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

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

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From the temperature dependency of the adiabatic compressibility in aqueous systems of nonelectrolytes, established by ultrasonic measurements, it is concluded that structural units to be termed "liquid clathrate hydrates" do exist for various systems, the concentration of the zero temperature coefficient of adiabatic compressibility representing the composition-mole-ratio, r_c^β(water/solute), for these hydrates. Hydrates with $r_c^\beta=7.2/3$ (for methanol, formamide, and urea) and 17 (for acetone and ethanol) correspond to the solid clathrate hydrates of Structures I and II respectively, while those with $r_c^\beta=24$, 28, 32, *etc*, can be explained on the basis of appropriate assumptions.

In the previous paper,[1] the sound velocity (V) and density (ρ) in aqueous solutions of urea (U), dimethylurea (DMU), thiourea (TU), acetamide (AA), acetone (A), and dimethylformamide (DMF) were measured, and the adiabatic compressibility (β) of solutions was calculated at various concentrations (μ: mole fraction) by means of the relation: $\beta=1/(\rho\cdot V^2)$. In that paper, it was found that, for each system, the V–μ curves and β–μ curves for various temperatures have a common intersection at the fixed concentrations of μ_c^V and μ_c^β respectively, the sound velocity (V_c) and adiabatic compressibility (β_c) of a solution at these concentrations being independent of the temperature over a certain range (ΔT_c^V and ΔT_c^β respectively). In the cases of aqueous solutions of A and ethanol (Et), the mole ratio r_c^V=(water/solute) at μ_c^β was equal to the number of water molecules in the framework of the solid clathrate hydrate (Structure II type). Therefore, we assumed that the structure of this type also exists in solutions, and named this structure "liquid clathrate hydrate". From these results, it may be expected that, for solutions other than A and Et, the value of r_c^β also corresponds to the number of water molecules of a liquid clathrate hydrate of another type characteristic of the respective solutes.

In the present study, the adiabatic compressibility of aqueous solutions of diethylurea (DEU), formamide (F), dimethylacetamide (DMAA), and diethylacetamide (DEAA) will be determined over the temperature range from 20 to 50 °C, and over that of hexamethylenetetramine (HMT) from 22 to 50 °C, by measuring the densities and the sound velocities of the solutions.

As in the previous paper,[1] the parameters, V_c, β_c, ΔT_c^V, ΔT_c^β, μ_c^V, and μ_c^β, are determined for these systems in order to examine their relation with the liquid structure. Two other parameters, v_c^V (volume fraction for 20 °C at μ_c^V) and v_c^β (volume fraction for 20 °C at μ_c^β), are introduced. On the basis of a model of the liquid clathrate hydrate, the properties and the dissolved states of a solute in water are discussed by means of the β_c—r_c^β relationships for various systems.

Experimental

Materials. The DEU and HMT were purified by the recrystallization of reagent-grade products from absolute alcohol. To purify F, DMAA, and DEAA, the reagent-grade products are distilled twice under reduced pressure before use.

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

Results

In Figs. 1—5, the sound velocity is plotted against the mole fraction for aqueous solutions of DEU, F, DMAA, and DEAA respectively over the temperature range of ΔT=20—50 °C and HMT over the range of ΔT=22—50 °C. All of the V–μ curves (Figs. 1—5) within a certain temperature range (ΔT_c^V) have a common intersection at a fixed concentration (μ_c^V). Although this temperature range (ΔT_c^V) is usually narrow (*ca.* 15—20 °C), this intersection is clearly discernible. The values of V_c, ΔT_c^V, and μ_c^V for the various aqueous systems here investigated are summarized in Table 1, together with the previous results[1] and a few data found in the literature.[2–6]

Figures 6—10 show the β–μ curves for aqueous solutions of DEU, F, DMAA, and DEAA respectively over the observed temperature range from 20 to 50 °C and HMT over the range of ΔT=22—50 °C. The β–μ curves for a certain temperature range also intersect at a common point. The numerical values of μ_c^β are slightly different from those of μ_c^V, while the temperature range, ΔT_c^β, is nearly the same as ΔT_c^V. The β_c, ΔT_c^β, and μ_c^β values at the converging point in the β–μ curves are summarized in Table 2. Table 2 also contains the data of the previous study[1] and those taken from other authors.[2–6]

In Fig. 11, V_c is plotted against the mole ratio r_c^V=(water/solute) at μ_c^V for various solutes. This plot shows that r_c^V shifts to a higher value with an increase in the molecular weight of solutes, but no clear

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[1] H. Endo, This Bulletin, **46**, 1106 (1973).

