BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1106—1111 (1973)

The Adiabatic Compressibility of Nonelectrolyte Aqueous Solutions in Relation to the Structures of Water and Solutions

Harumi Endo
Department of Applied Physics, Defense Academy, Yokosuka 239

(Received May 23, 1972)

The sound velocity (V) and density of aqueous solutions of urea, dimethylurea, thiourea, acetamide, acetone, and dimethylformamide have been measured, and the adiabatic compressibility (β) has been calculated at various concentrations (μ: mole fraction). The β-μ curves and V-μ curves at various temperatures have a common intersection at the fixed concentrations of μ_c^β and μ_c^V respectively. At these concentrations, the compressibility (β_c) and the sound velocity (V_c) of a solution are independent of the temperature over a certain range. When β_c is plotted against the mole ratio, r_c^β=(water)/(solute) at μ_c^β, the plots for acetyl-derivatives fall on one straight line, and those for urea-derivatives, on another line. In the cases of acetone and ethanol, the r_c^β values of these solutes coincide with the number of water molecules constituting the framework of the solid clathrate hydrate. Also, for the other aqueous solutions, it may be reasonable to conclude that the r_c^β value corresponds to the number of water molecules constituting some other type of liquid-clathrate hydrate characteristic of each solute.

A number of papers have been published on the properties of nonelectrolyte aqueous solutions from the view point of the dependence of the sound velocity (V) on the concentration (μ: mole fraction). The V-μ curves for the aqueous solutions of methanol (Me), ethanol (Et), propanol (Pr), acetone (A), *etc.*, have been known to show some unusual behaviors.

The V-μ curves of these solutions at a constant temperature exhibit maxima (maximum sound velocity: V_p) at certain concentrations[1-3] (velocity peak concentration: C_p). As both V_p and C_p decrease with an increase in the temperature, the V-μ curves for two different temperatures meet at a certain concentration (μ_c^V) ($<C_p$). Usually, a number of the V-μ curves within a certain temperature range (ΔT_c^V) have a common intersection[4,5] at a fixed concentration (μ_c^V), although Kuhnkies and Schaaffs[6] have pointed out the gradual displacement of the point of intersection with the temperature range in the case of alcohol solutions, among others. This behavior of the V-μ curves is found not only for the aqueous solutions of liquids of simple molecules, but also for those of complicated molecules such as morpholine[7] (Mo) $O(CH_2CH_2)NH$, for which the V_c at μ_c^V=0.0369 is constant in the temperature range of 20—60 °C.

In the present study, the adiabatic compressibilities, (β) of aqueous solutions of urea (U), dimethylurea (DMU), acetamide (AA), acetone (A), and dimethylformamide (DMF) are determined over the temperature range of 20—50 °C, and that of thiourea (TU), in the 50—60 °C range, by measuring the density and the sound velocity.

From these results, it is found that the β-μ curves of various temperatures also show a common intersection at a characteristic concentration (μ_c^β). At this concentration, the adiabatic compressibility (β_c) is independent of the temperature over a certain temperature range (ΔT_c^β). The parameters such as V_c, β_c, ΔT_c^V, ΔT_c^β, μ_c^V and μ_c^β are determined for these solutes in order to examine their relation with the solution structure.

When β_c is plotted against the mole ratio, r_c^β= (water)/(solute), the plots for acetyl-derivatives fall on one straight line, and those for urea-derivatives, on another line. From these $\beta_c - r_c^\beta$ curves, the properties and the dissolved state of solute in water are discussed. The reason why the peak concentration shifts to the lower-concentration side with an increase in the molecular weight in each homologue series is explained.

Experimental

Materials. The U, DMU, TU, and AA are purified by the recrystallization of reagent-grade products from absolute alcohol. To purify A and DMF, reagent-grade products are distilled twice before use.

---

[1] O. Nomoto and H. Endo, This Bulletin, **43**, 2718 (1970).

[2] W. Schaaffs, Landolt-Börnstein, Zahlenwerte und Funktionen. Gruppe II, Band5, "MolekularakustiK," Springer-Verlag, Berlin, Heidelberg, New York (1967), pp. 89—125.

[3] J. Saneyoshi, K. Kikuchi, and O. Nomoto, "Tyonpa Gizutu Binran," Nikkan Kogyo Shinbunsha, Tokyo (1966), pp. 1254—1267.

[4] A. Giacomini, *J. Acoust. Soc. Amer.*, **19**, 702 (1947).

[5] N. V. Chekalin and M. I. Schakhparonov, *Soviet Phys. Acoust.* (English Transl.) **17**, 147 (1971).

[6] R. Kuhnkies and W. Schaaffs, *Acustica*, **12**, 254 (1962).

