The Effect of Quaternary Phosphonium Halides on the Temperature of the Maximum Density of Water

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The shifts in the temperature of the maximum density(tmd) of water produced by quaternary phosphonium halides, $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PX}(n=0—4)$, were measured dilatometrically, and the Despretz constants, K_D, were determined. The K_D, which is positive when the tmd is lowered by a solute, increases nearly linearly with increasing n from 1.16 kK for $(n\text{-Bu})_3\text{PhPCl}$ to 1.57 kK for Ph_4PCl, while the K_D for Bu_4PCl, 0.933 kK, is considerably lower than that to be expected from those for other members. Since the standard partial molal volumes of the cations have been found to be nearly the same, the variation in K_D with n would originate from the difference in ion-water interaction between the cations. Some estimation was made for the contribution of the structural effect of the cations on the solvent water (K_st). The K_st is largely negative for the Bu_4P^+ ion, indicating that the cation is a structure maker. The K_st becomes less negative as n increases, indicating that the structure-making ability decreases with an increase in n.

The shifts in the temperature of the maximum density (tmd) of water produced by solutes contain information about the structural influence of the solutes on the solvent water. With nonelectrolytes as solutes, Franks and Watson[1] showed that the shifts (ΔT) are divided into two terms. One(ΔT_v) is dependent upon the size and expansibility of the solute in its pure liquid state, as derived by Wada and Umeda,[2] and it serves always to depress the tmd. The other(ΔT_st) is identified with the structural influence of the solute on the solvent water, positive for structure makers and negative for structure breakers. Some alcohols and amines[1,2] elevate the tmd at low concentrations.

On the other hand, the negative shifts alone have been found with electrolytes, including alkali metal halides and tetraalkylammonium halides. Darnell and Greyson[3] noticed, by comparing the tmd's of aqueous solutions of alkali metal halides with common ions, that the stronger the structure-breaking ability of the uncommon ions, the lower the tmd. They found, however, that tetraalkylammonium halides(R_4NX) depress the tmd; this effect becomes greater as the size of the alkyl group increases, contrary to our expectation that tmd would be raised as the size of the alkyl group increases because the structure-making ability of these groups increases with the alkyl-group size.[4] A similar trend was also found in D_2O as the solvent.[5] Darnell and Greyson interpreted their observation as showing that, at least in the neighborhood of the tmd, ion sizes play a more important role in influencing the water structure than the structure-making or structure-breaking properties of the ions which are observed at room temperature, and that, at low temperatures, R_4N^+ ions disrupt the water structure because of the incompatibility of the structure of the solvent.

However, this interpretation seems inconsistent with some facts which indicate that the lower the temperature, the greater is the structure-making ability of R_4N^+ ions, as found in the studies of the near-infrared spectra of Bu_4NBr and in the H_2O–D_2O mixture at 5 °C,[6] the NMR chemical shifts of the water proton in aqueous solution of R_4NX,[7] and the temperature dependence of the cationic partial molal heat capacities of R_4N^+ ions in water.[8] In order to discuss the influence of hydrophobic salts on the water structure, the extraction of ΔT_st from ΔT is essential. This is generally very difficult, however, because in this case we must be concerned with the volumetric properties of the salts in a hypothetical pure liquid state.

One way to approach the subject may be to examine the shifts produced by a series of salts which are nearly the same in their volumetric properties, but not in their interactions with water. Quaternary phosphonium salts, $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PX}(n=0—4)$, satisfy this requirement comparatively well; their standard partial molal volumes[9] tend to approach one another as the temperature is lowered, and the structure-making ability decreases with n.

Experimental

Apparatus and Measurements. Measurements of the volume changes of aqueous solutions of $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PX}(n=0—4)$ with the temperature were made in dilatometers of about 100-cm^3 capacity, calibrated triply with conductivity-grade water, at 0.5 K intervals in the temperature range of 0.5—6 °C. The dilatometers were constructed of Pyrex tubing about 35 mm i.d. and capillary tubing about 0.5 mm i.d. with minimum graduations of 0.0005 cm^3. The temperatures of the thermostat bath were controlled to within ±0.005 K. The temperatures of the bath were measured by a standard thermometer calibrated against a platinum-resistence thermometer (Leeds and Northrup).

The volume changes with the temperature were found to be approximately symmetrical near the tmd for all solutions. The tmd was obtained graphically from the temperature *vs.* volume curve, with a maximum error of ±0.05 K.

