October, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 3073—3078 (1982) 3073

Despretz Constants for Individual Ions

Toshiki WAKABAYASHI* and Katsuko TAKAIZUMI
The College of General Education, Tohoku University, Kawauchi, Sendai 980

(Received January 5, 1982)

The shifts (ΔT) in the temperature of maximum density (tmd) of water produced by electrolytes have been revised. It was found that the temperature dependences of S_V and/or b_V coefficients in the Redlich-Meyer equation should be taken into account, to obtain exactly the Despretz constants (K_D) or the standard partial molal expansibility ($\bar{E}^\circ$) from tmd data. The K_D's for 1 : 1 electrolytes were divided into the ionic components ($K_{D,i}$), by applying the value for $\bar{E}_i^\circ$ (H^+, 4 °C). Of the familiar monovalent ions, the $K_{D,i}$ values are negative ($\Delta T > 0$) only for H^+ and Li^+ ions and are positive for all the anions examined, including F^- ion. A further attempt was made to extract from $K_{D,i}$'s for organic ions the structural part $K_{st,i}$'s, based on a model. The $K_{st,i}$'s seem to reflect the structure-influencing ability of organic ions, but may not always be the case.

It has been recognized by many authors[1–7] that the shifts (ΔT) in the temperature of maximum density of water (tmd) produced by electrolytes as well as nonelectrolytes reflect the structural effects of ions on the solvent water. The shift produced by any solute at low concentrations is proportional to the solute concentration through the Despretz constant (K_D). Frank and Robinson[1] first noticed that K_D for alkali metal halides with a common anion increases in the order, $Li^+ < K^+ < Na^+$, in accordance with the effect of the cations on the relative partial molal entropy of water at 25 °C which were discussed in terms of the structural effect of ions. Darnell and Greyson[2] also noticed that with both alkali metal ions and halogenide ions, the ionic contributions to K_D seem to increase with increasing their structure-breaking ability with the exception of Na^+ ion.

With liquid nonelectrolytes as solutes, the observed ΔT's are usually divided into two parts, ΔT_V and ΔT_{st}, and hence K_D is also divided into K_D and K_{st}. The K_V is determined solely by the volumetric properties of the solute in its pure liquid state, while the K_{st}'s have been related qualitatively with the structural influences of the solutes on the solvent water,[8–14] that is, K_{st}'s have been confirmed to be positive for structure breakers ($\Delta T_{st} < 0$) and negative for structure makers ($\Delta T_{st} > 0$), though somewhat different approaches have been made by some authors.[15–17]

Some question has been recognized, however, with respect to tetraalkylammonium salts (R_4NX); the K_D increases with increasing alkyl-chain length.[2–4] This is contrary to the expectation that the hydrophobic nature of the alkyl radical would elevate the tmd of water similar to nonelectrolytes such as alcohols and some alkylamines.[7,8] Darnell and Greyson[2] inferred that the water structure-promoting characteristics of the species ordinarily found at room temperature would not be manifested in the neighbourhood of the tmd. They attributed the results to ion-size effects which would become important at temperatures approaching the tmd because of the enhanced structure of the solvent.

Estimating the K_{st}'s for R_4NBr, Wada and Miura[3] found that the K_{st} also increases with the alkyl-chain length. They proposed the idea that clathrate-like structures formed in the aqueous solution of $(n\text{-Bu})_4NBr$ contribute to the lowering of the tmd. Recently, Wada *et al.*[6] determined K_D's for twenty complex salts. They divided K_D's into ionic components ($K_{D,i}$) based on the assumption that $K_{D,i}(K^+) = K_{D,i}(Cl^-)$, and attempted further to extract the structural contributions of the complex ions from the $K_{D,i}$'s. They proposed that the hydrophobic ions may be divided into "iceberg" formations which elevate the tmd and "clathrate-like" formations which lower the tmd. In these estimations Wada and his coworkers employed the volumetric properties of the electrolytes in the solid state at 0 °C. As discussed later, the use of the volumetric properties of solutions in solid state seems questionable, particularly when the solutes are electrolytes.

In an earlier publication[7] we evaluated K_D's for some phosphonium halides, $(n\text{-Bu})_{4-n}Ph_nPX (n=0\text{—}4)$; the K_D for phosphonium chlorides increases with increasing the number of phenyl groups, indicating that in contrast to the conclusion obtained by other authors, the clathrate-like hydration would contribute toward elevating the tmd since the clathrate-like hydration supposed for the $(n\text{-Bu})_4P^+$ ion would successively disappear as the butyl groups are replaced by phenyl group since the K_V would decrease slightly with n.