[7] K. Mallikharjuna Swamy and P. Sitramaswamy, *J. Phys. Soc. Jap.*, **28**, 535 (1970).

Apparatus. A crystal-controlled ultrasonic interferometer operating at a frequency of 5 MHz is used to measure the sound velocity. To determine the wavelength, one hundred standing waves are used. The measuring cell containing the solutions is immersed in an oil bath, the temperature of which is kept constant within ±0.1 °C.

Results

In Figs. 1—6, the sound velocity is plotted against the mole fraction for aqueous solutions of U, DMU, AA, A, and DMF respectively, over the temperature range of ΔT=20—50 °C, while that for TU is plotted over the range of ΔT=50—60 °C. The sound velocity always increases with an increase in the concentration, reaches a maximum, and then decreases. In the cases of U and TU, no maximum was observed within the concentration range measured because of the solubility limit. It is found that V_p gradually decreases and shifts towards the lower-concentration side with an increase in the temperature (*cf.* Fig. 5 and Ref. 1). At the higher temperatures, the V-μ curves show no maximum and decrease nearly linearly.

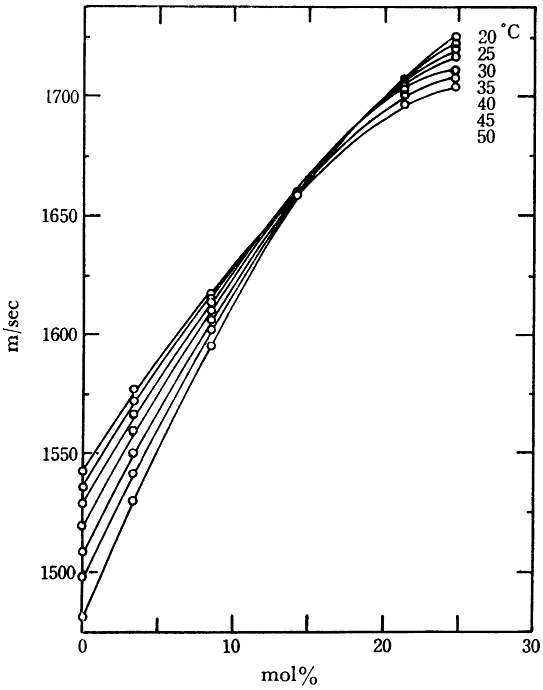

Fig. 1. Sound velocity *vs.* concentration of urea aqueous solutions.

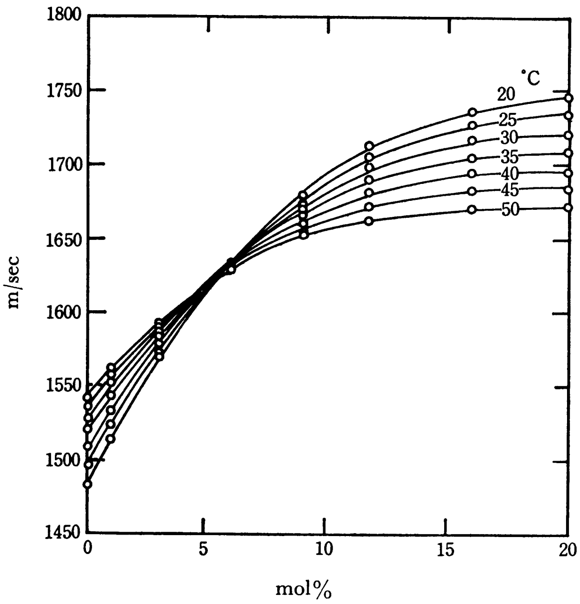

Fig. 2. Sound velocity *vs.* concentration of DMU aqueous solutions.

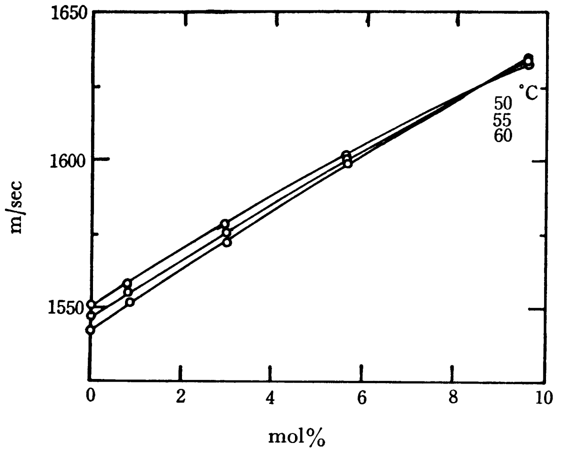

Fig. 3. Sound velocity *vs.* concentration of thiourea aqueous solutions.

