BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2715—2719 (1972)

Ultrasonic Study of Solute-Solvent Interaction in Aqueous Solutions of Tetraalkylammonium Salts

Fumio Hirata and Kiyoshi Arakawa
Research Institute of Applied Electricity, Hokkaido University, Sapporo

(Received September 6, 1971)

Ultrasonic velocity of aqueous solutions of tetraalkylammonium chlorides was measured over wide ranges of concentration and temperature in order to study the nature of solute-solvent interactions. Adiabatic compressibility was obtained from the data of sound velocity and density. The results were discussed in terms of the influence of solutes upon the structure of liquid water. It has been shown that Me_4N^+ is a structure breaker, while n-Bu_4N^+ forms a structure or "icebergs" around the cations evidently, and that the ability of iceberg formation begins at n-Pr_4N^+. It was concluded that the icebergs have a more rigid structure than the ice-like structure in bulk water.

Aqueous solutions of tetraalkylammonium salts show abnormal behavior in various physico-chemical properties, such as partial molal volume,[1-3] activity coefficient,[4-6] heat of solution,[7-10] conductance,[11] and viscosity.[12]

The behavior has been discussed mainly in terms of water-hydrocarbon interactions leading to recognition of hydrophobic interactions.

In recent years, the important role of hydrophobic interaction for the maintenance of higher order structure of protein molecules with non-polar side chains in aqueous solutions has become increasingly clear.[13,14]

When hydrocarbon molecules are dissolved in water, the entropy of solution becomes much more negative than in corresponding non-aqueous solutions. On this basis Frank and Evans[15] postulated the formation of "icebergs" around non-polar solute molecules in water.

Recently, Wen and Saito[1] have obtained remarkable results in the measurement of partial molal volume of tetraalkylammonium bromides in aqueous solutions.

A deep minimum appears for the partial molal volume of tetrabutylammonium bromides at about 1 mol/*l*.

It ascends with rising temperature. For the sake of interpretation, formation of a *clathrate-like structure* of water molecules around tetrabutylammonium cations was suggested.

---

1) W. Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964).

2) F. Franks and H. Smith, *Trans. Faraday Soc.*, **63**, 2586 (1967).

3) B. E. Conway, R. E. Verral, and J. E. Desnoyer, *ibid.*, **62**, 2738 (1966).

4) R. M. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963).

5) W. Y. Wen, S. Saito, and C. Lee, *ibid.*, **70**, 1244 (1966).

6) S. Lindenbaum and G. E. Boyd, *ibid.*, **68**, 911 (1964).

7) S. Lindenbaum, *ibid.*, **70**, 814 (1966).

8) W. Y. Wen and J. H. Hung, *ibid.*, **74**, 170 (1970).

9) T. S. Sarma, R. K. Mohanty, and J. C. Ahluwalia, *Trans. Faraday Soc.*, **65**, 2333 (1969).

10) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969).

11) D. F. Evans and R. L. Kay, *ibid.*, **70**, 366 (1966), R. L. Kay and D. F. Evans, *ibid.*, **70**, 2325 (1966).

12) E. R. Nightingale, Jr., *ibid.*, **63**, 1381 (1959), *ibid.*, **66**, 894 (1962).

13) W. Kauzman, *Advances in Protein Chem.*, **14**, 1 (1959).

14) G. Nemethy, *Angew. Chem. Int. Ed.*, **6**, 195 (1967).

15) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

Frank and Wen,[16] on the other hand, proposed a simple model for the modification of the structure of liquid water caused by the presence of ions.

A tetraalkylammonium cation is regarded as a fairly large spherical ion and a solute with hydrophobic surface. These two factors are supposed to influence the liquid structure of water. It is of interest to study the solute-solvent interaction in aqueous solutions of these salts.

The compressibility obtained from the measurement of sound velocity is determined primarily by intermolecular forces. It is useful to measure sound velocity for the purpose of studying the structural change of liquid water induced by solute molecules.

