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The Effects of Tetraalkylammonium Salts on the Structure and the Temperature of the Maximum Density of Water

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The effects of the tetraalkylammonium halides on the temperature of the maximum density of water were measured by means of dilatometry. Contrary to the expectation that the hydrophobic nature of the alkyl radicals would elevate the temperature of the maximum density of water, these salts lowered it, as other, more usual salts do, obeying the Despretz rule. Among the salts represented as R_4NBr, where R is either H or an *n*-alkyl radical, the Despretz constant, k_D, increases in the sequence: $H < CH_3 < C_2H_5 < n\text{-}C_3H_7 \ll n\text{-}C_4H_9$, while the deviation of k_D from k, which is a hypothetical constant of the ideal mixing where there is no interaction between the solute and the solvent, varies in the following sequence: $H \simeq CH_3 \simeq C_2H_5 \simeq n\text{-}C_3H_7 \ll n\text{-}C_4H_9$. The latter fact is attributable to the specific occurrence of a clathrate-like structure formed in the aqueous solution, only when R is $n\text{-}C_4H_9$. This is in accordance with another peculiarity of $(n\text{-}C_4H_9)_4NBr$ which shows a minimum in its partial molar volume at a certain concentration in water.

The phenomenon of the maximum density exhibited by water at 3.98°C under an atmospheric pressure is affected by the addition of a small amount of an electrolyte to it; this is in obedience to the Despretz rule,[1] which states that the lowering of the temperature of the maximum density (abbreviated as TMD) of water caused by a solute is linear with respect to its concentration. The rule has been almost uniformly confirmed by previous measurements of various electrolytes.[2] Recently, however, some alcohols, most markedly *t*-butyl alcohol, have been found to be in contradiction to the rule; their TMD is even elevated at dilute concentrations.[3] These observations have been interpreted as being attributable to the structure-promoting nature of the hydrophobic alkyl radicals bonded with the hydrophilic hydroxyl radical.

The present work has been undertaken in order to see how the tetraalkylammonium ions affect the TMD of water as the kind of the alkyl radicals is varied. As has been the recent trend, the characteristic properties of aqueous solutions of several

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[1] M. C. Despretz, *Ann. Chim. Phys.*, **70**, 49 (1839); **73**, 296 (1840).

[2] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, (1933), p. 107.

[3] G. Wada and S. Umeda, This Bulletin, **35**, 646 (1962).

tetraalkylammonium salts have been investigated from various points of view——the partial molar volumes,[4–10] the adiabatic compressibilities,[4,6] the transport properties,[11–14] the heats of dilution,[15] the solubilities,[16,17] the near-infrared spectra,[18] and the association equilibria.[19,20] According to their experimental results, the alkyl radicals generally interact with water molecules, with a structure-promoting tendency through the hydrophobic bonds, which sometimes leads to the formation of a clathrate-like structure around the solute ions. Simply judging from the fact that the structure-breaking nature of ions lowered the TMD of water, as in the case of simple ions,[2] while, on the contrary, the structure-promoting nature of the hydrophobic radicals in non-electrolytes elevated it, as in the case of some alcohols,[3] one might expect a slight elevation of the TMD by tetraalkylammonium ions. However, this was not found to be the case, as will be described below.

Experimental

Materials. The crystals used were of a guaranteed reagent grade and were obtained from the Tokyo Kasei Kogyo Co., Ltd., Tokyo, or from the Nakarai Chemicals, Ltd., Kyoto. Commercial NaSCN, NH_4Br, $(CH_3)_4NBr$, $(C_2H_5)_4NBr$, and $(C_2H_5)_4NI$ were recrystalized from water, $(n\text{-}C_3H_7)_4NI$, from ethanol, and $(n\text{-}C_4H_9)_4NBr$, from ethyl acetate. Pure water was prepared by repeating twice the cycles of treatment with ion-exchange resin and distillation.

Procedure. The TMD values of solutions were determined by the use of a dilatometer especially made for the present purpose; it had a capacity of about 300 m*l*, thus enabling us to detect a volume change of 3×10^{-5}%, as has been described in detail elsewhere.[3]

The thermal expansion coefficients, α, and the molar volumes at 0°C, V_{S0}, of the salts were determined by measuring the volumes of the crystals at various temperatures. In order to do that, a specific gravity bottle with a ground-in perforated glass stopper was used. In it a weighed amount of the crystal was put, after

