\mathrm{d}w}{\mathrm{d}m}\right)_0 = \frac{(1-w_0)}{z}\{\phi+w_0(z+1)-1\} \tag{23}$$

where w_0 is the value of w for pure water. Therefore, we obtain from Eqs. (22) and (23) the relation:

$$\frac{1}{V_0}\cdot\left(\frac{\mathrm{d}V}{\mathrm{d}m}\right)_0 = \frac{(1-w_0)}{w_0 z}\{\phi+w_0(z+1)-1\} + \frac{(\bar{V}_{\mathrm{ion}})_0}{V_0} \tag{24}$$

where $V_0(=w_0V_{\mathrm{fr}})$ and $(\bar{V}_{\mathrm{ion}})_0$ mean the molar volume of pure water and the molar volume at an infinite dilution of the ionic parts of SAS. The second term in parentheses in Eq. (21) becomes, at the limit of low concentrations:

$$\lim_{m\to 0}\left(\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}m}\right) = \frac{1}{A_0}\left(\frac{\partial A}{\partial w}\frac{\mathrm{d}w}{\mathrm{d}m}+\frac{\partial A}{\partial m}\right)_{m=0}$$

where:

$$A_0 = \frac{z}{w_0(1-w_0)\{w_0(z_0+1)-1\}},$$

$$\left(\frac{\partial A}{\partial w}\right)_0 = \frac{2w_0-1}{\{w_0(1-w_0)\}^2} - \frac{(z+1)\{2w_0(z+1)-1\}}{[w_0\{w_0(z+1)-1\}]^2},$$

and:

$$\left(\frac{\partial A}{\partial m}\right)_0 = \frac{z+1}{w_0\{w_0(z+1)-1\}} + \frac{z+1}{w_0{}^2z\{w_0(z+1)-1\}} + \frac{(\phi-1)}{[w_0\{w_0(z+1)\}]^2} + \frac{2(\phi-1)}{w_0{}^2\{w_0(z+1)-1\}}.$$

After some computation, we finally obtain the relaton:

$$\left(-\frac{\mathrm{d}\beta_{\mathrm{st}}}{\mathrm{d}m}\right)_0 = \beta_{\mathrm{st}}^0\left[\frac{3(1-w_0)}{w_0z} + \frac{(2w_0-1)\{w_0(z+1)-1\}}{w_0z^2} - \frac{(z+1)(1-w_0)^2\{2w_0(z+1)-1\}}{w_0z^2\{w_0(z+1)-1\}} + \frac{(1-w_0)}{w_0z\{w_0(z+1)-1\}}\right]\phi + \frac{(2w_0-1)\{w_0(z+1)-1\}^2}{w_0z^2} - \frac{(z+1)(1-w_0)^2\{2w_0(z+1)-1\}}{w_0z} + \frac{(1-z)(1-w_0)}{w_0z} + \frac{(1+z)(1-w_0)}{z} - \frac{(1-w_0)}{w_0z\{w_0(z+1)-1\}} + \frac{(1-w_0)\{w_0(z+1)-1\}}{w_0z} + \frac{(\bar{V}_{\mathrm{ion}})_0}{V_0} \tag{25}$$

where $\beta^0{}_{\mathrm{st}}$ is the structural compressibility of pure water. Using the concentration of C mol/l in place of the mole ratio, m, we obtain $(\mathrm{d}\beta_{\mathrm{st}}/\mathrm{d}C)_0=(1/55.5)\ (\mathrm{d}\beta_{\mathrm{st}}/\mathrm{d}m)_0$. Then we can obtain the theoretical relationship for the concentration dependence of the compressibility (extrapolated to infinite dilution) $(-\mathrm{d}\beta/\mathrm{d}C)_0$ in SAS solutions:

$$(\mathrm{d}\beta/\mathrm{d}C)_0 = (\mathrm{d}\beta_{\mathrm{st}}/\mathrm{d}C)_0 + (\Delta\beta_{\mathrm{ion}})_0 \tag{26}$$

where $(\Delta\beta_{\mathrm{ion}})_0$ is the decrease in the compressibility due to the ionic parts of SAS at an infinite dilution.

On the other hand, the partial molar volume at an infinite dilution being thermodynamically defined as $\bar{V}_0=\lim_{m\to 0}\left(\frac{\partial V}{\partial m}\right)_{\mathrm{N}}$ we get from Eq. (19):

$$\bar{V}_0 = V_{\mathrm{fr}}\left(\frac{\mathrm{d}w}{\mathrm{d}m}\right)_0 + (\bar{V}_{\mathrm{ion}})_0 \tag{27}$$

or, by substituting Eq. (23):

$$\bar{V}_0 = \frac{V_{\mathrm{fr}}(1-w_0)}{z}\cdot\phi + \frac{V_{\mathrm{fr}}(1-w_0)\{w_0(z+1)-1\}}{z} + (\bar{V}_{\mathrm{ion}})_0 \tag{28}$$

Numerical Computation

We[4)] have previously obtained w_0 and z as functions of the temperature using the data[5)] of Narten *et al.*; it has been shown that w_0 and z, at 30°C, are 0.808 and 0.295 respectively. The structural compressibility of pure water, β_{st}^0 is 26.7×10^{-12} cm^2/dyn[20)] at 30°C.