Materials. The tetraphenylphosphonium chloride was obtained from Merck. The other salts, $\text{Bu}_{4-n}\text{Ph}_n\text{PCl}(n=0—3)$, were synthesized from the corresponding phosphines. The method of purifying the salts and their purity were similar to those reported previously[9]. The stock solutions were filtered through a Millipore-filter. The solutions for dilatometric measurement were prepared by the dilution of the stock solutions by weight, all weighings being vacuum-corrected.

Results and Discussion

The shifts, ΔT, in the tmd of water produced by

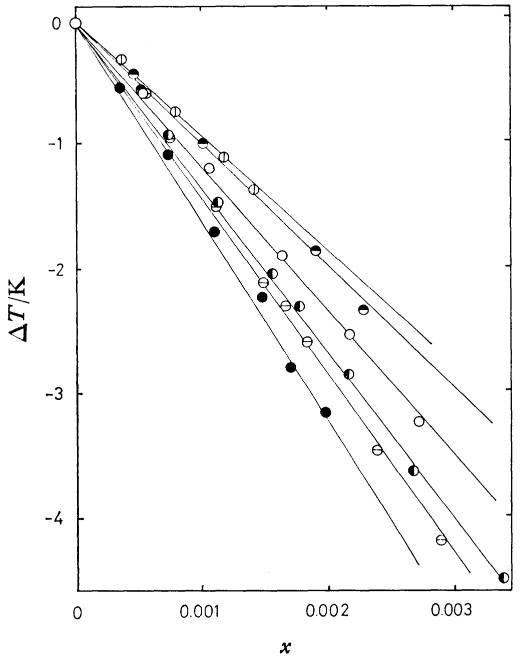

Fig. 1. Shifts(ΔT) in tmd produced by $Bu_{4-n}Ph_nPX$ as a function of salt mole fraction, x. ◓: Bu_4PBr, ⦶: Bu_4PCl, ○: Bu_3PhPCl, ◑: Bu_2Ph_2PCl, ⊖: $BuPh_3PCl$, ●: Ph_4PCl.

TABLE 1. DESPRETZ CONSTANTS(K_D) FOR PHOSPHONIUM HALIDES

Salts	$\frac{K_D}{10^3\,K}$	$\frac{\sigma^{a)}}{10^3}$
n-Bu_4PBr	0.982 (0.009)$^{b)}$	0.023
n-Bu_4PCl	0.933 (0.018)	0.032
n-Bu_3PhPCl	1.16 (0.019)	0.033
n-Bu_2Ph_2PCl	1.31 (0.02)	0.052
n-$BuPh_3PCl$	1.42 (0.029)	0.052
Ph_4PCl	1.57 (0.011)	0.016

a) Standard deviation. b) Uncertainty expected in K_D.

$Bu_{4-n}Ph_nPX$(n=0—4, X=Cl, Br) are shown in Fig. 1 as a function of the solute mole fraction, x. As may be seen from the figure, the ΔT for each salt seems to be nearly a linear function of x.

The Despretz constants, K_D, defined by:

$$\Delta T = -K_D x, \tag{1}$$

were determined by the least-squares method. The K_D values thus obtained are summarized in Table 1.

Table 2 lists the densities, d, of the solutions and the apparent molal volumes, ϕ_v, for $Bu_{4-n}Ph_nPCl$ at 5 °C in the concentration range of 0.02—0.2 mol kg^{-1}. The ϕ_v were calculated by means of the equation:

$$\phi_v = \frac{1}{m}\left(\frac{1000+mM}{d} - \frac{1000}{d_o}\right), \tag{2}$$

where m is the molality of salt; M, the formula weight of the salts, and d_o, the density of water at 5 °C, which was taken as 0.999965 g cm^{-3}.[10] The standard partial molal volumes, ϕ_v°, and the B_v coefficients for ϕ_v for the phosphonium halides were determined by fitting the ϕ_v data to Eq. 3 by the method of least squares;

$$\phi_v - A_v c^{1/2} = \phi_v^\circ + B_v c, \tag{3}$$

where A_v is the Debye-Hückel limiting slope and where the value at 5 °C was taken as 1.529 cm^3 dm$^{3/2}$ mol$^{-3/2}$.[11] The results are summarized in Table 3.