Thus, the studies about the effects of electrolytes on the tmd may provide useful information about ionic hydration, however, there seems to be two problems; one is the way to divide K_D's for electrolytes into the ionic components; the other is to find a suitable procedure to extract the structural components ($K_{st,i}$) for organic ions from the $K_{D,i}$'s.

In the present work, we revise the procedure to determine the Despretz constants for electrolytes and then attempt to approach these subjects.

Principle

The Despretz Constant of an Electrolyte. The shift in the tmd of water produced by a solute can be derived as follows. The apparent molal volume ϕ_2 of solute is defined by

$$\phi_2 = \frac{1}{m}\left(\frac{1000+mM}{d} - \frac{1000}{d_0}\right), \qquad (1)$$

where d is the density of solution, d_0 that of pure water, m the molality, and M the molecular weight of the solute. The molal volume of water, V_1, near the tmd can be expressed as

$$V_1 = V_1^*(1+\alpha_1(T-T_0^*)^2), \qquad (2)$$

where V_1^* is the molal volume at the tmd (T_0^*) of pure water, (namely 3.98 °C), and the value of α_1[8] is 7.8×10^{-6} deg^{-2}. Replacing $d_\circ$ in Eq. 1 by M_1/V_1, where M_1 is the molecular weight of water, differentiating with respect to temperature, and rearranging the result, we obtain

$$\Delta T = (T_\mathrm{m} - T^*_\circ) = -\frac{d^*_\circ}{2000\,\alpha_1}\frac{\partial \phi_2}{\partial T}m, \tag{3}$$

where the condition, $\partial d/\partial T=0$, at the tmd is considered; $d^*_\circ$ is the density of water at $T^*_\circ$.

For dilute aqueous solutions of electrolytes, ϕ_2 can be expressed as:

$$\phi_2 = \phi^\circ_2 + S_\mathrm{v}m^{1/2} + b_\mathrm{v}m, \tag{4}$$

where ϕ°_2 is the partial molal volume of the electrolyte at infinite dilution and S_V, the Debye-Hückel limiting slope, for which the exact values have been given by Redlich and Meyer,[18] and b_V, the excess volume coefficient which includes all the effects arising from ion-solvent and ion-ion interactions. Insertion of Eq. 3 into Eq. 4 gives

$$\Delta T = -\frac{d^*_\circ}{2000\,\alpha_1}\left(\bar{E}^\circ - \frac{\partial S_\mathrm{v}}{\partial T}m^{1/2} + \frac{\partial b_\mathrm{v}}{\partial T}m\right)m, \tag{5}$$

where $\bar{E}^\circ$ is the standard partial molal expansibility of electrolyte. The equation shows that, different from the case of nonelectrolyte solutes, for electrolytes the quantity that is directly proportional to concentration is not ΔT itself but a corrected one, and this is so even at low concentrations. Inserting the numerical values in Eq. 5, we obtain

$$\Delta T + 1.074\,m^{3/2} + 64.1\frac{\partial b_\mathrm{v}}{\partial T}m^2 = -64.1\bar{E}^\circ m, \tag{6}$$

where the value for $\partial S_\mathrm{V}/\partial T$ at 3.98 °C was obtained from Eq. 20 in Ref. 19, as 1.675×10^{-2} cm^3 mol$^{-3/2}$ kg$^{1/2}$K.

Thus, it is reasonable to define the Despretz constant by

$$K_\mathrm{D} = 64.1\,\bar{E}^\circ, \tag{7}$$

where the dimensions for K_D and $\bar{E}^\circ$ are mol^{-1} kg K and cm^3 mol^{-1} K^{-1}, respectively. The Despretz constant is obtainable by Eq. 6 from the tmd data or by Eq. 7 from $\bar{E}^\circ$.

It may be a fact worth noting that the contributions from the temperature dependences of S_V and b_V have scarcely been considered, though the equations equivalent to Eqs. 3 and 7 have been treated by many authors. This subject will be discussed in a later section.

Since $\bar{E}^\circ$ can be split into the contributions from cation and anion, $\bar{E}^\circ_+$ and $\bar{E}^\circ_-$, K_D can also be split into the separate contributions, $K_{\mathrm{D},+}$ and $K_{\mathrm{D},-}$. Determination of the ionic Despretz constants is, therefore, a straightforward matter, if a reliable value for $\bar{E}^\circ_\mathrm{ion}$ for any ion is available. Here the proton is chosen as the reference ion since for this $\bar{E}^\circ_+$ has been given as a function of temperature by Millero,[19]

$$\bar{E}^\circ_+(\mathrm{H}^+) = -0.008 - 3.40\times 10^{-4}t. \tag{8}$$

Combining Eq. 7 with Eq. 8, we obtain the value, -0.60 K mol^{-1} kg for $K_\mathrm{D}(\mathrm{H}^+)$.