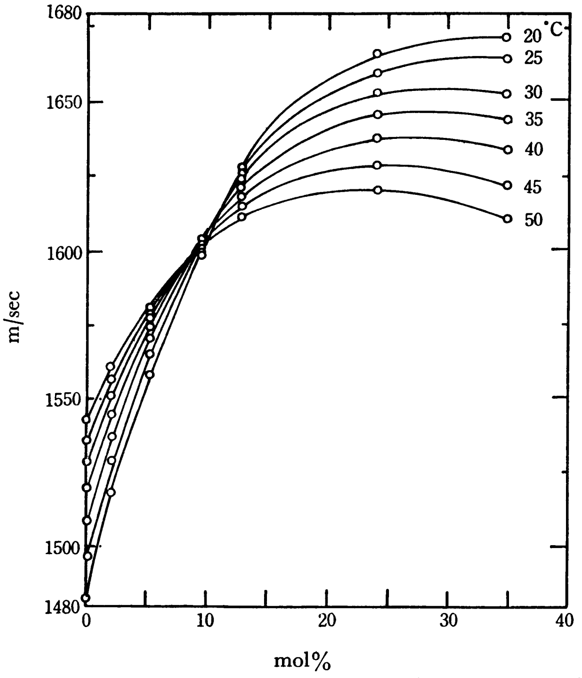

Fig. 4. Sound velocity *vs.* concentration of acetamide aqueous solutions.

For the aqueous solutions of TU and DMF, the intersection points of V-μ curves of various temperatures converge at one point over the observed temperature range (20—50 °C) (Figs. 3 and 6). For the aqueous systems of U, DMU, AA, and A (Figs. 1, 2, 4, and 5), on the other hand, the converging temperature range is rather narrower. The V_c, ΔT_c^V, and μ_c^V values at the converging point in the V-μ curves are summarized in the left-hand half of Table 1.

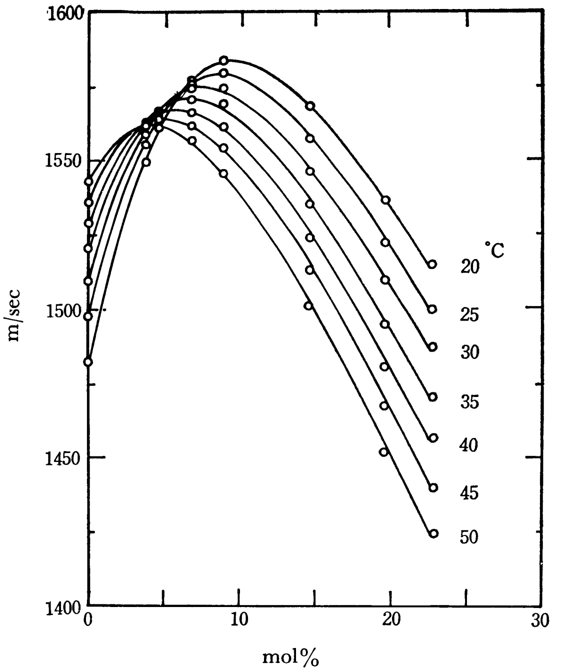

Fig. 5. Sound velocity *vs.* concentration of acetone aqueous solutions.

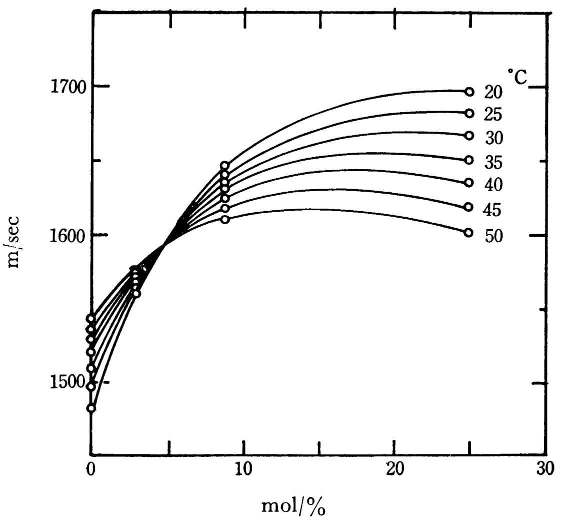

Fig. 6. Sound velocity *vs.* concentration of DMF aqueous solutions.