[2] K. Raghunath, Ph. D. Thesis, Univ. of Sri Venkateswara, Tirupati, 1968.

[3] N. Takenaka and K. Arakawa, 15th Meeting of the Onpa no Bussei to Kagaku Toron Kai, (1970), Preprints p. 64.

[4] F. Hirata and K. Arakawa, *ibid.*, 15th, p. 67.

[5] N. Takenaka and K. Arakawa, *ibid.*, 16th, 1971, p. 25.

[6] N. Kiyohara, N. Takenaka, and K. Arakawa, *ibid.*, 16th 1971, p. 16.

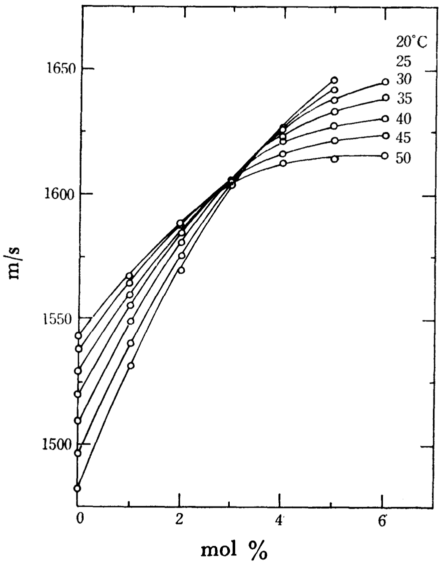


Fig. 1. Sound velocity *vs.* concentration of DEU aqueous solutions.

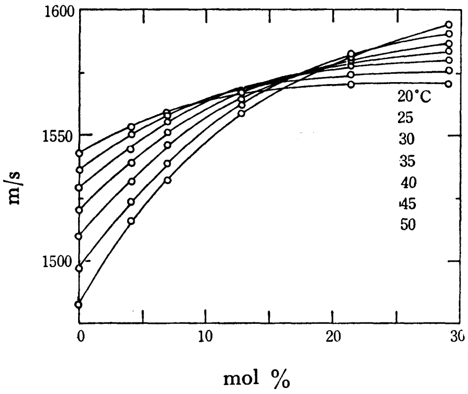


Fig. 2. Sound velocity *vs.* concentration of F aqueous solutions.

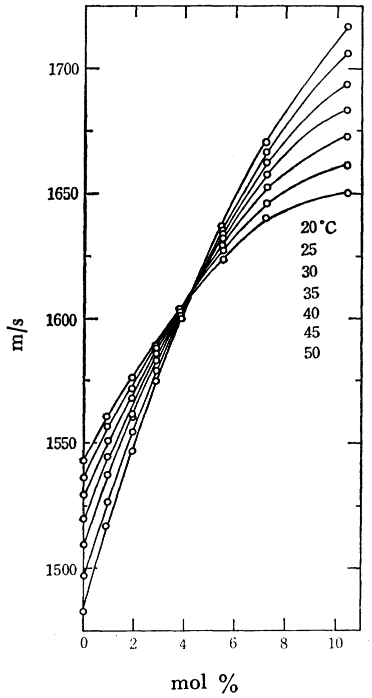


Fig. 3. Sound velocity *vs.* concentration of DMAA aqueous solutions.

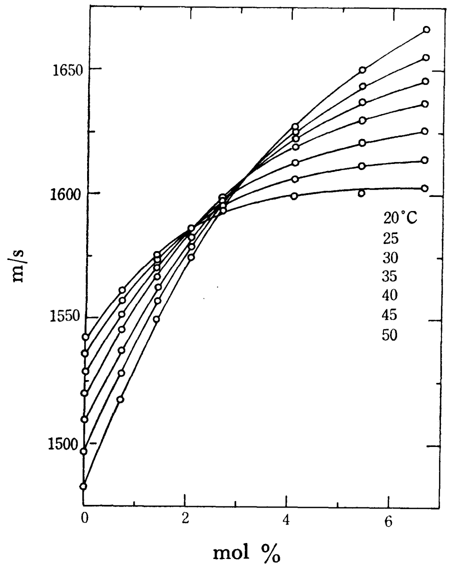


Fig. 4. Sound velocty *vs.* concentration of DEAA aqueous solutions.

