Estimation of the Amount of Hydration of Alcohols

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Introduction

The present authors have already calculated the volume of water of hydration (abbreviated to call hydration volume) of inorganic ions, assuming that both solute and hydration water are incompressible, and they have confirmed that such an assumption was permissible, for the values thus obtained ran parallel with the heat of hydration and electrostriction.[1] A similar calculation cannot however be applied in the case of hydration of alcohols in aqueous solution because the incompressibility of solute and hydration water, especially the latter, cannot be assumed. This comes chiefly from the difference between a strong interaction of ion~water dipole in the case of the aqueous electrolyte solution and a weak interaction of dipole~dipole or of hydrogen bond frequently pointed out to form in the case of aqueous solution of nonelectrolyte.[2] This problem can however be attacked from a somewhat different direction if we take up the sound velocity in aqueous solution instead of the compressibility.

Principle of Calculation

Recently, Rao[3] has pointed out that the function,

$$v^{1/3}M/D=V \qquad (1)$$

where v is the velocity of sound, M the molecular weight, and D the density, is a constant, characteristic of a pure liquid, and is additive and constitutive in that it may be computed by summing increments assigned to atoms and bonds. Lagemann and Corry[4] however proposed an alternative procedure for computing this constant, that is, there is an additivity only of what they choose to call "*bond velocities*" shown in the following table.

Table 1

Bond	Bond Increment	Bond	Bond Increment
C—H	95.2	C—Cl	230
C—C	4.25	C=C	129
C—O	34.5	C=O	186
O—H	99.0		

Now, we assume that this additivity rule also applies in the case of an ideal solution, just as the similar rule applies in the case of molecular polarization. Thus for an ideal solution

$$V_1N_1+V_2N_2=v^{1/3}\frac{M_1N_1+M_2N_2}{D} \qquad (2)$$

is assumed to hold, where N represents the molal fraction. In the case of an aqueous alcohol solution however, the above relation does not hold, because the solution is not a mere mixture of alcohol and water molecules. We may rather assume a ternary mixture composed of alcohol, bound or hydration water and free or solvent water for such a solution. Then we get the following equation instead of the equation (2),

$$V_1(N_1-x)+V_2N_2+V_1'x=v^{1/3}\frac{M_1N_1+M_2N_2}{D} \qquad (3)$$

where x and V_1' are the molal fraction and molecular sound velocity of hydration water respectively. From the equation (3), we obtain the amount of hydration per mole solute,

$$\frac{x}{N_2}M_1=\left[v^{1/3}\frac{M_1N_1+M_2N_2}{D}-(V_1N_1+V_2N_2)\right]\times M_1/V_1'V_1)N_2 \qquad (4)$$

Experimental Results and Discussions

First of all we checked the validity of the above mentioned additivity rule of bond velocity for water which differs widely in nature from other organic liquids checked by Lagemann and Corry.[4] We could confirm that

(1) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan*, **72**, 316 (1951).
(2) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945), A. L. Robinson, *J. Chem. Phys.*, **14**, 588 (1946).
(3) M. R. Rao, *J. Chem. Phys.*, **9**, 682 (1941).
(4) R. T. Lagemann, and J. E. Corry, *J. Chem. Phys.*, **10**, 739 (1942).

Table 2

Fraction by volume of heptane in mixture at 20°C.	Sound Velocity m./sec.	Density d_4^{20}	$V_1N_1+V_2N_2$	$v^{1/3}(M_1N_1+M_2N_2)/D$	% error
0.000	1039.4	0.6278	1163.2	(1163.2)	0.00
0.223	1058.4	0.6416	1245.6	1244.3	0.10
0.409	1082.3	0.6519	1314.3	1311.9	0.18
0.607	1107.1	0.6622	1387.5	1392.1	0.33
0.806	1130.1	0.6737	1461.0	1463.1	0.14
1.000	1152.4	0.6849	1532.7	(1532.7)	0.00

the equation (1) gave a numerical value of 201 for V of water while we obtained the value of 198 as twice the value of OH bond velocity. Thus we can safely apply the additivity rule for at least the pure liquids concerned.

Further we made an experimental confirmation of the equation (2). Fortunately we found data available for this purpose which has been offered by Jacobson[5] for the case of the mixture of heptane and pentane. In this case also, as is shown in Table 2, an excellent agreement can be seen between $V_1N_1+V_2N_2$ and $v^{1/3}(M_1N_1+M_2N_2)/D$.

We then proceeded to study the validity of the equation (3) or (4), for the case of aqueous alcohol solutions.