Figures 7—12 show the β-μ curves for aqueous solutions of U, DMU, AA, A, and DMF respectively, over the observed temperature range of 20—50 °C, and that for TU, over the range of ΔT=50—60 °C. Similarly, the β-μ curves of various temperatures intersect at one common point. The numerical values of the μ_c^β values of the β-μ curves are slightly different from those of the μ_c^V values of the V-μ curves, and the converging temperature range, ΔT_c^β, is nearly the same as ΔT_c^V. The values of β_c, μ_c^β, r_c^β, and ΔT_c^β are reproduced in the right-hand half of Table 1. Table 1 also contains the data for alcohol homologues, obtained from the data of Larionov.[8]

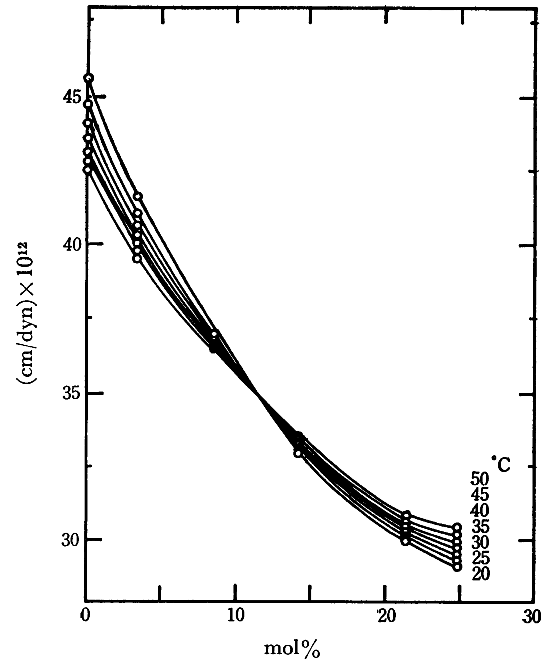

Fig. 7. Compressibility *vs.* concentration of urea aqueous solutions.

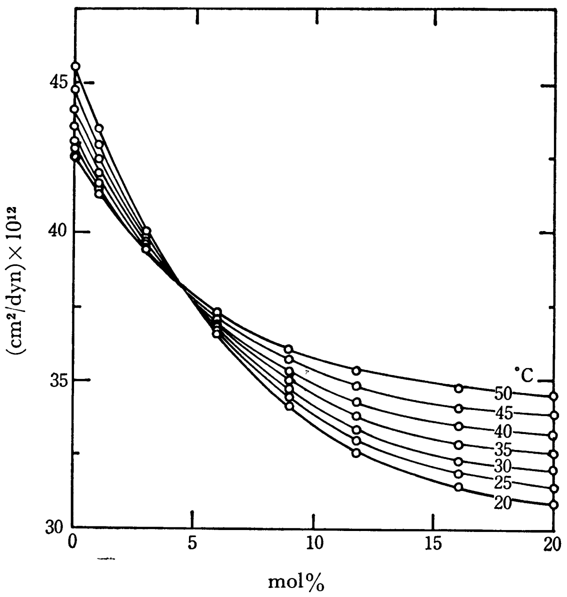

Fig. 8. Compressibility *vs.* concentration of DMU aqueous solutions.

In Fig. 13, β_c is plotted against r_c^β for various solutes. According to this plot, the solutes studied can be classified into two groups. One group consists of the urea-derivatives, for which

$$\beta_c = (0.22\, r_c^\beta + 33.3) \times 10^{-12}\ (\text{cm}^2/\text{dyn}) \qquad (1)$$

while the other group consists of the acetyl-derivatives, for which

$$\beta_c = (0.49\, r_c^\beta + 33.3) \times 10^{-12}\ (\text{cm}^2/\text{dyn}) \qquad (2)$$

They have a common intercept with the ordinate of $\beta_c^0 = 33.3 \times 10^{-12}$ (cm²/dyn).

Figure 14 shows a similar plot of V_c *vs.* r_c^V (mole ratio, = (water)/(solute) at μ_c^β). Here, however, no

---

[8] I. Larionov, Dissertation, MPPI (1951) in "The Use of Ultrasonic in Molecular Physics" by V. F. Nozdrev, translated from Russian by J. A. Carde, Pergamon Press, Oxford (1965), p. 354.

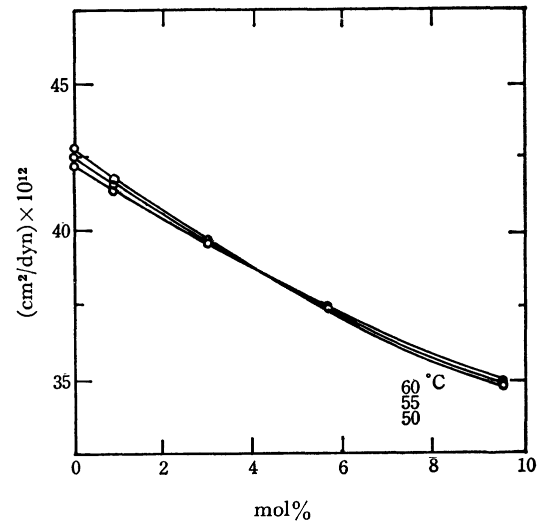

Fig. 9. Compressibility *vs.* concentration of thiourea aqueous solutions.

