Ultrasonic Study on Dilute Aqueous Solutions of Diamines

Katsutaka SASAKI and Kiyoshi ARAKAWA
Research Institute of Applied Electricity, Hokkaido University, Sapporo
(Received February 21, 1972)

Ultrasonic experiments were carried out on aqueous solutions of diamines (ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, and 1,6-hexanediamine) by means of pulse technique in order to study solute-solvent interactions. Sound velocity and absorption coefficient were determined in the frequency range 15—45 MHz. The magnitude of absorption coefficient for each solution increased rapidly with concentration up to about 0.4 mol%. It is concluded that the initial rapid increase is attributed to the proton transfer in base equilibria. The absorption coefficient at the same molar concentration of each solution increases appreciably with the size of hydrocarbon chain from $-(CH_2)_2-$ to $-(CH_2)_3-$. This is ascribed to the formation of icebergs around hydrocarbon groups.

The influence of solute molecules on the structure of liquid water has been discussed for dilute aqueous solutions,[1-3] and aqueous solutions of alcohols and amines have been extensively investigated.[4-7] However, many problems remain unsolved as yet. Alcohol-water and amine-water interactions have been explained on the basis of the following: polar group-water interaction and hydrocarbon group-water interaction ("hydrophobic interaction").

We have investigated the nature of solute-solvent interactions in various aqueous solutions by means of ultrasonic measurements.[8-10] We have carried out an ultrasonic study on dilute aqueous solutions of diamines with the intention of investigating the polar group-water interaction and hydrocarbon group-water interaction. These compounds are suitable, because of their large solubility in water despite relatively large hydrocarbon groups. This report describes the behavior of ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 1,5- pentanediamine and 1,6-hexanediamine in water.

Experimental

An ultrasonic pulse technique was used for the measurement of sound velocity and absorption coefficient. The apparatus and procedures of measurements have been described.[11] Sound velocity was measured at a fixed frequency, 5 MHz. The absorption coefficient was measured in the frequency range 15—45 MHz. Temperature range was 10—20°C, the accuracy being within ±0.1°C. Ethylenediamine and 1,3-propanediamine, obtained from Wako Pure Chem. Ind. Co., Ltd., were used after being refluxed and distilled over sodium metal. The boiling points of ethylenediamine and 1,3-propanediamine were 116±0.3°C and 137±0.3°C, respectively. 1,4-Butanediamine, 1,5-pentanediamine and 1,6-hexanediamine (m.p., 40±0.5°C) were obtained from Aldlich Co., Ltd. and were used without further purification. Viscosity coefficient and density of aqueous solutions of ethylenediamine, 1,3-propanediamine and 1,6-hexanediamine were measured by means of an Ostwald type viscometer and pycnometer at 20°C. The value of pH for each diamine solution was measured by a pH meter (model MH-5A, Toa Electronics Ltd.). The values of pH for ethylenediamine and 1,6-hexanediamine were found to be 11.8±0.1 and 12.2±0.1, respectively.

Results

Sound Velocity and Compressibility. The accuracy of sound velocity data was within±1 m/sec. The data obtained for aqueous solutions of 1,3-propanediamine are plotted against concentration in Fig. 1. It was found that the velocity *vs.* concentration curves for the solutions closely resemble each other. Compressibility *vs.* concentration relations calculated from velocity and density data at 20°C are given in Fig. 2, for solutions of ethylenediamine, 1,3-propanediamine and 1,6-hexanediamine. The compressibility data are

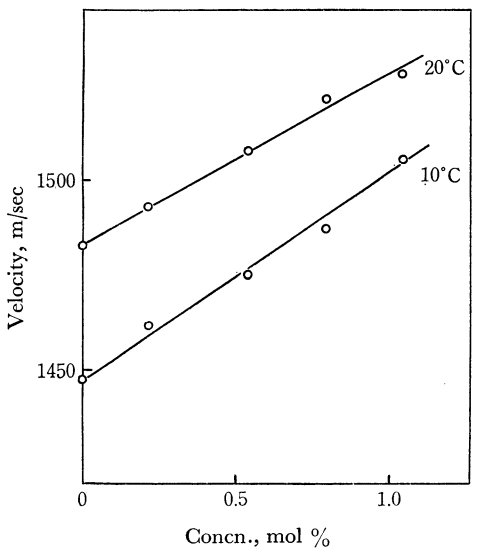

Fig. 1. Ultrasonic velocity for aqueous solutions of 1,3-propanediamine.