However, there have been very few studies along this line, except that reported by Conway and Verral which was made over a limited range of temperature at low concentrations[17] and also that by Allam and Lee.[18]

We have, thus, attempted to measure ultrasonic velocity of aqueous solutions of tetraalkylammonium chlorides over wide ranges of concentration and temperature.

Experimental

Samples of tetraalkylammonium chlorides, R_4NCl (R; Me, Et, Bu) were obtained from Wako Pure Chemical Industry Co., Ltd. and tetrapropylammonium chloride from Eastman Organic Chemicals, Rochester, New York. The samples were purified by recrystallization from ethanol-ether mixtures for tetramethylammonium chloride and chloroform-ether mixtures for tetraethylammonium chloride,[1] respectively.

All salts were dried in a vacuum at 60—70°C.

Concentrations of aqueous solutions of these four salts were determined by gravimetric analysis by precipitation with $AgNO_3$. The results agreed with the values calculated from the weight of dried samples before dissolution within small errors.

Sound velocity was measured using a crystal interferometer of the usual type at 3 MHz. The cell used was the same type as that previously described.[19]

Measurements were carried out at temperature from 20 to 35°C. Temperature was controlled within ± 0.05°C.

Density was measured using a pycnometer of the usual type.

Results

Ultrasonic Velocity. The ultrasonic velocity for aqueous solutions of tetraalkylammonium salts at 3 MHz is plotted against temperature and shown in Figs. 1 (a)—(d). We see that it increases linearly with the rise in temperature for tetramethylammonium chloride solutions, but temperature dependency is seen to be reversed at a certain concentration in the case of the other three salts.

Adiabatic Compressibility. Adiabatic compressibility κ_s is obtained from the sound velocity and density of solutions. Values of κ_s for aqueous solutions of tetraalkylammonium chlorides are plotted against temperature in Figs. 2 (a)—(d).

Similarly to sound velocity *vs.* temperature curves, the temperature dependence of κ_s is reversed at a certain concentration for solutions of Et_4NCl, Pr_4NCl, and Bu_4NCl, respectively. The values of κ_s at 25°C for each 1 mol/*l* solution is shown in Fig. 3 as a function of the number of carbon atoms in each salt. It is seen that adiabatic compressibility decreases with the number of carbon atoms and that the temperature dependence is reversed between Et_4NCl and Pr_4NCl.

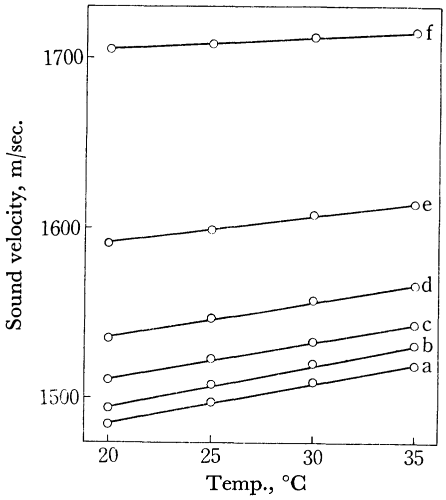

Fig. 1(a). Ultrasonic velocity of aqueous solutions of tetramethylammonium chloride. Concn. (M: mol/*l*) (a) Pure water, (b) 0.10 M, (c) 0.25 M, (d) 0.50 M, (e) 1.01 M, (f) 2.02 M.

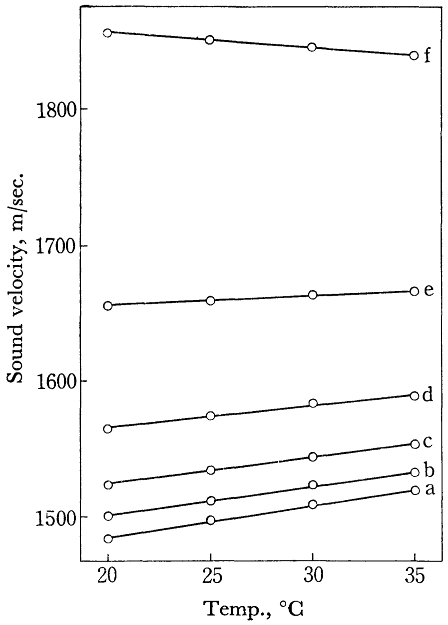

Fig. 1(b). Ultrasonic velocity of aqueous solutions of tetraethylammonium chloride. Concn. (M: mol/*l*) (a) Pure water (b) 0.13 M (c) 0.26 M, (d) 0.52 M, (e) 1.03 M, (f) 2.06 M.