Here we employed the fixed frequency type acoustic interferometer reported in a previous paper[6] to measure the sound velocity in a liquid mixture. The sound velocity measured was shown as a linear function of concentration in Fig. 1. From this figure, we can obtain the value for v of the equation (4), for a given concentration. To estimate the value V_1' in the equation (4), we assumed that hydration of alcohol is chiefly due to the hydrogen bridge between alcohol and water molecules, and approximated the hydration water to be ice. The value V_1' can then be calculated from the equation (1) using the values for ice. Thus we obtained $V_1'=259.7$.

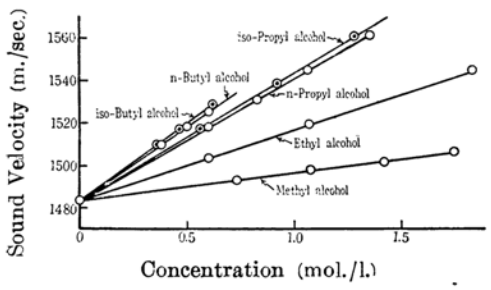

Fig. 1.—Sound velocity of aqueous alcohol solution at 20°C.

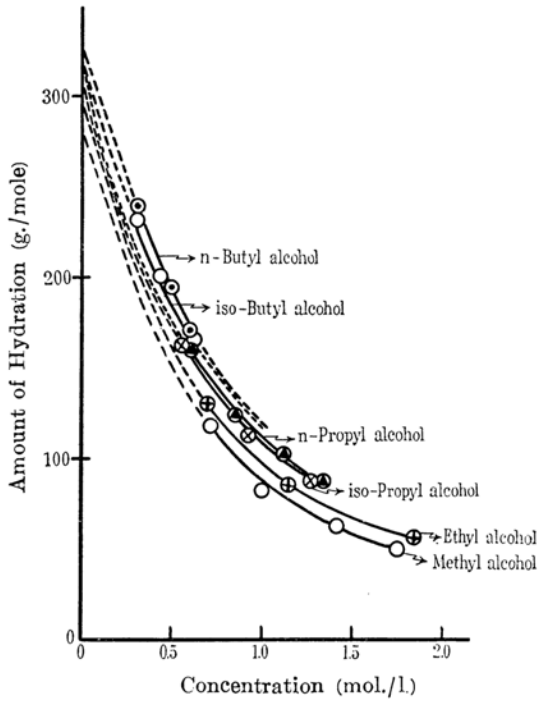

Fig. 2.—Amount of hydration per mole of alcohol at 20°C.

Using these values we calculated the amount of hydration as a function of concentration, from the equation (4). The results were shown in Fig. 2. In this figure we note a set of parallel curves for alcohol homologues. We fan also see that the amount of hydration increases with the number of carbon atoms in a molecule at constant concentration, and decreases with the concentration for one and the same alcohol which is in accord with the general behavior of the hydration. Further we compared the above value of amount of hydration (at 1 mol/liter concentration) with the known value of heat of hydration which was calculated for alcohols by Butler.[7] A

(5) B. Jacobson, *Arkiv Kemi.*, **2**, 177 (1950).
(6) T. Yasunaga, *J. Chem. Soc. Japan*, **72**, 87 (1951).
(7) J. A. V. Butler, "Structure and Molecular Forces in (a) Pure Liquids and (b) Solution", *Faraday Society*, 229 (1935).

fairly good proportionality between these quantities is noticed in Fig. 3. The fact again leads us to the conclusion that the amount of hydration hereby obtained is the quantity closely related to the actual amount of water of hydration.

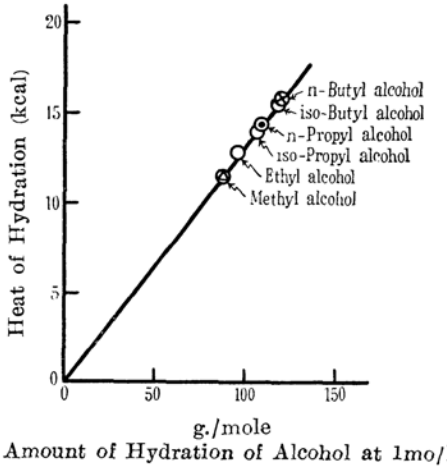

Fig. 3.—Relation between heat of hydration and amount of hydration at 1 mol/l.

Summary

The amount of hydration for alcohols in aqueous solution was estimated, assuming that the molecular sound velocity of a solution can be calculated from that for each constituent of the solution and their molal fraction, thereby regarding the water of hydration as the third component different from the free solvent and rather resembling ice as far as the sound velocity is concerned. The quantities thus calculated showed the general behavior of hydration water and also proved to be proportional to the heat of hydration.

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