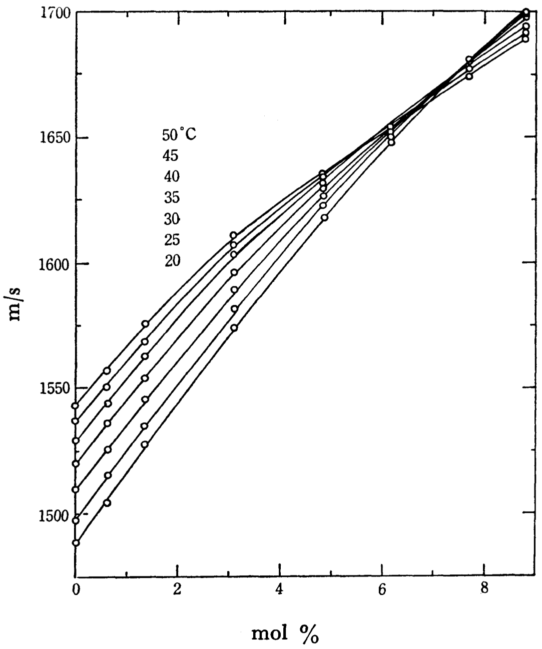


Fig. 5. Sound velocity *vs.* concentration of HMT aqueous solutions.

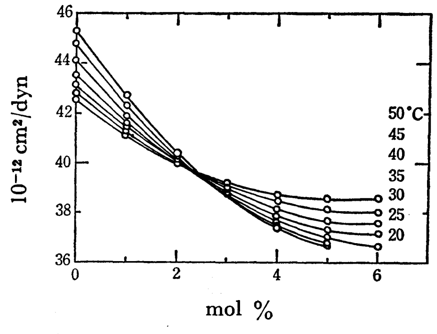


Fig. 6. Adiabatic compressibility of DEU aqueous solutions.

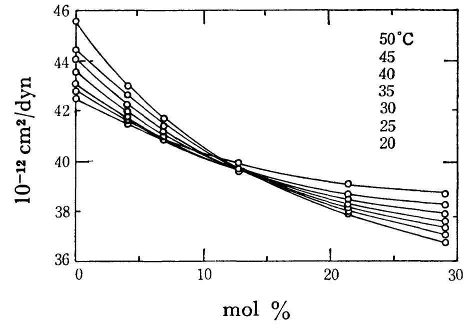


Fig. 7. Adiabatic compressibility *vs.* concentration of F aqueous solutions.

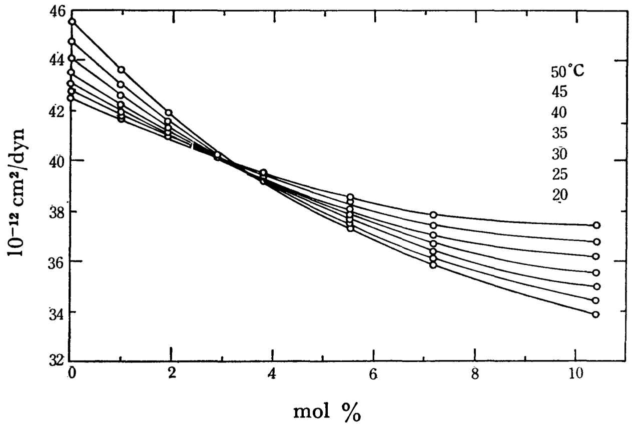


Fig. 8. Adiabatic compressibility *vs.* concentration of DMAA aqueous solutions.

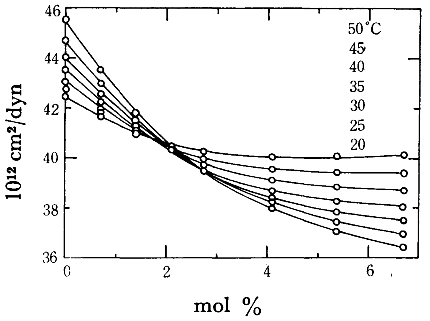


Fig. 9. Adiabatic compressibility *vs.* concentration of DEAA aqueous solutions.

