Ultrasonic Studies of the Hydration of Various Compounds in an Ethanol-Water Mixed Solvent. I. Hydration of Inorganic Compounds

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The problem of the hydration of electrolytes in an aqueous solution has been studied in our laboratory for the past few years. One of the present authors[1] determined the amount of hydration by measuring the ultrasonic velocity and density on the basis of the assumption that the hydrated water molecules are incompressible because of the strong electrostatic interaction between the ion and the surrounding water. A theoretical study on this problem has also been reported by Yasunaga,[2] who assumed that the strength of interaction between the ion and the surrounding water molecules depends only on the distance between them for the ions of identical charge, and that the lower limit of the strength of interaction is that of a hydrogen bond in ice.

In general, the definitions of hydration in the various methods hitherto reported are somewhat arbitrary, and the discordance among the data of hydration numbers found in the literature suggests the need of further research. The hydration numbers obtained by various methods are compared in Table III.

It has been known that the velocity of sound in an ethanol-water mixture[3] shows unusual behavior withre spect to its concentration dependence as do such other physical properties as viscosity, volume contraction, heat capacity, heat of mixing, and sound absorption. According to Parshad,[4] a maximum in the plot of the velocity of sound against the concentration is shifted to the lower concentration side by the addition of electrolytes.

In the present study, an attempt is made to determine the degree of the hydration of electrolytes by using this phenomenon, assuming that the shift of the peak is caused only by the decrease in the amount of free water in the solution.

Theoretical

As has been mentioned above, the plot of the velocity of sound against the concentration of ethanol in water exhibits a peak, the maximum of which is shifted toward the lower concentration side by the addition of an electrolyte. Now it is assumed that this shift is caused only by the hydration, and that there is no interaction between the electrolyte dissolved and the ethanol. Therefore, the amount of hydration can be estimated from the relationship:

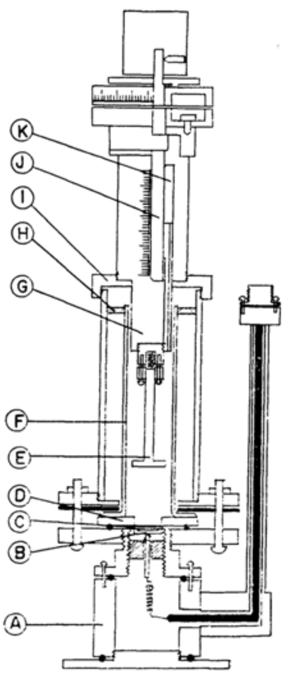

Fig. 1. Ultrasonic interferometer.

A	Base	B	Crystal supporter
C	Crystal	D	Terex glass plate
E	Reflector	F	Cell
G	Reflector shaft	H	Neoprene
I	Cell cap	J	Leading screw
K	Threaded bushing		

1) T. Yasunaga, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 87, 89 (1951); T. Sasaki, T. Yasunaga and H. Fujiwara, ibid., **73**, 181 (1952).

2) T. Yasunaga, *J. Sci. Hiroshima Univ., Ser. A*, **23**, 133 (1959).

3) P. Vigoureux, "Ultrasonics," John Wiley & Sons Inc., New York (1951), p. 116.

4) R. Parshad, *J. Acoust. Soc. Am.*, **21**, 175 (1949).

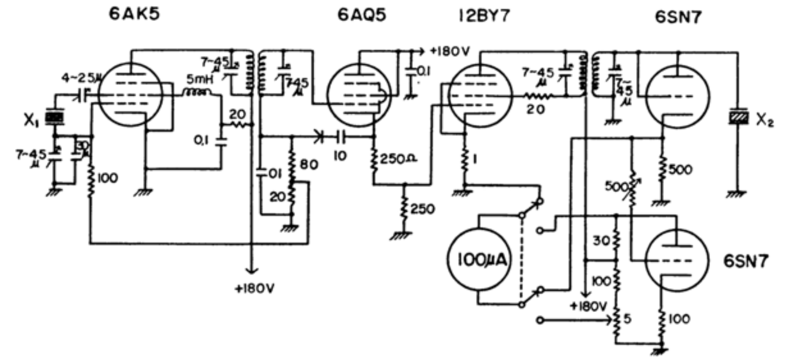

Fig. 2. Electronic circuits for the interferometer.