---

[16] H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

[17] B. E. Conway and R. E. Verral, *J. Phys. Chem.*, **70**, 3952 (1966).

[18] D. S. Allam and W. H. Lee, *J. Chem. Soc.*, *A*, 426 (1966).

[19] O. Kiyohara and K. Arakawa, This Bulletin, **43**, 3037 (1970).

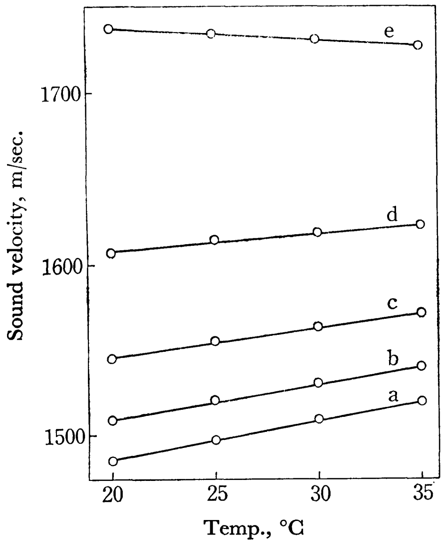

Fig. 1(c). Ultrasnonic velocity of aqueous solutions of tetrapropylammonium chloride. Concn. (M: mol/l) (a) Pure water, (b) 0.10 M, (c) 0.25 M, (d) 0.51 M, (e) 1.01 M.

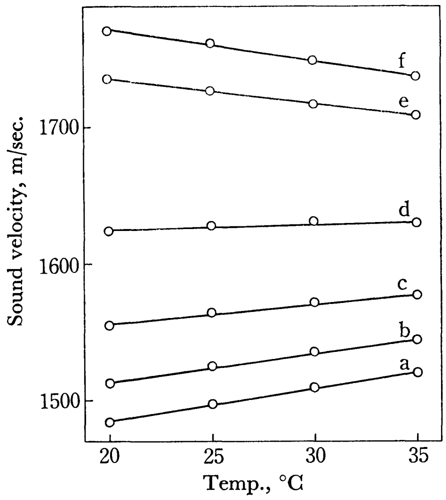

Fig. 1(d). Ultrasonic velocity of aqueous solutions of tetrabutylammonium chloride. Concn. (M: mol/l) (a) Pure water, (b) 0.08 M, (c) 0.22 M, (d) 0.44 M, (e) 0.88 M, (f) 1.15 M.

Discussions

Compressibility in Water. Water is regarded as an equilibrium mixture of two structures such as an *ice-like structure* and a *close packed structure*.[20,21]

Compressibility of liquid water is given by

$$\kappa = \kappa_\infty + \kappa_{relax.}/(1+\omega^2\tau^2) \qquad (1)$$

where κ_∞ is an instantaneous part of compressibility and $\kappa_{\mathrm{relax.}}$ a relaxational part of compressibility.[20]

The relaxation time τ corresponding to $\kappa_{\mathrm{relax.}}$ is of the order of 10^{-11} sec. The relation $\omega\tau \ll 1$ holds in the present experiment, where ω is the angular frequency. Thus, the adiabatic compressibility obtained is equal to $\kappa_\infty + \kappa_{\mathrm{relax.}}$.

With the rise in temperature, κ_∞ increases due to thermal expansion, and $\kappa_{\mathrm{relax.}}$ decreases due to thermal rupture of the ice-like structure.

Thus, the decrease of compressibility at temperatures 20—35°C is attributed to the decrease of $\kappa_{\mathrm{relax.}}$, which is dominant over the increase of κ_∞.