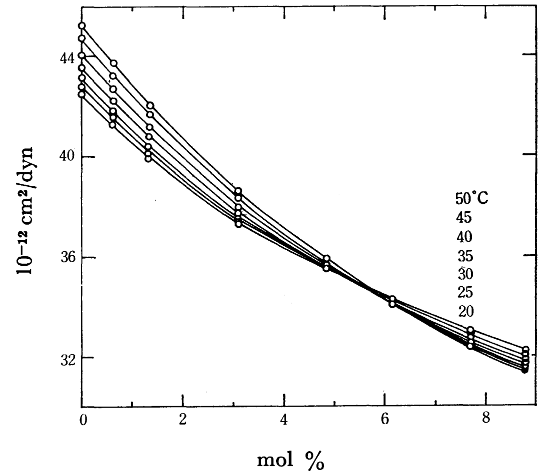


Fig. 10. Adiabatic compressibility *vs.* concentration of HMT aqueous solutions.

TABLE 1. DATA CONCERNING SOUND VELOCITY

	V_c m/s	μ_c^V mol%	r_c^V	v_c^V vol%	ΔT_c^V °C
U	1688	18.0	4.5	35.6	20—40
DMU	1641	6.5	14.3	22.9	20—35
TU	1628	8.8	10.3	22.5	50—60
AA	1615	11.2	7.9	26.3	20—35
A	1573	6.2	15.1	21.2	20—30
DMF	1591	4.7	20.3	17.5	20—50
Me	1574	13.5	6.3	25.9	20—30
Et	1605	6.8	13.7	19.1	20—40
Pr	1580	5.2	18.2	18.5	0—20
Mo	1565	3.7	26.1	15.6	20—60
DEU	1620	3.6	26.8	18.7	20—30
F	1575	17.3	4.8	31.5	25—40
DMAA	1620	4.6	21.5	20.0	20—35
DEAA	1610	3.3	29.7	19.1	20—35
HMT	1681	7.8	12.0	32.8	22—35
D[2]	1574	5.4	17.4	21.2	30—40
G[2]	1690	12.0	7.3	35.5	30—50
DGDE[3]	1610			20	10—30
TEAC[4]					
DGDM[5]	1610			18	10—30
DMSO[6]	1605	6.0	15.7	20	25—45

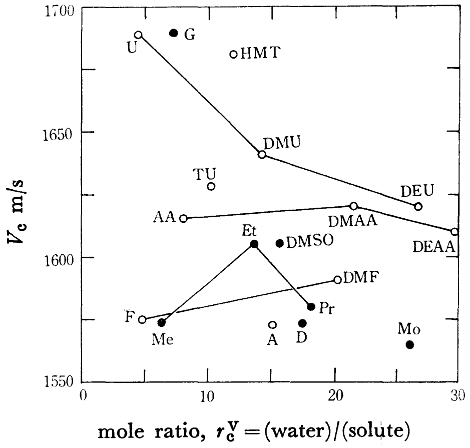


Fig. 11. V_c *vs.* r_c^V for various solutes.
○: present study, ●: others, ——: homolog series.

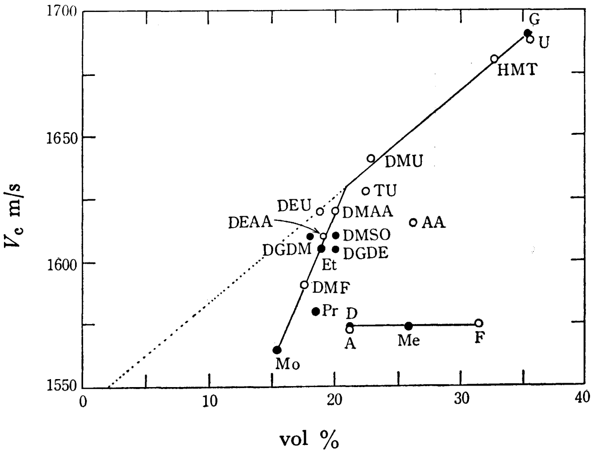


Fig. 12. V_c *vs.* v_c^V (vol % at 20 °C) for various solutes.