Resistances in kiloohm unless marked Ω; capacitances in microfarads unless marked μ (micromicrofarad)

TABLE I. SOME RECENT VALUES OF THE VELOCITY OF SOUND IN WATER AT 25°C

Author	Method	Frequency Mc./sec.	Velocity m./sec.
Hubband and Loomis[5] (1928)	Interferometer	0.5	1498.1
Seifen[6] (1938)	Optical	5	1497.15
Schreuer[7] (1939)	Optical	6~12	1497.2
Gucker and Haag[8] (1953)	Interferometer	4	1497.0
Owen and Simons[9] (1957)	Interferometer	2.5~10	1496.7
Ours (1963)	Interferometer	5	1496.8

TABLE II. SOLUBILITIES OF SOME INORGANIC COMPOUNDS IN ETHANOL[10]

Salt	Solubility
NaCl	0.065 g./100 g. ethanol (25°C)
KCl	0.022 g./100 g. ethanol (25°C)
K_2CO_3	0.095 g./100 g. solution of 90.65% ethanol (23~26°C)
$BaCl_2$	0.014 g./100 g. ethanol 97% (15°C)

$$\frac{W_{alc.0}}{W_{w.0}}=\frac{W_{alc}}{W_w-W_x}=a \qquad (1)$$

where W_{alc}, W_w and W_x are the amounts of ethanol, total water and hydrated water at the peak point respectively, and the subscript 0 refers to the values at infinite dilution with respect to the electrolyte. This equation is derived on the basis of a working hypothesis that the position of the maximum is determined only by the ratio of the amounts of ethanol and free water.

Experimental

Apparatus.—The velocity of sound was measured with an ultrasonic interferometer. A partially-exploded diagram of the interferometer-cell is show in Fig. 1. A vertical glass tube 15 cm. long and 3.8 cm. in diameter is sealed with a glass plate of 4.213 mm. thick, without grease at the bottom, below which is placed a gold plated x-cut quartz crystal with a resonance frequency of 5 Mc.

The reflector is made of a plane glass plate, which moves vertically without and rotation, and its position is determined within an accuracy of 0.002 mm. with a micrometer with a travelling range of 5 cm.

The electronic circuits are given in Fig. 2. The temperature change of the frequency was minimized by keeping the quartz crystal of the main oscillator in a thermostat. The frequency of the oscillator was measured in each experimental run with the standard frequency of the JJY station. The drift of frequency was less than 10 c./day.

The velocity of sound in water as measured with the present apparatus is given in Table I, together with the data found in the literature. The present result is in good agreement with those results, especially with those of Owen and Simons, and with those of Gucker and Haag, who used interferometers of a similar type.

Materials.—Sodium chloride, potassium chloride, potassium carbonate, and barium chloride were used

5) J. C. Hubbard and A. L. Loomis, *Phil. Mag.*, **5**, 1177 (1928).
6) N. Seifen, *Z. Physik*, **108**, 681 (1938).
7) E. Schreuer, *Akust. Z.*, **4**, 215 (1939).
8) F. T. Gucker and R. M. Haag, *J. Acoust. Soc. Am.*, **25**, 470 (1953).
9) B. B. Owen and H. L. Simons, *J. Phys. Chem.*, **61**, 479 (1957).
10) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," D. Van Nostrand Company, Inc., New York (1940).

as the electralytes. The mutual interaction between the ion and ethanol for these electrolytes is negligible, as is seen from their solubilities in ethanol as shown in Table II. Guaranteed pure reagents were used without further purification. Ethanol was purified by the usual method to a purity of 99.86%.