Structure Breaking Effect of Tetramethylammonium Cations. Compressibility decreases rapidly from pure water to aqueous solutions of tetramethylammoium chloride (Fig. 3). This might be ascribed to three effects: (1) the effect of Cl^- on the structure of water, (2) the decrease of compressibility caused by the introduction of large incompressible cations Me_4N^+, (3) the influence of Me_4N^+ on the structure of the surrounding water.

The difference between partial molal volume, $\bar{V}$, and intrinsic volume, V^0, estimated from crystal radius of

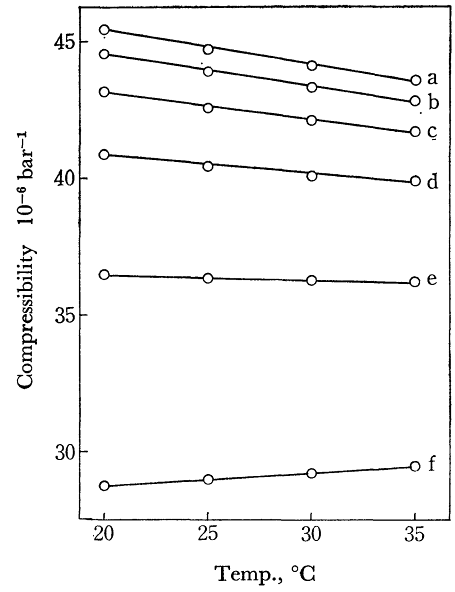

Fig. 2(a). Compressibility of aqueous solutions of tetramethylammonium chloride. Concn. (M: mol/l) (a) Pure water, (b) 0.10 M, (c) 0.25 M, (d) 0.50 M, (e) 1.01 M, (f) 2.02 M.

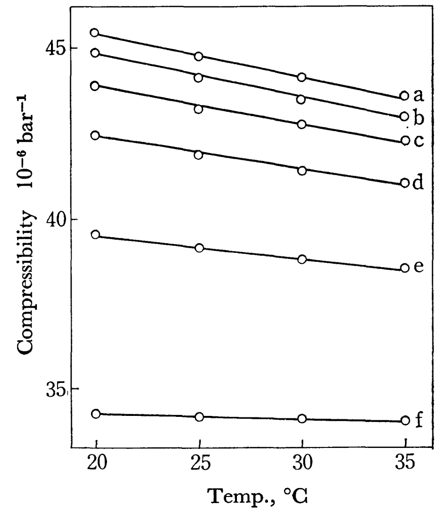

Fig. 2(b). Compressibility of aqueous solutions of tetraethylammonium chloride. Concn. (M: mol/l) (a) Pure water, (b) 0.13 M, (c) 0.26 M, (d) 0.52 M, (e) 1.03 M, (f) 2.06 M.

---

20) L. Hall, *Phys. Rev.*, **73**, 775 (1948).

21) K. Arakawa and K. Sasaki, This Bulletin, **42**, 303(1969).

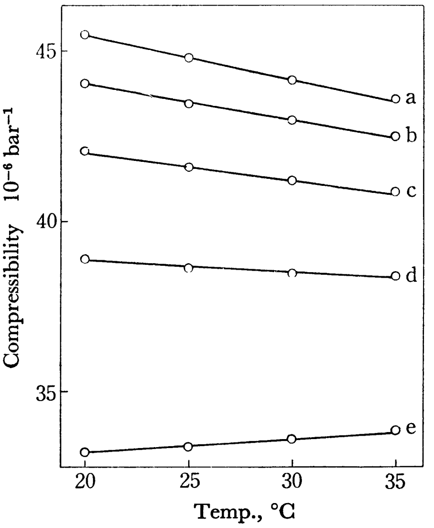

Fig. 2(c). Compressibility of aqueous solutions of tetrapropylammonium chloride. Concn. (M: mol/l) (a) Pure water, (b) 0.10 M, (c) 0.25 M, (d) 0.51 M, (e) 1.01 M.