Table 2. Data concerning adiabatic compressiblity

	$\beta_c\times10^{-12}$ cm^2/dyn	μ_c^β mol%	r_c^β	v_c^β vol%	ΔT_c^β °C
U	34.8	11.8	7.4	25.2	20—50
DMU	37.5	5.2	18.2	19.0	20—40
TU	38.7	4.0	24.0	11.1	50—60
AA	39.0	8.0	11.5	19.7	20—35
A	41.6	5.6	16.8	19.4	20—30
DMF	39.9	4.2	22.8	15.8	20—40
Me	42.1	10.5	8.5	20.8	20—40
Et	40.7	5.5	17.2	15.8	20—30
Pr	41.7	4.1	23.4	15.1	10—30
Mo					
DEU	38.3	3.3	29.8	17.2	20—30
F	39.5	12.8	6.8	24.4	25—40
DMAA	39.5	3.5	27.6	15.7	20—40
DEAA	39.6	2.7	36.0	16.3	20—35
HMT	34.0	6.3	15.0	27.9	22—35
D[2]	40.7	4.0	24.0	16.4	30—40
G[2]	36.2	6.0	15.8	20.4	30—50
DGDE[3]					
TEAC[4]	34	3	32.6	19.9	20—35
DGDM[5]					
DMSO[6]	39.5	4	24	14	25—35

relationship is found between V_c and r_c^V, even among the items of the homolog series.

In Fig. 12, V_c is plotted against the volume fraction (v_c^V) at 20°C at μ_c^V. According to this plot, however, the points for AA, A, Me (methanol), and F markedly deviate from the plotted curve, the latter three having nearly the same sound velocity. Each of them, other than A, is the lowest-molecular-weight substance in the homolog.

It is possible that the smooth curve can be subdivided into two straight lines meeting at (1630 m/s, 21.0 vol %). One group consists of the U-homolog series, HMT, and G, for which:

$$V_c = 403\,v_c^V + 1547 \text{ (m/s)} \quad (v_c^V \text{ in volume fraction})$$

while the other consists of the F-, AA-, and alcohol-homolog series, except for the lowest-molecular-weight substances in each homolog, for which:

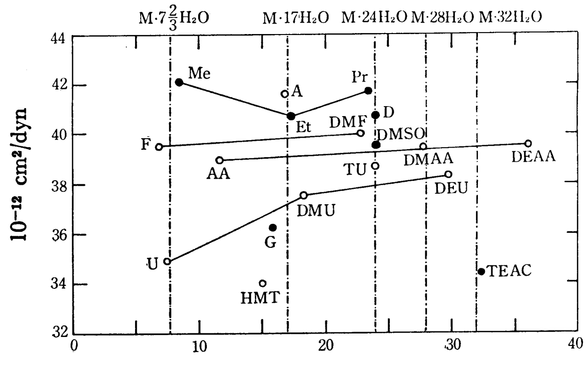
$$V_c = 1143\,v_c^V + 1390 \text{ (m/s)}$$

In Fig. 13, β_c is plotted against r_c^β for various solutes. According to this plot, the homolog series may be classified into two groups. The first group is that of the AA-homolog series, for which an approximately linear relationship between β_c and r_c^β holds:

$$\beta_c = (0.0225\,r_c^\beta + 38.7) \times 10^{-12} \text{ (cm}^2\text{/dyn)}$$

The second group is that of another homolog series, for which the β_c—r_c^β curves are not linear.

In Fig. 14, β_c is plotted against v_c^β, the volume fraction at 20 °C at μ_c^β, instead of at r_c^β. According to this plot, in a manner similar to that in the case of V_c—v_c^V plot, the solutes studied fall on a smooth curve independent of the sort of solute. Here also, as in the case of the V_c—v_c^V plot, the points for AA, A, Me and F deviate from a smooth curve, these solutes, other than A, being the lowest-molecular-weight substances in each homolog. The plots in Fig. 14 may be divided into three groups. The first group is the U-homolog series, HMT, dimethyl sulfoxide (DMSO), glycerin (G), *etc.* The second group is the F-, AA-, and alcohol-homolog series, except the lowest-molecular-weight substances in each homolog, and dioxane (D). The third group is the remaining substances (the lowest-molecular-weight substance in each homolog and A).



mole ratio, r_c^β = (water)/(solute)

Fig. 13. β_c *vs.* r_c^β for various solutes.
○: present study, ●: others, ——: homolog series.