Results

The velocities of sound in the solutions of sodium chloride, potassium chloride, potassium carbonate and barium chloride in the mixture of ethanol and water are shown in Figs. 3—6. The concentration of ethanol at the maximum velocity of sound decreased with the increase in the concentration of electrolytes, as has been reported by Parshad.[4] The concentration of ethanol at the maximum velocity of sound is plotted against that of the electrolyte in Fig. 7. The degrees of hydration at various concentrations of the electrolytes calculated from these data by using Eq. 1 are shown in Fig. 8. The degree of hydration of sodium chloride and potassium chloride decreased slightly with the increase in the concentration, while that of potassium carbonate and that of barium chloride were constant over the range of concentration studied. The values for the degree of hydration at infinite dilution, as obtained from Fig. 8 by extrapolation, are

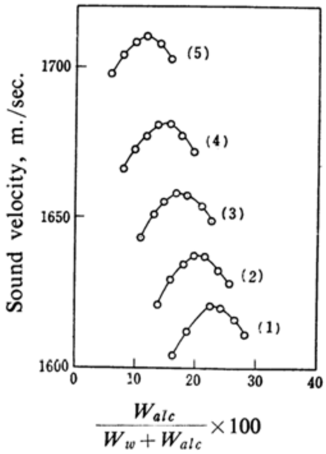

Fig. 3. Sound velocity in ethanol-water solutions of sodium chloride.

The concentration of sodium chloride in M;
(1) 0 (2) 0.689 (3) 1.478
(4) 2.227 (5) 3.063

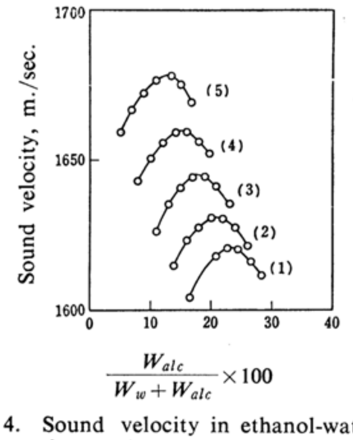

Fig. 4. Sound velocity in ethanol-water solutions of potassium chloride.

The concentration of potassium chloride in M;
(1) 0 (2) 0.692 (3) 1.417
(4) 2.215 (5) 3.021

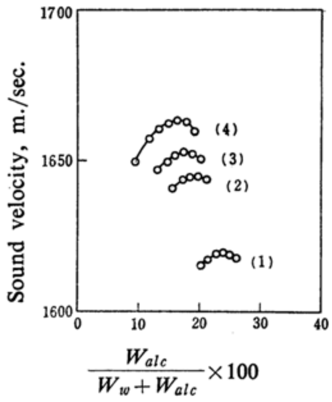

Fig. 5. Sound velocity in ethanol-water solutions of potassium carbonate.

The concentration of potassium carbonate in M;
(1) 0 (2) 0.505 (3) 0.640 (4) 0.789

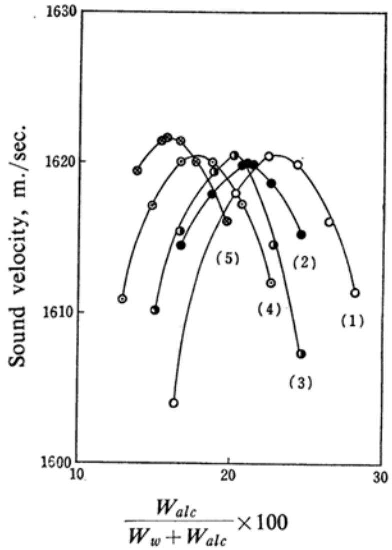

Fig. 6. Sound velocity in ethanol-water solutions of barium chloride.

The concentration of barium chloride in M;
(1) 0 (2) 0.282 (3) 0.375
(4) 0.657 (5) 0.886

TABLE III. COMPARISON OF THE HYDRATION NUMBER

Author	Method	Hydration number			
		NaCl	KCl	K_2CO_3	$BaCl_2$
Ulich[11]	Ionic entropy	7	6		14
Haggis[12]	Dielectric	6±1	5±1		
Yasunaga[1]	Compressibility	6.7	5.2	21.7	14.8
Azzam[13]	Theoretical	7.4	5.8		
Yasunaga[2]	Theoretical	2.31	1.99		
Present work	Sound velocity	8.5	7.1	24.4	14.8