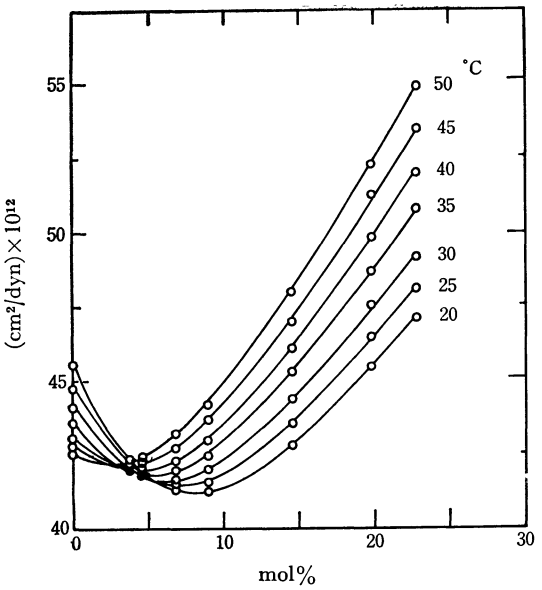

Fig. 11. Compressibility *vs.* concentration of acetone aqueous solutions.

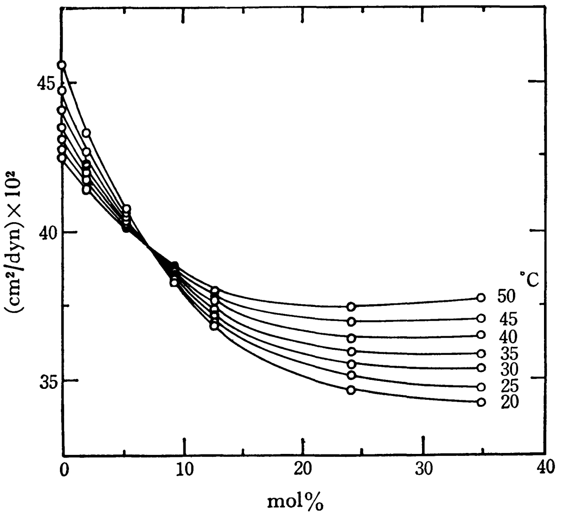

Fig. 10. Compressibility *vs.* concentration of acetamide aqueous solutions.

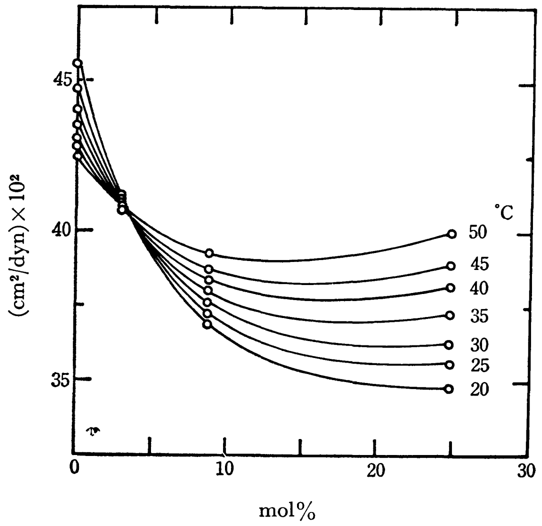

Fig. 12. Compressibility *vs.* concentration of DMF aqueous solutions.

TABLE 1. THE PARAMETERS AT A COMMON INTERSECTION OBTAINED FROM BOTH CURVES $V-\mu$ AND $\beta-\mu$.

	Data concerning sound velocity				Data concerning adiabatic compressibility			
	V_c m/sec	μ_c^V mol%	r_c^V	ΔT_c^V °C	β_c $\times 10^{-12}$ cm²/dyn	μ_c^β mol%	r_c^β	ΔT_c^β °C
U	1688	18.0	4.5	20—40	34.8	11.8	7.4	20—50
DMU	1641	6.5	14.3	20—35	37.5	5.2	18.2	20—40
TU	1628	8.8	10.3	50—60	38.7	4.0	24.0	50—60
AA	1615	11.2	7.9	20—35	39.0	8.0	11.5	20—35
A	1573	6.2	15.1	20—30	41.6	5.6	16.8	20—30
DMF	1591	4.7	20.3	20—50	39.9	4.2	22.8	20—40
Me[a]	1574	13.5	6.3	20—30	42.1	10.5	8.5	20—40
Et[a]	1605	6.8	13.7	20—40	40.7	5.5	17.2	20—30
Pr[a]	1580	5.2	18.2	0—20	41.7	4.1	23.4	10—30
Mo[b]	1565	3.7	26.1	20—60				

a) Ref. 8. b) Ref. 6.