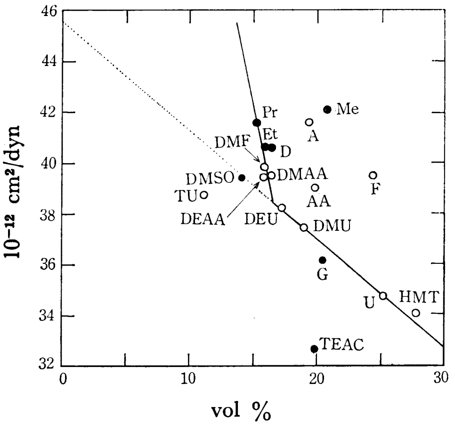


Fig. 14. β_c *vs.* v_c^β (vol % at 20°C) for various solutes.
○: present study, ●: otheres.

In the first group, a plot of β_c against v_c^β gives a straight line:

$$\beta_c = (45.6 - 42.7\,v_c^\beta) \times 10^{-12} \text{ (cm}^2\text{/dyn)} \tag{1}$$

where 45.6×10^{-12} cm²/dyn is the compressibility of water at 20 °C. The second group corresponds to the following equation:

$$\beta_c = (77.5 - 236.7\,v_c^\beta) \times 10^{-12} \text{ (cm}^2\text{/dyn)} \tag{2}$$

Here, the range of v_c^β is given by ($0.135 \leqq v_c^\beta \leqq 0.165$). The two straight lines (1) and (2) meet at a point of (38.5×10^{-12} cm²/dyn, 16.5 vol%). In the third group, however, no such relationship exists between β_c and v_c^β.

Discussion and Considerations

The X-ray diffraction studies of liquid water suggest that the water has long-range ordered structure.

The framework of the structure in liquid water consists of a hexagonal ice-1 structure with numerous cavities, which can accommodate another species of water, the non-hydrogen-bonded water.

The compressibility (β) of liquid water consists of two parts:

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

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. Therefore, the temperature derivatives of β in aqueous solution are given by:

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

It may be assumed that Eq. (3) is also applicable to nonelectrolyte aqueous solutions. Also, it may be assumed that the number of clusters of water molecules does not change appreciably up to μ_c^β, the solute molecules being all accommodated in water-clusters. The instantaneous compressibility, β_∞, consists of two parts, one due to the instantaneous compression of clusters and the other due to the compression of the intercluster distance. The former does not change appreciably because the elasticity of the cluster is mainly caused by the framework, the cavity-site water molecules, and the solute molecules adopted in water-clusters not contributing to the elasticity. Also, the latter does not change up to μ_c^β, because the number of clusters does not change up to μ_c^β: there are no free solute molecules, either. Therefore, it may be concluded that β_∞ is quite constant and that $d\beta_\infty/dT = 0$ up to μ_c^β. This solution model, accommodating all the solute molecules in water-clusters up to a certain concentration, is presumably consistent also with the partial molal volume data. It has been reported that the value of the partial molal volume of water in ethanol solution[7] is independent of the concentration up to about 10-mol% Et, nearly corresponding to our, μ_c^β, while the partial molal volume of Et diminishes up to this concentration, and then increases again. For higher concentrations, $\mu > \mu_c^\beta$, it may be assumed that the increase in the number of solute molecules accompanies the increase in the number of clusters, this decreasing β_{st} and increasing β_∞. On the basis of this model we obtain Table 3 showing the temperature derivatives of β_∞ and β_{st} for various concentration ranges. In the aqueous solutions at μ_c^β within ΔT_c^β, it can be seen from Figs. 6—10 that $d\beta/dT = 0$. As it is assumed that $d\beta_\infty/dT = 0$ for $\mu \leqq \mu_c^\beta$, it follows that $d\beta_{st}/dT = 0$ at $\mu = \mu_c^\beta$. It follows that $d\beta_{st}/dT = 0$ for $\mu > \mu_c^\beta$ also, because $\beta_{st} \doteqdot 0$ for this concentration range, according to our model. Therefore, it may be concluded that the structure of a solution at the crossing concentration for the β–μ curves consists of repeat-units with a mole ratio of r_c^β, which may be termed "liquid clathrate hydrate". The repeat-unit, presumably being a caga-like structure, may be similar to the solid clathrate hydrate known for a few solutes.