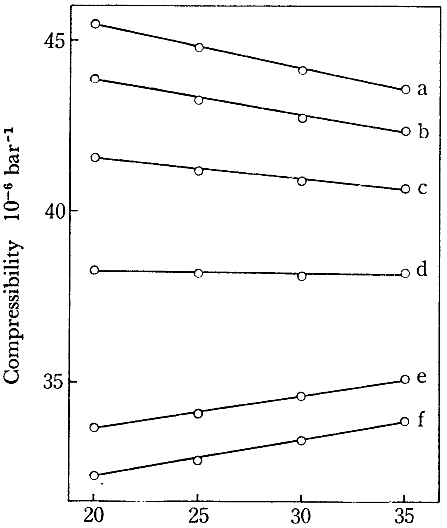

Fig. 2(d). Compressibility of aqueous solutions of tetrabutylammonium chloride. Concn. (M: mol/l) (a) Pure water, (b) 0.08 M, (c) 0.22 M, (d) 0.44 M, (e) 0.88 M, (f) 1.15 M.

ions represents the volume change of water caused by the action of ions. The values of $(V^0\text{-}\bar{V})$ of Cl^- and Me_4N^+ are estimated to be 1.7 and 21.4 cm^3/mol, respectively.[3] The effect of Cl^- is regarded to be negligible as compared with that of Me_4N^+.

Thus, only the contribution from Me_4N^+ might be taken into consideration.

The values of $(V\kappa_s)$ of an 1 mol/l solution of tetramethylammonium chloride is given by

$$V\kappa_s = N_1V_1\kappa_1 + N_2(V^0_{NMe_4^+}\kappa^0_{NMe_4^+} + V^0_{Cl^-}\kappa^0_{Cl^-}) \qquad (2)$$

where

V; volume of an 1 mol/l aqueous solution
κ_s; adiabatic compressibility of 1 mol/l aqueous solution
κ_1; average compressibility of solvent water in the solution

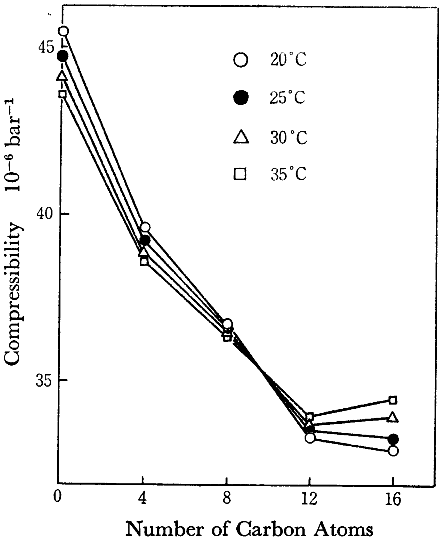

Fig. 3. Compressibility of 1 M aqueous solutions of tetraalkylammonium chlorides as a function of the number of carbon atoms in each salt.

V_1; volume of solvent water in the solution
N_1; number of moles of water in the solution
$V^0_{NMe_4^+}$; intrinsic volume of Me_4N^+
N_2; number of moles of Me_4NCl
$\kappa^0_{NMe_4^+}$; intrinsic compressibility of Me_4N^+
$V^0_{Cl^-}$; intrinsic volume of Cl^-
$\kappa^0_{Cl^-}$; intrinsic compressibility of Cl^-

In this equation, $(V^0_{Cl^-}\kappa^0_{Cl^-})$ is practically zero and can be neglected. Thus we obtain the magnitude of κ_1 by the equation

$$\kappa_1 = \frac{V\kappa_s - N_2V^0_{NMe_4^+}\kappa^0_{NMe_4^+}}{N_1V_1} \qquad (3)$$

The intrinsic volume of Me_4N^+, $V^0_{NMe_4^+}$, is estimated with large uncertainty from 90 to 105 cm^3/mol.[1–3,12]

When we use the largest value[22] 105 cm^3/mol for $V^0_{NMe_4^+}$ and the value 3×10^{-6} bar^{-1} for $\kappa^0_{NMe_4^+}$ we find the average compressibility of water in the solution at 25°C to be smaller than the compressibility in pure water at the same temperature.[27] Thus, the sharp decrease of compressibility from pure water to a 1 mol/l aqueous solution of Me_4NCl is primarily ascribed to the structure-breaking effect of Me_4N^+.