Separation of Structural Contribution from $K_{\mathrm{D,i}}$ for Organic Ions. It is of interest to separate $K_{\mathrm{D,i}}$ for large organic ions into two terms, a volumetric term, $K_{\mathrm{V,i}}$, and a structural term, $K_{\mathrm{st,i}}$. The latter term is considered to reflect the structural influence of the ion on the solvent water.

For nonelectrolyte solutes that are liquid at temperatures in the region of the tmd, Frank and Watson[9] have derived the following equation and confirmed its validity:

$$\Delta T = -\frac{x\alpha_2 V^\circ_2}{2(1-x)\alpha_1 V^*_1} - \frac{1}{2(1-x)\alpha_1 V^*_1}\frac{\partial \Delta V^\mathrm{M}_\mathrm{x}}{\partial T}, \tag{9}$$

where x is the mole fraction of the solute, V°_2 and α_2 are the molar volume and the thermal expansion coefficient of the solute in pure liquid state at the tmd, and $\Delta V^\mathrm{M}_\mathrm{x}$ is the excess volume of mixing referred to a mixture of solute mole fraction x. The first term on the right hand side of the equation, first derived by Wada and Umeda,[8] is determined solely by the volumetric properties of the two pure liquids. This term expresses the shift in the tmd in an ideal mixture for which $\Delta V^\mathrm{M}_\mathrm{x}$ is 0 for all compositions, it is often referred to as the ideal term, and is always negative. The second term, on the other hand, expresses the effect arising from the solute-solvent interactions which induce the system to become nonideal.

Making an approximation, $\Delta V^\mathrm{M}_\mathrm{x} = bx(1-x)$,[20] and converting the mole fraction into molality, we can write the Despretz constant as:

$$K_\mathrm{D} = K_\mathrm{v} + K_\mathrm{st}, \tag{10}$$

where

$$K_\mathrm{v} = d^*_\circ\alpha_2 V^\circ_2/(2000\,\alpha_1), \tag{11a}$$

and

$$K_\mathrm{st} = d^*_\circ(\partial b/\partial T)/(2000\alpha_1), \tag{11b}$$

where in dilute solution $\partial\Delta V^\mathrm{M}_\mathrm{x}/\partial T$ and hence K_st are found to be negative for some organic compounds such as alcohols, alkylamines and tetrahydrofuran; most of these are known as the structure makers for the solvent water.

Equations 9—11 are valid for nonelectrolytes, but not for electrolytes. However, as shown by Wada and his coworkers,[3,6] we may consider that the $K_{\mathrm{D,i}}$'s should also consist of two terms similar to the case of nonelectrolytes. The contribution of the volumetric term, $K_{\mathrm{V,i}}$, may be significant for organic ions, since they are much larger in size than simple inorganic ions and their intrinsic expansibilities would be relatively large. In an ideal mixture, both the partial molal volume and the expansion coefficient are the same as those in the pure liquid for each component, and hence, the K_V does not contain any contribution from the structural changes of the solvent water induced by the solute. The thermal expansion coefficient of any substance is in general larger in the liquid state than in the solid state; therefore an excessively small value for K_V should be obtained if the solid expansibility is used in place of the liquid one. With electrolytes another factor should be taken into account; this is the electrostatic interactions between the ions in salt crystals. These result in much smaller expansibilities than those of molecular crystals, while in dilute electrolyte solutions the interactions are much weaker. Thus, it is obvious that to use the expansibilities for salt crystals in estimating K_V's would yield excessively

TABLE 1. THE DESPRETZ CONSTANTS, K_D/K mol^{-1} kg, FOR 1 : 1 ELECTROLYTES (Eq. 6)[a),b)]

	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
Cl^-	5.9_5	5.1_8	12.4_8	11.0_3	11.0_9	11.5_9	6.5_1
	(5.9_5)	(5.0_0)	(12.6_6)	(11.0_3)	(11.3_2)	(11.5_8)	(6.5_9)
Br^-	6.5_5	6.4_7	14.0_1	12.2_8	12.8_8		7.8_2[c)]
	(7.3_5)	(6.4_0)	(14.0_6)	(12.4_3)	(12.7_2)	(12.9_8)	(7.9_9)
I^-	9.0_0	7.7_1	16.6_0	15.0_4	15.2_2		10.3_0[d)]
	(9.8_3)	(8.8_8)	(16.5_4)	(14.9_1)	(15.2_0)	(15.4_6)	(10.4_0)
NO_3^-	11.9_5	11.8_0	18.7_2	16.9_6	17.2_8	17.4_7	12.8_0
	(11.9_5)	(11.0_0)	(18.8_6)	(17.0_3)	(17.3_2)	(17.5_8)	(12.5_9)

a) Tmd data were, unless otherwise specified, taken from Ref. 21. The last term of the left hand side of Eq. 6 was ignored for all the salts. b) The bracketed values are reproduced from $K_{D,i}$. c) Ref. 3. d) Ref. 2.