TABLE 3. THE CONCENTRATION DEPENDENCE OF TEMPERATURE DERIVATIVES OF ADIABATIC COMPRESSIBILITY IN AQUEOUS SOLUTIONS

Concentration	Model		Experimental
	$\frac{d\beta_\infty}{dT}$	$\frac{d\beta_{st}}{dT}$	$\frac{d\beta}{dT} = \frac{d\beta_\infty}{dT} + \frac{d\beta_{st}}{dT}$
$\mu < \mu_c^\beta$	0	<0	<0
$\mu = \mu_c^\beta$	0	0	0
$\mu > \mu_c^\beta$	>0	0	>0

In Fig. 13, β_c is plotted against r_c^β for all the substances listed in Table 2. As can be seen in Fig. 13, most of the solutes fall nearly on parallel (dotted) straight lines $r_c^\beta = \text{const}$. Some of these mole ratios correspond to those known in solid clathrate hydrates: we can assume the existence of liquid clathrate hydrates with the same structure, while other can be be explained on the basis of some simplified assumptions.

There are two sorts of hydrates which are known as Structures I and II respectively. Structure I includes hydrates of small molecules, such as Cl_2, SO_2, and ethylene oxide. Structure II for hydrates has been found in larger hydrating molecules, such as A, Et, and tetrahydrofuran. The unit cell of Structure I, containing 46 water molecules, consists of a close packing of two dodecahedra, consists of 20 water molecules and with a radius of 5.2 Å, and six tetradecahedra, consisting of 24 water molecules and with a radius of 5.9 Å.

If the guest molecules, M, occupy only the larger cavity, the ideal stoichiometrical composition will be $6M \cdot 46H_2O$, *i. e.*, $r_c^\beta = 7.2/3$. When the tetradecahedra containing a solute are freely floating in the liquid water in the isolated state, without composing a solid clathrate hydrate of the Structure-I type, the composition of this polyhedra is $M \cdot 24H_2O$, *i. e.*, $r_c^\beta = 24$. In the Structure II solid clathrate hydrate, the unit cell containing 136 water molecules consists of 16 dodecahedra with a radius of 4.8 Å, and 8 hexadecahedra with a radius of 6.9 Å. Here, the hexadecahedra consist of 28 water molecules. If only the larger cavity is occupied by a guest molecule, the ideal stoichiometrical composition in Type II will be $8M \cdot 136H_2O$, *i. e.*, $r_c^\beta = 17$. When the hexadecahedra containing a solute are freely floating in solution, the composition of this polyhedra is $M \cdot 28H_2O$, *i. e.*, $r_c^\beta = 28$. As can be seen in Fig. 13, $r_c^\beta = 20$ is absent in $\beta_c^\beta - r_c^\beta$ curves for various solutes. From these results, it can be concluded that the dodecahedra with a radius of 4.8—5.2 Å are too small to accommodate a solute in their cavity.

It should be noted that among the many quaternary ammonium salts, only tetrabutyl- and tetraamylammonium salts form solid clathrate hydrates, while no solid clathrate hydrate is known for tetraethylammonium chloride (TEAC). As may be seen from Ref.

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

4, TEAC has a converging point in the β–μ curves. Here, the value of r_c^β is found to be 32.6. This r_c^β, 32, presumably corresponding to that of the octadecahedra. Therefore, it may be concluded that TEAC also forms a liquid clathrate hydrate in liquid water in a manner similar to that in the cases of other nonelectrolyte solutes.

It may be noticed in Fig. 13 that a larger solute molecule exhibits a lower compressibility, β_c, for the same r_c^β, *i. e.*, for the same liquid clathrate structure. This is to be expected, because cavities accommodating larger solute molecules are more "rigid" when the polyhedra are crushed by acoustic pressure; this may correspond to the so-called "rigidity" of icebergs around a solute molecule (*e. g.*, tetraalkylammonium salts[8]).

It is known that, in some cases,[9,10] the framework-structure of water in solid clathrate hydrates may be replaced by solute molecules. Therefore, it seems reasonable to assume that the framework-structure of water in aqueous solutions may also be replaced by a solute molecule in some cases. It may be seen in Eqs. (1) and (2) that the coefficient of v_c^β in the latter is remarkably larger than that in the former. This presumably indicates that the latter group of molecules (such as the F-, AA, and alcohol-homolog series, except for the lowest-molecular-weight substances in each homolog) fill up the cavity only, while the former group (such as the U-homolog series, DMSO, and TU) also collaborates as constitutive parts in forming the framework.

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[8] E. Wicke, *Angew. Chem., Int. Ed.*, **5**, 106 (1966).

[9] D. Glew, *Nature*, **201**, 922 (1964).

[10] T. Mark and R. McMullan, *J. Chem. Phys.*, **42**, 2732 (1965).