1) F. Franks and B. Watson, *Trans. Faraday Soc.*, **65**, 2339 (1969).
2) M. J. Blandamer, N. J. Hidden, M. C. R. Symons, and N. C. Treloar, *ibid.*, **65**, 2663 (1969).
3) F. Franks and D. J. G. Ives, *Quart .Rev.*, (London), **20**, 1 (1966).
4) M. J. Blandamer, N. J. Hidden, and M. C. R. Symons, *Trans. Faraday Soc.*, **66**, 316 (1970).
5) C. J. Burton, *J. Acoust. Soc. Amer.*, **20**, 186 (1948).
6) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).
7) J. Kozak, W. S. Knight, and W. Kauzmann, *ibid.*, **48**, 675 (1968).
8) K. Sasaki and K. Arakawa, This Bulletin, **42**, 2485 (1969).
9) K. Arakawa, N. Takenaka, and K. Sasaki, *ibid.*, **43**, 636 (1970).
10) K. Sasaki and K. Arakawa, *ibid.*, **44**, 3223 (1971).
11) K. Arakawa and N. Takenaka, *ibid.*, **39**, 447 (1966).

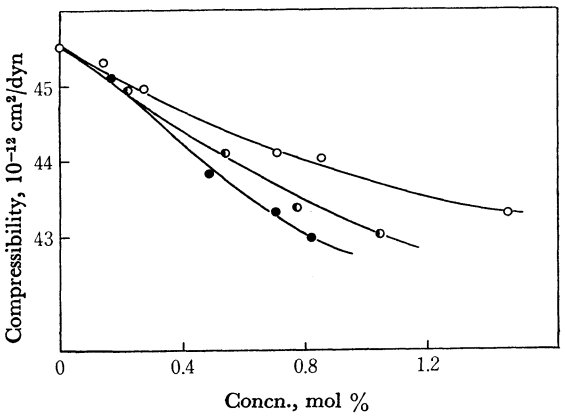

Fig. 2. Compressibility for aqueous solutions of diamines at 20°C.
○: ethylenediamine ◐: 1,3-propanediamine
●: 1,6-hexanediamine

consistent with the results obtained by Hirata and Arakawa,[12] in which the structure of icebergs is found to be more incompressible than ice-like structure in liquid water.

Ultrasonic Absorption. The data of absorption coefficient α were reproducible within $\pm 2\%$. The absorption coefficient *vs.* frequency curves for 1,3-propanediamine solutions are given in Fig. 3. The magnitude of α/f^2 decreases gradually with $\log f$ (f, frequency) for all solutions. α/f^2 *vs.* concentration curves at 35 MHz are given in Fig. 4. The results of α/f^2 *vs.* concentration for ethylenediamine are consistent with the data obtained by Blandamer *et al.*[4] We see that the magnitude of α/f^2 increases rapidly with concentration up to about 0.4 mol%, and increases slightly at higher concentrations.

Viscosity coefficient η was measured in order to obtain the values of classical absorption, which is given by

$$(\alpha/f^2)_{class.} = \frac{8\pi^2\eta}{3\rho V^3} \qquad (1)$$

where ρ is density and V sound velocity. The structural absorption is given by

$$(\alpha/f^2)_{struct.} = (\alpha/f^2)_{obsd.} - (\alpha/f^2)_{class.} \qquad (2)$$

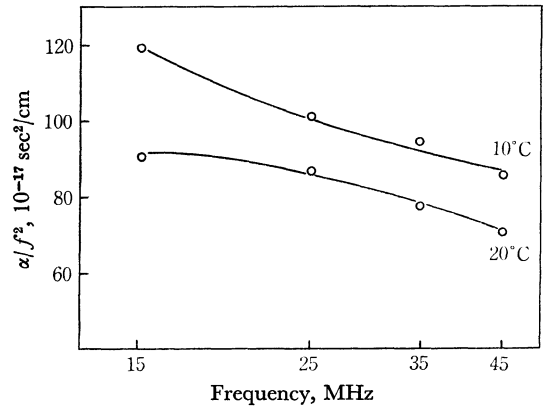

Fig. 3. Ultrasonic absorption for aqueous solutions of 1,3-propanediamine at 0.19 mol % (1 vol %).

12) F. Hirata and K. Arakawa, to be published.

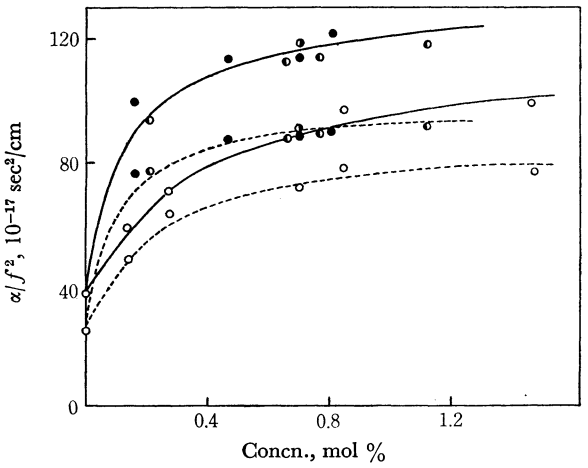

Fig. 4. Concentration dependence of ultrasonic absorption for aqueous solutions of diamines at 35 MHz. (solid line, at 10°C, broken line, at 20°C)
○: ethylenediamine, ◐: 1,3-propanediamine,
◑: 1,4-butanediamine, ●: 1,6-hexanediamine.