Generally, the hydration number of ions depends on the methods[21,22)] used. The hydration numbers for $\mathrm{SO_4^{2-}}$, as obtained by various methods, range from 4 to 16,[21–23)] and those of Na,$^+$ from 1 to 71.[22,23)] Here we used the values obtained by the ultrasonic method,[23)] *i.e.*, 16 for $\mathrm{SO_4^{2-}}$ and 4.7 for Na,$^+$ and assumed the hydration number for the $\mathrm{OSO_3^-}$ ion to be 3/4 the value(=12) for $\mathrm{SO_4^{2-}}$. Then, the hydration number for $\mathrm{OSO_3^-}$ and $\mathrm{Na^+}$ amounts to 16.7. The decrease in compressibility $(\Delta\beta_{\mathrm{ion}})_0$ due to ionic parts becomes -13.4×10^{-12} (cm^2/dyn)/(mol/l). Then, we obtain the theoretical relationship for the concentration dependence of the compressibility (extrapolated to an infinite dilution) $(-\mathrm{d}\beta/\mathrm{d}C)_0$ as a function of the carbon number, ϕ, of the alkyl group in SAS solutions:

$$(-\mathrm{d}\beta/\mathrm{d}C)_0 = (2.02\phi+6.45)\times10^{-12}\ (\mathrm{cm^2/dyn})/(\mathrm{mol}/l) \tag{29}$$

The dotted line in Fig. 4 shows this relation.

Now let us consider the partial molar volume. We assume the partial molar volume of $\mathrm{HOSO_3Na}$ to be equal to 32.0 cm^3/mol at moderate concentrations,

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where the solution is considered to contain $HOSO_3^-$ and Na^+ ions. Here, we assume the $(\bar{V}_{\text{ion}})_0$ of SAS to be equal to the partial molar volume of SHS. On this assumption, we obtain, as the theoretical relationship between the carbon number, ϕ, in SAS and the partial molar volume at an infinite dilution $(\bar{V}_0)$, the following equation:

$$\bar{V}_0 = 14.6\phi + 32.7 \ (\text{cm}^3/\text{mol}) \qquad (30)$$

The dotted line in Fig. 5 shows this relation.

Disscussion

According to the interstitial model, we can explain the linear chage in the sound velocity and compressibility *vs.* the concentration for the systems of SMS, SES, and SBS. The marked deviation from linearity of these quantities in the SHS solution (*cf.* Figs. 2 and 3) is attributable to the dissociation[24] of the HSO_4^- into H^+ and SO_4^{2-} at low concentrations. At moderate concentrations, SHS behaves as a uni-divalent electrolyte because of its dissociation into Na,+ H,+ and SO_4^{2-}. The $(d\beta/dC)$ in the SHS solution slowly decreases untill the limiting value of about -5.9×10^{-12} (cm^2/dyn)/(mol/l) is reached at *ca.* 15 mmol/l; it is considered to act as a uni-univalent electrolyte composed of HSO_4^- and Na.+

The linear dependence of $(d\beta/dC)_0$ on the carbon number ϕ in the alkyl chain can also be explained. The approximate agreement between the constant terms in Eqs. (1) and (29) may indicate that our assumption regarding the hydration number of the ionic parts (OSO_3^- and Na^+) is rather adequate.

The slope of the $(d\beta/dC)_0$ *vs.* ϕ curve, however, indicates that the theoretical dependency on the carbon number is about three times larger than the experimental value. In the theoretical calculation, we used the seventh assumption, that a cavity may be occupied by only one methylene (or methyl) radical. The experimental results may be explained by allowing one cavity to be occupied by up to three radicals. The length of the hydrogen bond in water is 2.76[25]—2.88[5] Å, the diamater of the hexagonal cavity is about 6 Å, and the cavity is wide enough to accommodate up to three methylene radicals, since the length of the C–C bond is about 1.5[26] Å.

As regards the relationship between $\bar{V}_0$ and ϕ, on the other hand, the theoretical dependency on the carbon number is nearly in agreement with the experimental value, while the constant term is different. Also, from the studies of $\bar{V}_0$[27] for the homologue series of alkylamine hydrogen halides and tetraalkylammonium salts, it has been reported that the increment per CH_3 (or CH_2) radical added to the homologue series is $\bar{V}_0$=*ca.* 16.7 ml/mol, a value which is nearly in agreement with the present results per carbon atom.

The modification of the theory to admit up to three methylene groups may decrease the slope of the $\bar{V}_0-\phi$ curves. This results that the slope deviates from the experimental results, although the avarage value of $\bar{V}_0$ may approach the experimental value.

An interstitial-solute model similar to that employed here has also been proposed by Glew[28] on the basis of studies of hydrates. Evidence of the occupation of the cavity by the solute is also given by the kinetic study in the solvolysis of *t*-butyl chloride in an alcohol–water system.[29] More direct evidence is afforded by the X-ray diffraction study of aqueous solutions.[7,8]

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