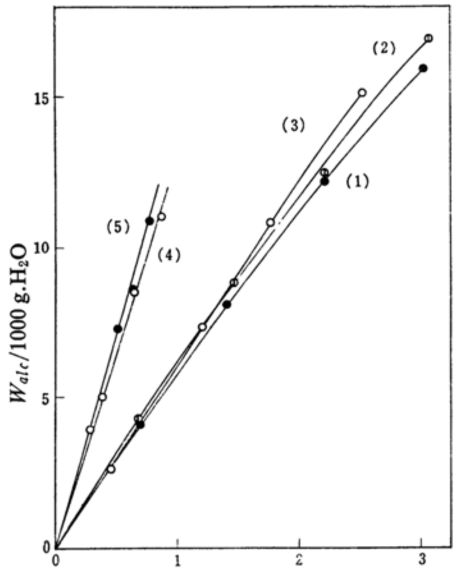

Fig. 7. Relation between the concentration of solute and that of ethanol at the maximum in the velocity of sound.
(1) KCl (2) NaCl (3) NaCl+KCl
(4) $BaCl_2$ (5) K_2CO_3

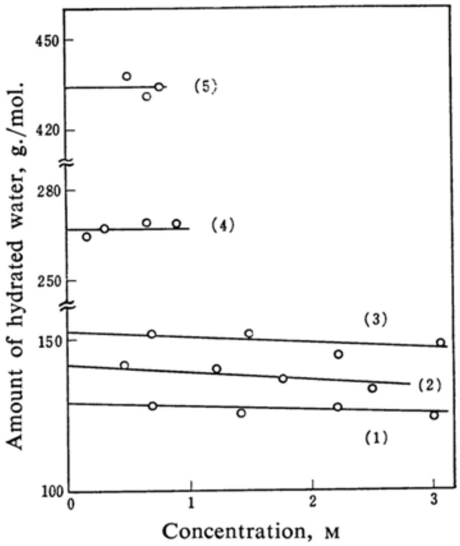

Fig. 8. Amount of hydration.
(1) KCl (2) NaCl+KCl (3) NaCl
(4) $BaCl_2$ (5) K_2CO_3

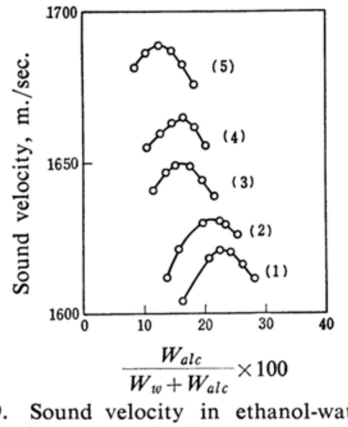

Fig. 9. Sound velocity in ethanol-water solution of sodium chloride and potassium chloride.
The concentration of each of sodium chloride and potassium chloride in M;
(1) 0 (2) 0.464 (3) 1.224
(4) 1.777 (5) 2.523

shown in Table III, where the data found in the literature are appended. As may be seen in Table III, the present result is slightly higher than the other data.

The results obtained for the mixtures of sodium chloride and potassium chloride are shown in Figs. 7, 8 and 9. As may be seen in the figures, the degree of hydration in the mixture of two electrolytes is just the arithmetic sum of those of the individual ions.

Discussion

The significant points in the present results are as follows. 1) The degree of hydration is independent of the concentration. The slight deviation from constancy for the concentrated solutions of sodium and potassium chloride can be ascribed to the ion association. 2) The degree of hydration of a mixture of two electrolytes is additive. 3) The amounts of hydration are in good agreement with those

11) H. Ulich, *Z. physik. Chem.*, **168**, 141 (1934).
12) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).
13) A. M. Azzam, *Z. Elektrochem.*, **58**, 889 (1954).

obtained by various methods. These facts confirm, at least empirically, the validity of our assumption that the position of the maximum of sound velocity is determined by the relative concentration of free water.

The extension of the research with different types of compounds is in progress; this will shed light on the problems of hydration and of the solution properties of a three-component system.

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