The results at 20°C are given in Fig. 5. Since the magnitude of classical absorption is found to increase slowly in this concentration range, the initial rapid increase of α/f^2 is attributed to the increase of $(\alpha/f^2)_{struct.}$

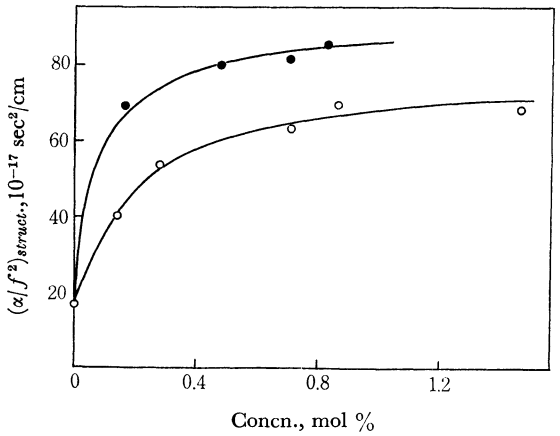

Fig. 5. Concentration dependence of structural absorption for aqueous solutions of diamines at 20°C (35 MHz).
○: ethylenediamine, ●: 1,6-hexanediamine

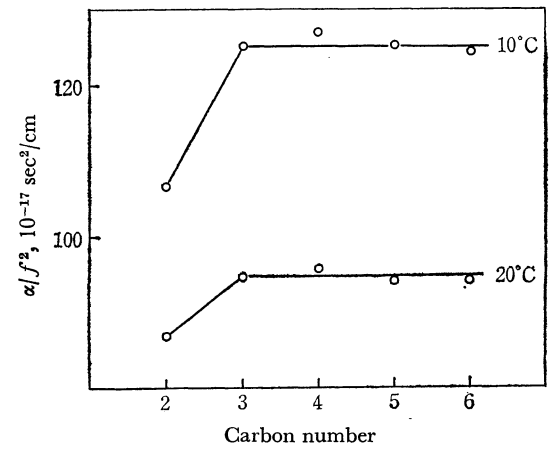

Fig. 6. Ultrasonic absorption for aqueous solutions of diamines as a function of the carbon number in solute molecules. (25 MHz).

The magnitude of α/f^2 in Fig. 6 at the same molar concentration (0.7 mol%) is plotted against the size of hydrocarbon chain of solute molecules. We see that the magnitude of α/f^2 for ethylenediamine is less than that of other higher homologues.

Discussion

Polar Group-Water Interaction. Let us first discuss the initial rapid increase of α/f^2 appearing in all diamine solutions (Fig. 4). It has been pointed out that for dilute aqueous solutions of alcohols, dioxane, urea *etc.*, the value of α/f^2 are nearly equal to those for pure water.[2,9,13] The magnitude of α/f^2 for aqueous solutions of dioxane is nearly the same as that of pure water up to about 4 mol%.[9] On the other hand, for aqueous amine solutions, there is a significant increase in extremely dilute concentration of the order of 1 mol%.[2,4,14] A similar increase of α/f^2 is observed for diamines (Fig. 4). The origin of the initial rapid increase seems to be ascribed to amino groups.

Blandamer *et al.* attributed the ultrasonic absorption caused by the addition of amine molecules to the acid-base equilibria.[14]

$$RNH_2 + H_2O \rightleftarrows RNH_3^+ + OH^- \quad (3)$$

On the other hand, Berfield and Schneider,[15] and Mckellar and Andrea[16] concluded that the hydrogen-bond formation and breaking between amine and water molecules cause the increase of α/f^2.

Alei *et al.*[17,18] showed that the proton negative shift by amino groups in aqueous solutions of ethylenediamine as well as the viscosity coefficient reaches maximum at 33 mol% concentration. They proposed that there is a stable dihydrate complex linked with hydrogen-bond in aqueous solutions of ethylenediamine. If the presence of dihydrate complex give rise to the initial excess ultrasonic absorption in dilute aqueous solutions of diamines, the magnitude of α/f^2 should increase linearly with concentration. However, the α/f^2 *vs.* concentration curves become nearly flat above 0.4 mol% after the initial rapid increase (Figs. 4 and 5). Thus we might say that the behavior of α/f^2 in dilute aqueous solutions of diamines does not result from the formation and breaking of hydrogen-bond.