TABLE 1. THE INCREASE IN THE TMD, ΔT, AT THE MOLE FRACTION x OF VARIOUS SALTS

Salt	$x\times10^3$	ΔT °C
NaSCN	0.10	−0.10
	0.73	−0.83
	1.46	−1.62
	2.33	−2.53
	2.94	−3.22
NH_4Br	0.11	−0.04
	1.16	−0.54
	2.34	−1.00
	2.87	−1.38
	4.14	−1.96
	5.22	−2.41
$(CH_3)_4NBr$	1.15	−0.67
	1.75	−0.97
	2.39	−1.33
	3.33	−1.85
	4.88	−2.64
$(C_2H_5)_4NBr$	0.67	−0.39
	1.11	−0.63
	1.76	−1.05
	2.48	−1.45
	2.90	−1.73
	4.55	−2.73
$(C_2H_5)_4NI$	0.43	−0.30
	1.17	−0.71
	1.38	−0.93
	2.18	−1.60
	2.93	−2.13
	3.68	−2.73
$(n\text{-}C_3H_7)_4NI$	0.34	−0.20
	0.68	−0.45
	0.91	−0.64
	1.11	−0.83
	1.54	−1.21
$(n\text{-}C_4H_9)_4NBr$	0.23	−0.18
	0.47	−0.42
	1.07	−1.12
	1.79	−1.89
	2.36	−2.52
	3.42	−3.80

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4) B. E. Conway and R. E. Verral, *J. Phys. Chem.*, **70**, 3952, 3961 (1966).

5) J. Padova and I. Abrahamer, *ibid.*, **71**, 2112 (1967).

6) S. Schiavo, B. Scrosati and A. Tommasini, *Ric. Sci.*, **37**, 211, 219 (1967).

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

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11) R. L. Kay, T. Vituccio, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **70**, 2336 (1966).

12) D. F. Evans, G. P. Cunningham and R. L. Kay, *ibid.*, **70**, 2974 (1966).

13) R. A. Horne and R. P. Young, *ibid.*, **72**, 1763 (1968).

14) R. Fernandez-Prini, *Trans. Faraday Soc.*, **64**, 2146 (1968).

15) R. H. Wood, H. L. Anderson, J. D. Beck, J. R. France, W. E. de Vry and L. J. Soltzberg, *J. Phys. Chem.*, **71**, 2149 (1967).

16) F. Franks and D. L. Clarke, *ibid.*, **71**, 1155 (1967).

17) H. E. Wirth and A. Lo Surdo, *ibid.*, **72**, 751 (1968).

18) K. W. Bunzl, *ibid.*, **71**, 1358 (1967).

19) H. E. Wirth, *ibid.*, **71**, 2922 (1967).

20) P. R. Danesi, F. Orlandini and G. Scibona, *J. Inorg. Nucl. Chem.*, **30**, 2513 (1968).

which it was filled with an inert liquid, such as toluene or cyclohexane. The bottle was filled with the liquid under reduced pressure to prevent bubbles from being occluded in the small openings between the pieces of the crystal. The temperature variation of the molar volumes in the temperature range of about 2—25°C was linear and gave the α from the slope and the V_{S_0} from the intercept at 0°C, as calculated by the method of the least squares.

Results and Discussion

The observed shifts in the TMD from 3.98°C, ΔT, at various concentrations expressed in mole fractions, x, are listed in Table 1. Some of them agree well with the data appearing in the literature.[21,22] The good linear relationships between ΔT and x for the individual salts may be seen in Fig. 1. Therefore, the Despretz constant, k_D, may be defined empirically as:

$$\Delta T = -k_D x \tag{1}$$

Its values for the salts are shown in Table 2.

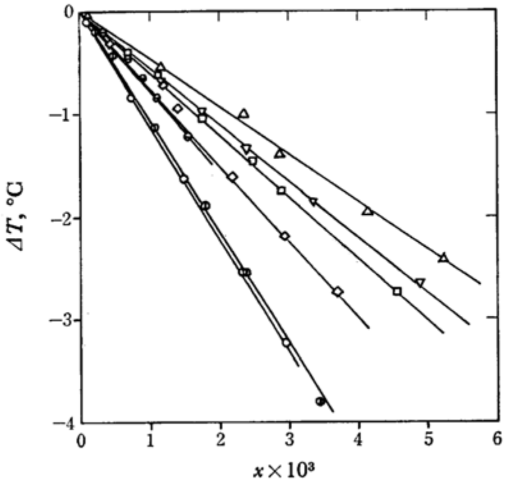

Fig. 1. The linear relationships between ΔT and x for various salts.
○ NaSCN, △ NH_4Br, ▽ $(CH_3)_4NBr$,
□ $(C_2H_5)_4NBr$, ◇ $(C_2H_5)_4NI$, ⊖ $(n\text{-}C_3H_7)_4NI$,
◐ $(n\text{-}C_4H_9)_4NBr$