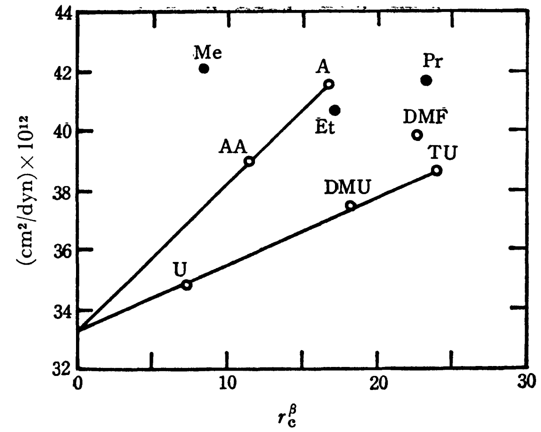

Fig. 13. β_c *vs.* r_c^β for various solutions.
○ present study, ● others study (*cf.* Ref. 8).

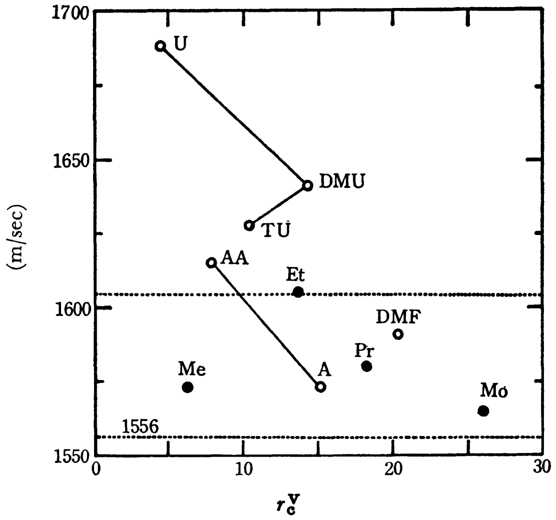

Fig. 14. V_c *vs.* r_c^V for various solutes.
The region between two dotted lines corresponds to that of 1580 m/sec±1.5%.
○ present study, ● others study (*cf.* Refs. 6 and 8)

clear relationship between them is found.

Discussion

As is well known, the X-ray diffraction studies of liquid water[9,10] suggest that it has a long-range ordered structure. The number of nearest neighbors in liquid water is slightly larger than in ice, and it increases slightly with an increase in the temperature. The framework of the structure of liquid water consists of a hexagonal ice-1 structure with numerous cavities, which can accommodate another species of water (non-hydrogen-bonded water); this structure is very stable against thermal agitation up to higher temperatures.

According to Hall,[11] the compressibility (β) of liquid water is given by:

$$\beta = \beta_\infty + \beta_{st} \tag{3}$$

where β_∞ is the instantaneous compressibility due to the compression of the molecules and the intermolecular distance, and where β_{st} is the structural compressibility due to the breakdown of intermolecular bonds accompanying the destruction of the open structure.

The mechanism of ultrasonic absorption in water has been studied by Hall[11] and by others.[12–14] By using the two-state-model theory of water, they have explained the bulk viscosity and the relaxational compressibility of water. In Hall's paper, it is assumed that β_∞ is independent of the temperature (T), *i.e.*, that $\mathrm{d}\beta_\infty/\mathrm{d}T=0$. On the basis of the X-ray diffraction data of liquid water obtained by Narten *et al.*[10], we[15] have previously studied the mechanism of ultrasonic absorption in water in relation to the liquid-water structure.

It is assumed that Eq. (3) is also applicable for nonelectrolyte aqueous solutions. The temperature derivatives of β in aqueous solutions are given by:

$$\frac{\mathrm{d}\beta}{\mathrm{d}T} = \frac{\mathrm{d}\beta_\infty}{\mathrm{d}T} + \frac{\mathrm{d}\beta_{st}}{\mathrm{d}T} \tag{4}$$

In the aqueous solutions at μ_c^β in ΔT_c^β, Eq. (4) leads to $\mathrm{d}\beta/\mathrm{d}T=0$. Accordingly, from the assumption that $\mathrm{d}\beta_\infty/\mathrm{dT}$ is zero, $\mathrm{d}\beta_{st}/\mathrm{d}T$ becomes zero also. For $\mu<\mu_c^\beta$, $\mathrm{d}\beta/\mathrm{d}T$ becomes negative from Figs. 7—12; therefore, $\mathrm{d}\beta_{st}/\mathrm{d}T$ also becomes negative. On the other hand, for $\mu>\mu_c^\beta$, $\mathrm{d}\beta_{st}/\mathrm{d}T$ is also equal to zero, because $\mathrm{d}\beta_{st}/\mathrm{d}T$ cannot become positive because of physical considerations. Therefore, it is found from Figs. 7—12 that $\mathrm{d}\beta_\infty/\mathrm{d}T>0$. A schematical illustration of the relationship between $\mathrm{d}\beta/\mathrm{d}T$ and μ is shown in Figs. 15 (a) and 15 (b).