The ΔT for liquid nonelectrolytes can be expressed as:

TABLE 2. DENSITIES AND APPARENT MOLAL VOLUMES OF $Bu_{4-n}Ph_nPX$ AT 5 °C

$\frac{m}{\text{mol kg}^{-1}}$	$\frac{d}{\text{g cm}^{-3}}$	$\frac{\phi_v}{\text{cm}^3\,\text{mol}^{-1}}$
n-Bu_4PBr(n=0)		
0.02613	1.000722	310.11
0.05692	1.001661	309.00
0.10329	1.003073	308.28
0.12751	1.003874	307.47
0.20075	1.006089	306.95
n-Bu_3PhPCl(n=1)		
0.05956	1.000726	301.86
0.09170	1.001169	301.38
0.12130	1.001600	300.91
0.15123	1.002020	300.68
n-Bu_2Ph_2PCl(n=2)		
0.02930	1.000927	301.72
0.04245	1.001368	301.39
0.06283	1.002042	301.18
0.08685	1.002797	301.40
0.09832	1.003181	301.18
0.12020	1.003867	301.23
0.14859	1.004794	300.92
0.18875	1.006092	300.57
n-$BuPh_3PCl$(n=3)		
0.04120	1.002154	301.05
0.08237	1.004272	301.27
0.09234	1.004776	301.31
0.10126	1.005272	300.85
0.16062	1.008218	300.99
Ph_4PCl(n=4)		
0.06118	1.004330	302.18
0.08189	1.005795	301.89
0.09447	1.006648	302.09
0.10949	1.007675	302.09

TABLE 3. STANDARD PARTIAL MOLAL VOLUMES(ϕ_v°) AND B_v COEFFICIENTS FOR PHOSPHONIUM HALIDES AT 5 °C

Salts	$\frac{\phi_v^\circ}{\text{cm}^3\,\text{mol}^{-1}}$	$\frac{B_v}{\text{cm}^3\,\text{dm}^3\,\text{mol}^{-2}}$
n-Bu_4PBr	310.0 (0.37)$^{b)}$	−24.6 (3.2)$^{c)}$
n-Bu_4PCl	303.2$^{a)}$	
n-Bu_3PhPCl	302.4 (0.12)	−16.5 (1.1)
n-Bu_2Ph_2PCl	301.6 (0.12)	−8.7 (1.2)
n-$BuPh_3PCl$	301.0 (0.25)	−3.7 (2.5)
Ph_4PCl	301.9 (0.38)	−3.8 (4.5)

a) Estimated value from $\bar{V}^\circ$(Br$^-$, 5°) and $\bar{V}^\circ$(Cl$^-$, 5°); *cf.* Ref. 9. b) Uncertainty in ϕ_v°. c) Uncertainty in B_v.

$$\Delta T = T - T^* = \frac{-\alpha_2 V_2^\circ x}{2\alpha_1(1-x)V_1^*} + \frac{-1}{2\alpha_1(1-x)V_1^*}\frac{\partial \Delta V_\mathrm{x}^\mathrm{M}}{\partial T}, \tag{4}$$

where the T and T^* are the temperature of the maximum density of a solution and of pure water(3.98 °C) respectively; x is the mole fraction of the solute; α_2 the thermal expansion coefficient of the solute, and α_1, a coefficient in a quadratic equation of T expressing the molal volume of pure water around $T^*(\alpha_1 = 7.80\times10^{-6}\ \mathrm{K}^{-2})$,[2] $V_1{}^*$ and $V_2{}^\circ$ are the molal volume of pure water at T^* and that of the solute in the pure liquid state at T, and $\Delta V_\mathrm{x}^\mathrm{M}$ is the excess volume of mixing referred to a mixture of the solute mole fraction, x. For dilute solutions, Eq. 4 is reduced to:

$$\Delta T = -\left(\frac{\alpha_2 V_2^\circ}{2\alpha_1 V_1^*} + \frac{1}{2\alpha_1 V_1^*}\frac{\partial b}{\partial T}\right)x = -(K_\mathrm{v} + K_\mathrm{st})x, \tag{5}$$

under the assumption that $\Delta V_\mathrm{x}^\mathrm{M} = bx(1-x)$,[12] where b is a constant with regard to the mole fraction. Thus, the Despretz constant can be divided into the volume-dependent term, K_v, and the structural term, K_st. With electrolytes containing large organic ions, as in the present case, the K_v would contribute largely to K_D.