---

22) The value V_{ion} was calculated from the ionic radius in crystal r_x by the equation

$$V^0_{ion} = \frac{4}{3}\pi N_A r_x^3 \qquad (N\text{: Avogadro's number})$$

This value is supposed to be too large in the case of Me_4N^+, as compared with reported values of V_{ion}.[1–3,13,23–26]

23) L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957).

24) P. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, **53**, 301 (1957).

25) R. Mukerjee, *J. Phys. Chem.*, **65**, 740, 744 (1961).

26) E. Gleuckauf, *Trans. Faraday Soc.*, **61**, 914 (1965).

27) The value of $\kappa_{NMe_4^+}$ has not been determined. It might be estimated to be larger than 3×10^{-6} bar^{-1} which is nearly equal to the value for fused quartz, flint glass, LiCl crystal (*cf.* Cho-onpa Gijutsu Binran (Handbook for Ultrasonic Technique), Nikkan Kogyo Shinbun Co., Ltd. (1966), p. 1325). When $\kappa_{NMe_4^+}\geq3\times10^{-6}$ bar^{-1}, the value of $\kappa_1<44.7_5\times10^{-6}$ bar^{-1} which is the value for bulk water at 25°C.

This conclusion is also supported by the fact that the temperature dependence of compressibility of a 1 mol/*l* solution of Me_4NCl is smaller than that of pure water (Fig. 3).

Moreover, it is consistent with the results of studies for physico-chemical properties of the solution such as partial molal volume,[1)] heat capacity[9)], and conductivity.[11)]

Iceberg Formation Around Tetrabutylammonium Cations. Several papers have peported that Bu_4N^+ ions form icebergs around themselves.

Wen and Saito[1)] stated in 1964 that the structure of icebergs is "*clathrate like*". However, Wen and Hung[8)] stated recently that "the nature of structure promotion by hydrocarbons or tetraalkylammonium salts is not well defined". Wicke[28)] stated on the basis of NMR data that the icebergs around non-polar solutes have a "rigid" structure involving non-tetrahedral linking of H_2O molecules.

The values of κ_s of 1 mol/*l* solution of Bu_4NCl increase with rising temperature (Fig. 3).

The amount of icebergs is supposed to decrease with the rise in temperature. Thus, our result supports the idea that the icebergs around Bu_4N^+ cations have a smaller compressibility than bulk water, and that the structure of the icebergs is more rigid than ice-like structure.

The Nature of Icebergs. Conway and Verral discussed the molal adiabatic compressibility of solutes in aqueous solutions of tetraalkylammonium halides at infinite dilution.[17)] They calculated the difference of molal values of κ_s at infinite dilution,

$$\phi^0_{K(s),Me_4NX} - \phi^0_{K(s),Et_4NX},\ \phi^0_{K(s),Et_4NX} - \phi^0_{K(s),Pr_4NX},\ etc.$$

From the difference the contribution from co-anions to the compressibility of solutions was cancelled out.

We have calculated the difference of κ_s for solutions $\kappa_{Me_4NCl,1M} - \kappa_{Et_4NCl,1M}$, *etc.* at concentration 1 mol/*l*, and have compared the results with the values of Conway and Verral at infinite dilution (Table 1).

In the case of tetramethylammonium salt, tetraethylammonium salt and tetrapropylammonium salt solutions, the values of the difference at infinite dilution and those at 1 mol/*l* are nearly the same, but those between tetrapropylammonium salt solutions and tetrabutylammonium salt solutions at infinite dilution are much larger than the values at 1 mol/*l*.