It can be said that in dilute aqueous diamine solutions, the initial rapid increase of absorption and saturation of its magnitude above 0.4 mol% concentration is caused by the proton transfer of base equilibria:

$$NH_2RNH_2 + H_2O \rightleftarrows NH_2RNH_3^+ + OH^- \quad (4a)$$

$$NH_2RNH_3^+ + H_2O \rightleftarrows NH_3^+RNH_3^+ + OH^- \quad (4b)$$

The measured value of pH for each diamine solution is found to correspond to the value of pK in the second dissociation.[19] Thus, it is concluded that the cause of the initial rapid increase of absorption observed for all solutions is the dissociation given by (4b).

Hydrocarbon Group-Water Interaction. We have pointed out the initial rapid increase of α/f^2 as a general property of each diamine solution (Fig. 4). It is seen that the magnitude of α/f^2 above 0.4 mol% becomes nearly flat with concentration (Figs. 4 and 5). We see that the magnitude of α/f^2 increases with the size of hydrocarbon chain of solute molecules from $-(CH_2)_2-$ to $-(CH_2)_3-$ and exhibits a saturation effect in higher homologues (Fig. 6).

We observed[10] that the magnitude of α/f^2 for aqueous solutions of α-amino acids is independent of the size of hydrocarbon chain in solute molecules. Thus, it was concluded that the behavior of neutral α-amino acids in water is essentially similar to each other, and the structure-forming effect due to alkyl groups in amino acid molecules was cancelled out by the strong structure-breaking effect due to the dipolar field by zwitter-ions irrespective of their size.

On the other hand, for aqueous non ionic solutions (alcohols, ethers *etc.*), we see that the formation of icebergs becomes significant around hydrocarbon groups which are larger than methyl groups.[20,21] In liquid water, 1,3-dimethylurea molecules behave as a weak structure breaker but 1,3-diethylurea molecules behave as a structure former.[8]

In diamine solutions, the structure-breaking effect due to ionic dissociation of amino groups is less than that due to dipolar field by zwitter-ions in amino acid solutions. The structure-forming effect by hydrocarbon groups in diamine molecules can not be cancelled out completely by the structure-breaking effect due to ionic dissociation of amino groups. The increase of α/f^2 with the size of hydrocarbon chain from $-(CH_2)_2-$ to $-(CH_2)_3-$ in Fig. 6 can be attributed to the structure-forming effect of hydrocarbon chain in diamine molecules.

Thus, it is concluded that the iceberg formation becomes appreciable above the carbon number 3 in diamine molecules. The structure of icebergs is more incompressible than ice-like structure in liquid water (Fig. 2). This is in line with the idea of Wicke.[22] However, it should be pointed out that the iceberg formation is not dependent linearly on the size of hydrocarbon chain in these molecules, since the magnitude of α/f^2 is saturated above the carbon number of 3.

Concluding Remarks

The following conclusions are obtained from ultrasonic measurements.

1) An initial rapid increase of ultrasonic absorption for the diamine solutions is attributed to the proton

13) M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symons, *Chem. Comm.*, 342 (1966).
14) M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symons, *Trans. Faraday Soc.*, **63**, 66 (1967).
15) R. N. Berfield and W. G. Schneider, *J. Chem. Phys.*, **31**, 488 (1959).
16) J. F. Mckellar and J. H. Andrea, *Nature*, **195**, 778 (1962).
17) M. Alei, W. B. Lewis, A. B. Denison, and L. O. Morgan, *J. Chem. Phys.*, **47**, 1062 (1967).
18) M. Alei and A. E. Florin, *J. Phys. Chem.*, **72**, 550 (1968).
19) J. J. Christensen, R. M. Izatt, D. P. Wrathsll, and L. D. Hansen, *J. Chem. Soc., A*, 1212 (1969).
20) D. B. Wetlaufer, S. A. Malik, L. Stoller, and R. I. Coffin, *J. Amer. Chem. Soc.*, **86**, 509 (1964).
21) N. Takenaka and K. Arakawa, The 16th Annual Symposium on Ultrasonic and Chemical Physics, Oct., 1971 Sapporo.
22) E. Wicke, *Angew. Chem. Internat. Edit.*, **5**, 106 (1966).

transfer in base equilibria (the second dissociation).

2) The iceberg formation around hydrocarbon groups in diamine molecules become appreciable at the hydrocarbon chain of $-(CH_2)_3-$ and in higher homologues.

The authors wish to thank Mr. Nobuo Takenaka for his cooperation in this study.