TABLE 2. VARIOUS CONSTANTS FOR THE SALTS

Those in the parentheses are estimated values

Salt	k_D	$\alpha \times 10^4$ deg^{-1}	V_{S_0} ml/mol	k	Δk
NaSCN	1095	1.83	46.0	30	1065
NH_4Br	465	1.99	40.1	28	437
$(CH_3)_4NBr$	549	1.97	98.7	69	480
$(C_2H_5)_4NBr$	596	3.15	150	169	427
$(n\text{-}C_3H_7)_4NBr$	(610)	—	—	(210)	(400)
$(n\text{-}C_4H_9)_4NBr$	1086	2.47	280	246	840
$(C_2H_5)_4NI$	726	2.25	164	131	595
$(n\text{-}C_3H_7)_4NI$	747	2.14	237	181	566

When it is assumed that there is no interaction between the ions and the solvent molecules, and that, consequently, the resultant volume after the solute and the solvent have been mixed is the algebraic sum of the volumes of the components, the ideal depression of the TMD, ΔT_n, may be expressed as follows:[3)]

$$\Delta T_n = -\frac{x}{1-x}\,\frac{\alpha}{2\beta}\,\frac{V_{S_0}}{V_{W_m}} \tag{2}$$

where V_{W_m} is the molar volume of water at 3.98°C, 18.016 ml/mol, and where β is also a constant, 7.80×10^{-6} deg^{-2}, related to the thermal expansion of water near the TMD, as defined by the equation:

$$V_W = V_{W_m}\{1 + \beta(\theta - 3.98)^2\} \tag{3}$$

in which θ is the temperature in Celsius. This equation is only applicable at temperatures close to the TMD of water. According to Eq. (2), ΔT_n is approximately linear with respect to x, with a proportional constant of $k = (\alpha/2\beta)(V_{S_0}/V_{W_m})$ at concentrations so dilute that $1-x$ can be regarded as being equal to unity. Then, the following relationship can be established:

$$\Delta T_n = -kx \tag{4}$$

For the calculation of k's, the values of α and V_{S_0}, tabulated in Table 2, are necessary.

Generally, the observed k_D and the calculated k do not coincide with each other; rather, the former predominates over the latter. Therefore, the difference between them, $\Delta k = k_D - k$ (shown in the last column of Table 2), is a useful clue for any discussion of the discrepancy from the ideal mixing.

In the present work, since experimental data on $(n\text{-}C_3H_7)_4NBr$ are lacking because of the difficulty of purifying it, $(n\text{-}C_3H_7)_4NI$ was used instead, with $(C_2H_5)_4NI$ as a reference.

TABLE 3. COMAPRISON OF THE VALUES OF k_D BETWEEN BROMIDES AND IODIDES

Cation	Br^-	I^-	Diff (I^-–Br^-)
Li^{+} [2)]	390	460	70
Na^{+} [2)]	820	950	130
K^{+} [2)]	740	860	120
$(C_2H_5)_4N^+$	596	726	130

Table 3 lists the values of k_D for the bromides and iodides of several common cations; it indicates that the differences between the bromides and iodides are almost constant unless the size of the cation is extremely small.

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21) G. Wada and S. Umeda, This Bulletin, **35**, 1797 (1962).

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

Because of this additive nature of ions, the k_D of $(n\text{-}C_3H_7)_4NBr$ can be roughly estimated as is shown in the parentheses in Table 2. The k value for the same salt can also be estimated by simply assuming that it may come in the middle between those for $(C_2H_5)_4NBr$ and $(n\text{-}C_4H_9)_4NBr$. Consequently, its Δk may be supposed to be approximately 400.

A survey of the Δk values of tetraalkylammonium bromides (R_4NBr) in Table 2 will show that Δk does not vary greatly so long as R corresponds to either H, CH_3, C_2H_5, or $n\text{-}C_3H_7$, but that it suddenly doubles when R is altered to $n\text{-}C_4H_9$.

According to the general tendency already found in the cases of simple salts, Δk is always positive and is larger for the stronger structure-breakers or for the weaker structure-formers. Water is considered to be an equilibrium mixture between the molecules of an ice-like structure (iceberg) and of a structure without hydrogen bondings.[23] When the ice-like structure is destroyed by ions, the TMD of water must be lowered to a larger extent than could be expected on the basis of k; this corresponds to the transition of the ice-like structure to a more packed one, because the water in the ice-like structure has a larger molar volume than otherwise. Since the alkyl radicals have a hydrophobic nature, and, since, therefore, they may be considered to promote the ice-like structure around them, the Δk's for tetraalkylammonium bromides have been expected to be negative, much as *t*-butyl alcohol really behaves.[3] However the facts found here are quite contrary to this expectation.