As may be seen from Table 1 and Fig. 2, K_D increases with an increase in the number of phenyl groups on the cations. The $K_\mathrm{D}(\mathrm{Bu_4PBr})$ is larger by about 70 K than $K_\mathrm{D}(\mathrm{Bu_4PCl})$, indicating that the anionic contribution of $\mathrm{Br^-}$ to K_D is larger than that of the $\mathrm{Cl^-}$ ion. This difference is comparable to that, 50 K,[3] found for a set, $K_\mathrm{D}(\mathrm{Et_4NBr})$ and $K_\mathrm{D}(\mathrm{Et_4NCl})$. The contribution of the $\mathrm{Br^-}$ (and also of $\mathrm{Cl^-}$) ion to K_D's would be comparatively small, say around 5×10^2 K for the $\mathrm{Br^-}$ ion, which is the mean value of K_D for HBr and KBr.[20] Thus, it appears that the cationic contribution to K_D increases with an increase in n, from 5×10^2 K for the $\mathrm{Bu_4P^+}$ ion to 1.1×10^3 K for the $\mathrm{Ph_4P^+}$ ion, assuming that the volumetric properties, V_+° and α_+, of the cations are nearly the same, as is suggested by the equality in their standard partial molal volumes(Table 2). This point is discussed below more elaborately.

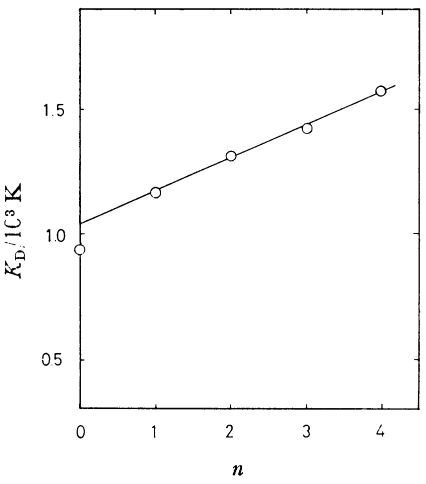

Fig. 2. Despretz constants(K_D) for $\mathrm{Bu}_{4-n}\mathrm{Ph}_n\mathrm{PCl}$ as a function of n.

The $\overline{V}_+^\circ$ may be written as the sum of the contributions of several factors: the intrinsic volume of the cation, $\overline{V}_\mathrm{in}$; the structural volume change associated with the shift of the H-bond equilibria of the solvent water in the presence of the ion, $\overline{V}_\mathrm{st}$, and the packing effect of the ion in the cavities in water structures, $\overline{V}_\mathrm{c}$. The electrostriction effect can be neglected here because of the large cationic sizes. $\overline{V}_\mathrm{in}$ will decrease with an increase in n, as is suggested by the molal volume of benzene and liquid butane at 25 °C, 89.4 and 100 $\mathrm{cm^3\,mol^{-1}}$ (extrapolated values from higher homologs) respectively. $\overline{V}_+^\circ(\mathrm{Bu_4P^+})$ in methanol was estimated as 267, and that of the $\mathrm{Ph_4P^+}$ ion, as 264 $\mathrm{cm^3\,mol^{-1}}$,[13] where the structural effects are much lower than in water. Thus, the $\overline{V}_+^\circ$ values of the present cations are expected to decrease as n increases. The expansion coefficients of the cations would also decrease with n because the polarizability of the butyl group is expected to be smaller than that of the phenyl group, and hence the dispersion force would increase with n.[14] Thus, the conclusion is obtained that K_v decreases somewhat with an increase in n and that, therefore, K_st increases with n. Since it has been confirmed that, with a nonelectrolyte as a solute, $\partial\Delta V_\mathrm{x}^\mathrm{M}/\partial T$ and so $\partial b/\partial T$ are negative for structure-makers and positive for structure-breakers,[2] the phenyl group may be either a structure-breaker or a weaker structure-maker than the butyl group. This conclusion is in agreement with the information obtained from the studies of the viscosity,[15] the molal volume,[9] the molal heat capacity,[13] and the differential near-infrared spectra[16] for $\mathrm{Bu_4PBr}$ or $\mathrm{Bu_4NBr}$ and $\mathrm{Ph_4PCl}$ solutions.