The effect of solute to surrounding water per mole in the 1 mol/*l* solution is clearly less than the effect at infinite dilution owing to an overlapping effect (Fig. 4).[29)]

TABLE 1. THE DIFFERENCE OF MOLAL ADIABATIC COMPRESSIBILITY

This work (10^{-6} bar^{-1} mol^{-1} *l*)		Conway and Verral (10^{-6} bar^{-1} mol^{-1} *l*)	
$\kappa_{Me_4NCl,\ 1M} - \kappa_{Et_4NCl,\ 1M}$,	2.6_3	$\phi^0_{K(s),\ Me_4NX} - \phi^0_{K(s),\ Et_4NX}$,	2.4
$\kappa_{Et_4NCl,\ 1M} - \kappa_{Pr_4NCl,\ 1M}$,	3.0_6	$\phi^0_{K(s),\ Et_4NX} - \phi^0_{K(s),\ Pr_4NX}$,	3.7
$\kappa_{Pr_4NCl,\ 1M} - \kappa_{Bu_4NCl,\ 1M}$,	0.2_0	$\phi^0_{K(s),\ Pr_4NX} - \phi^0_{K(s),\ Bu_4NX}$,	10.6

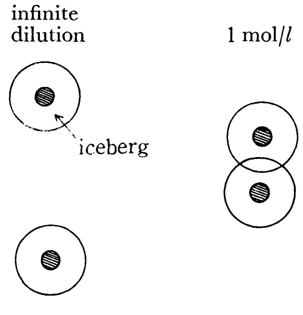

Fig. 4. Overlapping effect of solute-solvent interactions.

The fact that the difference between our data and those of Conway and Verral becomes appreciable (last row, Table 1) supports the idea that the overlapping effect appears typically in Bu_4N^+ ions. This is consistent with the above conclusion.

Dernell and Greyson[30)] found that the tetraalkylammonium salts depress the temperature of maximum density of water T_m and the order of the effect increases in sequence $H_4N^+ < Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Am_4N^+$. They concluded that "the water structure-promoting characteristics of the species ordinarily found at room temperature do not manifest themselves in the neighborhood of T_m". Sarma and Ahluwalia,[31)] however, rejected the conclusion from their measurements of heats of solution ΔH_s^0.

Heat capacity changes ΔC_p in aqueous solutions of Bu_4NBr, Pr_4NI, and $NaBPh_4$ derived from ΔH_s^0 values show no appreciable change as temperature falls from 30 to 4°C. They suggested that the hydration sheath around non-polar groups is not definitely ice-I-like but rather resembles a Pauling-type clathrate cage or some other polymorphic modification of ice. Our concept of rigid icebergs is consistent with this idea.

Relation between the Ability of Iceberg Formation and Ionic Size. As seen in Fig. 3, a marked difference appears in the temperature dependence of Pr_4NCl, where it is reversed, and the tendency is more remarkable in the solution of Bu_4NCl. Thus, the ability of iceberg formation seems to be appreciable at Pr_4N^+.

This agrees with the results obtained by Lindenbaum[7)] from a study of thermodynamic excess functions in which the magnitude of excess enthalpy and entropy for Pr_4NCl solutions are very large in comparison with those for Me_4NCl and Et_4NCl solutions and the trend becomes more marked for Bu_4NCl solution.

On the other hand, several papers state that the behavior of Me_4N^+ differs from that of R_4N^+ (R; Et, *n*-Pr, *n*-Bu).[5,9,32)]

This discrepancy may be at least partly ascribed to the difference of the nature of physico-chemical properties treated in those studies.

Our thanks are due to the kind cooperation of Mr. Nobuo Takenaka, Dr. Osamu Kiyohara, and Mr. Keiji Hasegawa.

---

28) E. Wicke, *Angew. Chem. Int. Ed.*, **5**, 106 (1966).

29) H. S. Frank, "Chemical Physics of Ionic Solutions" (ed., B. E. Conway and R. G. Barradas) p. 53, John, Wiley and Sons. Inc., (1966).

30) A. J. Darnell and J. Greyson, *J. Phys. Chem.*, **72**, 3021 (1968).

31) T. S. Sarma and J. C. Ahluwalia, *J. Phys. Chem.*, **74**, 3547 (1970).

32) E. R. Nightingale, Jr., "Chemical Physics of Ionic Solutions" (ed., B. E. Conway and R. G. Baradas) John, Wiley and Sons. Inc. (1966), p. 87.