It is assumed that the cavities contained in the framework of the water-cluster are gradually filled up by the solutes, or that the framework water in the lattice of clusters involves an exchange of solute molecules with an increase in the concentration up to μ_c^β with a maintenance of the structure of ice-1. This accompanies a decrease in the β_{st} and also in the $\mathrm{d}\beta_{st}/\mathrm{d}T$ of the solution. When a nonelectrolyte is dissolved in water, a new structure is formed of the water and solute molecules. This structure change accompanies a decrease in the compressibility of liquid water (*cf.* Fig. 15 (c)).

Also, it is assumed that the number of clusters of water molecules does not change appreciably up to μ_c^β. The instantaneous compressibility, β_∞, consists of two parts, one due to the compression of the clusters

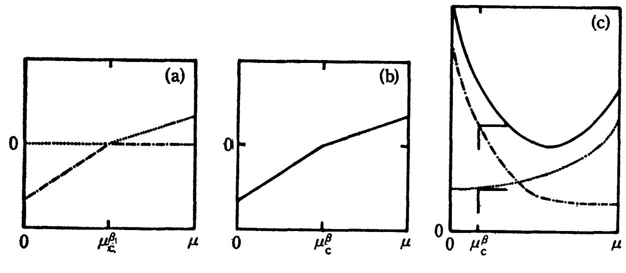

Fig. 15. $\frac{\mathrm{d}\beta_\infty}{\mathrm{d}T}$, $\frac{\mathrm{d}\beta_{st}}{\mathrm{d}T}$, $\frac{\mathrm{d}\beta}{\mathrm{d}T}$, β_∞, β_{st}, and β of aqueous solutions *vs.* concentration.

(a) …… $\frac{\mathrm{d}\beta_\infty}{\mathrm{d}T}$, —·— $\frac{\mathrm{d}\beta_{st}}{\mathrm{d}T}$

(b) —— $\frac{\mathrm{d}\beta}{\mathrm{d}T}$, Here $\frac{\mathrm{d}\beta}{\mathrm{d}T}=\frac{\mathrm{d}\beta_\infty}{\mathrm{d}T}+\frac{\mathrm{d}\beta_{st}}{\mathrm{d}T}$

(c) —— β, —·— β_{st}, …… β_∞, Here $\beta=\beta_\infty+\beta_{st}$

---

[9] J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

[10] H. Narten, M. Danford and H. Levy, *Disscus. Faraday Soc.*, **43**, 97 (1967).

[11] L. Hall, *Phys. Rev.*, **73**, 775 (1948).

and the other due to the compression of the intermolecular distance. The former does not change appreciably when we adopt the solute molecules in cavities because the elasticity of a cluster is mainly caused by the framework. Also, the latter does not change up to μ_c^β, because the number of the cluster does not change up to μ_c^β. Therefore, we may conclude that β_∞ is appreciably constant and that $d\beta_\infty/dT=0$ up to μ_c^β.

For higher concentrations, it is assumed that the increase in the number of solute molecules accompanies an increase in the number of clusters, thus decreasing β_{st} and increasing β_∞ (*cf.* Fig. 15 (c)). These two opposite effects serve to form a minimum of compressibility, or a maximum of sound velocity, at C_p.

A model of the structure of a solution has been proposed by Glew[16] on the basis of density measurements of an Et aqueous solution; there the name "solution hydrate" has been suggested. It seems better, however, that this structure of solution be named "liquid-clathrate hydrate," because the composition of this structure in Et is the same as that of the solid clathrate hydrate.[17] In this model, the solute is surrounded by a three-dimensionally hydrogen-bonded framework of water molecules. The solute molecules in the liquid-clathrate hydrate may be oriented in the cavity of a water-cluster hydrogen-bonded with framework-water molecules. In talking about the "solution hydrate"[16] or the "liquid-clathrate hydrate" in solution, it must be emphasized that the meaning of the definite composition in a hydrate does not indicate the hydration number of the solute, but is, rather, a structural unit.