The estimation of K_st for the present cations is of interest and may be possible in the case of the $\mathrm{Bu_4P^+}$ ion. Since $\mathrm{Bu_4PBr}$ is similar in molecular structure to $\mathrm{Bu_4NBr}$, the K_st can be assumed to be nearly the same with these two salts, and we can obtain the following relation by subtracting $K_\mathrm{D}(\mathrm{Bu_4NBr})$ from $K_\mathrm{D}(\mathrm{Bu_4PBr})$:

$$K_\mathrm{D}(\mathrm{Bu_4PBr}) - K_\mathrm{D}(\mathrm{Bu_4NBr}) = \frac{\alpha_2}{2\alpha_1 V_1^*}(V_2^\circ(\mathrm{Bu_4PBr}) - V_2^\circ(\mathrm{Bu_4NBr})), \tag{6}$$

where the thermal expansion coefficient, α_2, is assumed to be equal. From the equation, the value for α_2 is estimated by inserting the standard partial molal volumes, $\overline{V}_2^\circ(5\ ^\circ\mathrm{C})$, in place of V_2°. This approximation seems reasonable because $\overline{V}_\mathrm{st}$ and $\overline{V}_\mathrm{c}$ are expected to be equal for the two cations, and these contributions cancel each other out upon the subtraction. The value obtained for α_2 is $1.8\times10^{-3}\ \mathrm{K^{-1}}$, with 310.0 and 295.15[8] $\mathrm{cm^3\,mol^{-1}}$ at 5 °C for $\overline{V}_2^\circ$ of $\mathrm{Bu_4PBr}$ and $\mathrm{Bu_4NBr}$ respectively, and 888 K for $K_\mathrm{D}(\mathrm{Bu_4NBr})$.[5] The α_2 value is of the same order as those for $\mathrm{C_5}$—$\mathrm{C_9}$ alkanes,[14] and seems reasonable. From Eq. 5 with the α_2 value, we obtain 1.8 kK for $K_\mathrm{v}(\mathrm{Bu_4P^+})$, where $\overline{V}_+^\circ(\mathrm{Bu_4P^+})$ is taken as 281.1 $\mathrm{cm^3\,mol^{-1}}$, which is obtained by subtracting $\overline{V}_-^\circ(\mathrm{Br^-}, 5^\circ)$ 28.9 $\mathrm{cm^3\,mol^{-1}}$,[9] from $\overline{V}_2^\circ(\mathrm{Bu_4PBr}, 5^\circ)$. The estimation shows that $K_\mathrm{st}(\mathrm{Bu_4P^+})$ is largely negative, about -1.3 kK, indicating a strong structure-making ability of the cation, but overshadowed by the larger $K_\mathrm{v}(\mathrm{Bu_4P^+})$.

It is noticeable that the K_D for $\mathrm{Bu_4PCl}$ is considerably smaller than that extrapolated from those for other members (Fig. 2). This would suggest the presence of a clathrate-like structure of Bu_4P^+ ion, which was proposed by Wen and Saito[17] for the hydration model for Bu_4N^+ and Pr_4N^+ ions. The cooperative nature in forming a hydrogen-bonded structure of water[18,19] may be responsible for the large increase in K_{st} value from the Bu_4P^+ to the Bu_3PhP^+ ion because of a different kind of water structure in the cosphere of the phenyl group. The aqueous-solution behavior of the Ph_4P^+ ion can, in comparison with that of the Bu_4P^+ ion, be characterized by the following: A low activation energy for viscous flow,[15,21] a low partial molal heat capacity,[13] a large molal expansibility with a negative temperature dependence,[9] a low negative value of B_V(Table 3) with a negative temperature dependence, in contrast with a positive dependence for Bu_4PBr,[9] *etc.* All these facts suggest that the water molecules in the phenyl-cosphere are less structured, and hence less hydrogen-bonded, than those in the butyl-group cospheres; in other words, the phenyl groups are hydrophilic rather than hydrophobic. This character of the phenyl groups would arise from delocalized charges on the phenyl groups[22] and the structure-breaking effect due to the poor fit of planar phenyl groups into the partly tetrahedral structure of water. The volumetric properties of the present salts, including a discussion of the B_V-coefficients, will be given in detail elsewhere.[23]

The approach attempted here seems promising for obtaining information, from the tmd data, about the structural influence of organic ions on the solvent water. The division of K_D for electrolytes into ionic contributions based on a sounder basis is required for a more comprehensive treatment of the tmd data. This will be one next subject.[24]

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