Among many tetraalkylammonium salts, only some tetra-*n*-butyl-ammonium salts are known to form clathrate hydrate crystals, such as $(n\text{-}C_4H_9)_4NBr\cdot 32.8H_2O$ and $(n\text{-}C_4H_9)_4N\text{-}C_6H_5COO\cdot 39.5H_2O$, in which the four $n\text{-}C_4H_9$ radicals are wrapped in individual polyhedral cages composed of water molecules and in which the nitrogen atom of the ammonium is located at the point of contact of these four cages.[24] Alkyl radicals smaller than the *n*-butyl do not form such clathrates because they are too small in comparison with the cage.

When the partial molar volumes of $(n\text{-}C_4H_9)_4NBr$ in its aqueous solutions are plotted against the square root of the concentrations, the curve exhibits a minimum value at the concentration of about 1 mol/*l*. The ratio of the number of moles of the solute to that of the solvent at this concentration corresponds to $(n\text{-}C_4H_9)_4NBr\cdot(60\pm 10)H_2O$.[25] In the cases of other simpler salts, no phenomenon like this is seen; in such cases there are only the monotonous curves of the partial molar volumes *vs.* the square root of the concentration approximately obeying the Debye-Hückel law.[26,27]

Therefore, the characteristic behavior of $(n\text{-}C_4H_9)_4NBr$ in exhibiting both an extraordinarily large value in Δk and a minimum value in the partial molar volume in aqueous solutions might be closely related to the fact that $(n\text{-}C_4H_9)_4NBr$ is the only one among the tetraalkylammonium bromides used that forms the clathrate hydrate. The number of water molecules involved in the clathrate-like structure in solution at the concentration of the minimum partial molar volume is approximately twice as many as in the crystal. Although the clathrate-like structure of $(n\text{-}C_4H_9)_4NBr$ in water is, therefore, in a less-established order than in the crystalline state, the water molecules around the $n\text{-}C_4H_9$ radicals are more ordered and more effectively packed than in the free water, similarly as the structure-breaking ions break the bulky, ice-like structure up into a more packed one. However, one important difference between the shrinks of the volumes due to the formation of the clathrate-like structure and to the destruction by the structure-breaking ions is that the former is accompanied by an increased order, but the latter, by an increased disorder.

The chemical shifts in the NMR signals due to the protons in the water molecules caused by the structure-promoting ions are usually negative, while they are positive upon the disappearance of the hydrogen bonds caused by the structure-breaking ions. The observed chemical shifts caused by the tetraalkylammonium ions are, on the contrary, positive, as if they were weak structure-breakers.[28] The tetraalkylammonium ions are large enough for them to be a likely kind of structure-breaker. However, the hydrophobic nature of the alkyl radicals must promote the structure around the ions by the so-called hydrophobic bonds.[29] This contradiction can be clearly interpreted by the fact that the covalent character of the hydrogen bonds in water causes a chemical shift towards a higher applied field of the water-proton resonance, as has been revealed by the measurements of the sodium alkyl sulfate solutions.[30]

Thus, in summary, the phenomena observed on the shifts in the TMD by the tetraalkylammonium ions may be said to be affected by three factors. First, the tetraalkylammonium ions are ions of such

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[23] G. Wada, This Bulletin, **34**, 955 (1961).

[24] G. A. Jeffrey and R. K. McMullan, *J. Chem. Phys.*, **37**, 2231 (1962); R. K. McMullan, M. Bonamico and G. A. Jeffrey, *ibid.*, **39**, 3295 (1963).

[25] W. Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964); S. Saito, *Hyomen (Surface)*, **4**, 584 (1966).

[26] L. G. Hepler, J. M. Stokes and R. H. Stokes, *Trans. Faraday Soc.*, **61**, 20 (1965).

[27] B. J. Levien, *Australian J. Chem.*, **18**, 1161 (1965).

[28] H. G. Hertz and W. Spathoff, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.*, **63**, 1096 (1959).

[29] W. Kauzmann, *Advances in Protein Chem.*, **14**, 1 (1959).

[30] J. Clifford and B. A. Pethica, *Trans. Faraday Soc.*, **60**, 1483 (1964).

large radii that they behave like structure-breakers, making k_D larger than k. Second, the alkyl radicals are hydrophobic and so are likely to have the effect of depressing k_D. Third, only the tetra-*n*-butylammonium ion specifically serves to form a clathrate-like structure, a structure which makes the apparent partial molar volume of water smaller; consequently, the k_D of $(n\text{-}C_4H_9)_4NBr$ is one of the largest k_D's among the salts of the 1 : 1 type. Sodium thiocyanate was chosen as a typical structure-breaking salt; it has the very high k_D value of 1095, as is shown in Table 2.