It may be suggested here that the number of water molecules composing the framework of the liquid-clathrate hydrate corresponds to r_c^β for each solute. Also, the empirical relation between β_c and r_c^β may be indicative of the change in the water structure. From Eqs. (1) and (2), we obtained the following equations for the decrease in the strucutural compressibility in water caused by the solute. Here, the value of β_0, the compressibility of liquid water, is 45.6×10^{-12} cm^2/dyn at 20 °C: for the urea-derivatives,

$$\Delta\beta = \beta_0 - \beta_c = (12.3 - 0.22 r_c^\beta) \times 10^{-12}\ (\mathrm{cm^2/dyn}) \quad (5)$$

and for the acetyl-derivatives:

$$\Delta\beta = \beta_0 - \beta_c = (12.3 - 0.49 r_c^\beta) \times 10^{-12}\ (\mathrm{cm^2/dyn}) \quad (6)$$

Since we have assumed that the number of clusters in water remains appreciably constant up to the concentration of r_c^β (μ_c^β mole fraction), the β_∞ values are nearly the same for both water and the solution at this concentration; therefore, $\Delta\beta$ indicates the difference in the structural compressibility of a solution, *i.e.*, $\Delta\beta_{st}$. For the solutes with larger r_c^β values, the water strucuture is less modified, or the cavities are less occupied, so the decrease in $\Delta\beta_{st}(=\Delta\beta)$ is smaller. This explains the negative signs of the coefficients of r_c^β in Eqs. (5) and (6). By comparing the urea-derivatives and the acetyl-derivatives, it is obvious from Eqs. (5) and (6) that the coefficient of r_c^β in the latter is nearly twice that for the former. This presumably indicates that the latter fills up the cavity only, while the former also collaborates to make the framework[18] as a constitutive part.

For Et[17] and A[19,20] aqueous solutions, it may be seen in Table 1 that r_c^β is equal to the composition in the Structure-II solid clathrate hydrate with the formula of $M\cdot 17H_2O$.[21] Here, M is the guest molecule. Glew has proposed, in an Et aqueous solution over the temperature range of 0—30 °C, the existence of the liquid-clathrate-hydrate (Structure-II type of composition, $Et\cdot 17H_2O$) to account for an anomaly molar volume at $\mu = ca.\ 0.06$. For other aqueous solutions, it may be reasonable to assume that r_c^β corresponds to the number of water molecules constituting some other type of liquid-clathrate hydrate characteristic for each solute. Accordingly, the discussion and interpretation of results may be based on the following non-stoichiometric reaction scheme:

$$M + r_c^\beta H_2O \rightleftarrows M\cdot r_c^\beta H_2O \quad (7)$$

Since the number of water molecules constituting the liquid-clathrate hydrate in a homologues series increases with an increase in the molecular weight, r_c^β decreases with the molecular weight. Accordingly, μ_c^β (as well as C_p of aqueous solution) also shifts to a lower-solute concentration with an increase in the molecular weight of the homologue series.

It may be seen in Table 1 that the upper limiting temperature (T_c^u) of ΔT_c^β decreases with the addition of a non-polar group to the derivatives of urea and acetyl, so it may be reasonable to assume that the strength of the water-water hydrogen bond adjacent to the non-polar group is weaker than that of the polar group. Accordingly, it may be concluded that the framework of the liquid-clathrate hydrate adjacent to a non-polar group is selectively decomposed by the thermal agitation of molecules with a rise in the temperature. T_c^u is higher for the urea-derivatives than for the acetyl-derivatives for this same reason.

Chekalin *et al.*[5] report that V_c is independent of the sort of solute and that it is equal to 1580 m/sec within ±1.5% (*ca.* 1556—1604 m/sec). This rule is, however, not of universal validity, as may be seen in Fig. 14.

The author wishes to thank Prof. Tsunetaka Sasaki of the Tokyo Metropolitan University for his helpful discussions and generous support of this research and also Prof. Otohiko Nomoto of the Defense Academy for his valuable suggestions and discussions.

---

12) A. Smith and A. Lawson, *J. Chem. Phys.*, **22**, 351 (1954).

13) T. Litovitz and E. Carnevale, *J. Appl. Phys.*, **26**, 816 (1955).

14) C. Davis and T. Litovitz, *J. Chem. Phys.*, **42**, 2563 (1965).

15) O. Nomoto and H. Endo, This Bulletin, 44, 1519 (1971).

16) D. N. Glew, *Nature*, **195**, 698 (1962).

17) A. D. Potts and D. W. Davidson, *J. Phys. Chem.*, **69**, 996 (1965).

18) M. Abu-Hamidiyyah, *J. Phys. Chem.*, **69**, 2720 (1965).

19) A. S. Quist and H. S. Frank, *ibid.*, **65**, 560 (1961).

20) G. J. Wilson and D. W. Davidson, *Can. J. Chem.*, **41**, 264 (1963).

21) R. M. Barrer in "Non-Stoichiometric Compounds" ed. by L. Mandelcorn, Academic Press, New York and London (1964). p. 313.