small values which in turn would lead to excessively large values for K_{st}'s. This will at least be one of the reasons for finding unexpected values for K_{st}'s for hydrophobic salts.[3)]

Another approach may be possible: Consider a 1 : 1 electrolyte as the solute. Transfer of one ion pair from the solid phase to the solvent water produces two hydrated ions. For each ion we may divide this action into two processes. The first is the transfer of a hypothetical molecule (which is the same in the molecular structure as that of the ion but with no electric charge) from its hypothetical pure liquid to water; the second is the charging process of the molecule in water to yield the ion. The latter process should change the hydration state of the hypothetical molecule, other than possible volume change of the solute molecule itself by electrostriction effect. The changes in the hydration state would be significant for ions of small size while for large sized ions the changes would be comparatively minor due to their low electric fields, *i.e.*, the water structure around the hypothetical molecule will be less affected. In any case, the changes accompanied by the charging process are now all included in the $K_{st,i}$ term except for the volume change due to the electrostriction of the ion itself which should be included in $K_{V,i}$ term.

Thus, we can evaluate the $K_{st,i}$'s for ions by Eq. 11a, and hence, also the $K_{vt,i}$'s, if proper estimation is possible for V_2° and α_2 of hypothetical pure liquids.

Results and Discussion

Table 1 lists the Despretz constants for 1 : 1 electrolytes which were obtained by Eq. 6 from the tmd data found in the literature. For most of the simple electrolytes treated, Eq. 6, neglecting the second correaction term, gave reasonable results, as evidenced by the fact that the standard deviations (σ) between the observed tmd's and those reproduced from the K_D are reduced by one order or more by applying the first correction. As a whole, the contributions to K_D from the correction term amount to about 0.7 K mol^{-1} kg. The second correction term, $(\partial b_V/\partial T)m^2$, seems to be essential for the salts containing so-called hydrophobic ions. For instance, the tmd data for Bu_4NBr[3)] show that the K_D calculated from each tmd at each concentration increases successively with concentration from 782 K (referred to mole fraction scale) at mole fraction 2.3×10^{-4} to 1110 K at 3.42×10^{-3}. The reported value for K_D is 1086 K (σ=0.026 K), which was obtained without any corrections. Equation 6 gives 945 K with $\sigma=6.3\times10^{-3}$ K, where the value for $(\partial b_V/\partial T)$ was taken as 0.209 cm^3 mol^{-2} kg K^{-1}.[22)] On the other hand, $(\partial b_V/\partial T)$'s for Me_4NBr and Et_4NBr are slightly negative[22)] and the two correction terms partially set off each other.

Table 2 lists the ionic Despretz constants which are referred to the standard, $K_{D,+}(H^+)=-0.60$ K mol^{-1} kg. It is of interest to compare $K_{D,-}$'s for Cl^- and Br^- ions in the table with those obtained by extrapolation of the curve obtained by plotting K_D for R_4NX's *vs.* molecular weight of the cation, to zero molecular weight of the cation. Attempts of this kind have been made by other authors to determine the absolute partial molar volumes of halogenide ions[23)] or the absolute ionic molal expansibility for the Cl^- ion.[24)] As in the case of $\bar{E}^\circ$ (R_4NCl, 25 and 35 °C),[24)] the extrapolation was made by using only two lower members for both sets of salts, since the plots were not linear. The $K_{D,-}(Cl^-)$ found from tmd data for R_4NCl[2)] was 7.3 K mol^{-1} kg and $K_{D,-}(Br^-)$, from those for R_4NBr,[3)] 8.4. These are somewhat larger than those in Table 2. Although this may be one possible way to determine $K_{D,-}$, more reliable data are required to do this since disagreement among tmd data for R_4NX's are found (Table 2).

TABLE 2. THE DESPRETZ CONSTANTS FOR INDIVIDUAL IONS, $K_{D,i}$/K mol^{-1} kg[a)]

Ion	$K_{D,i}$	Ion	$K_{D,i}$		
H^+	-0.60	NH_4^+	-0.0_4[b)]	-0.1_3[c)]	
Li^+	-1.5_5	Me_4N^+	*2.0_6*[b)]	*1.8_5*[c)]	*0.8_5*[d)]
Na^+	6.1_1	Et_4N^+	*3.1_9*[b)]	2.6_6[c)]	2.6_5[d)]
K^+	4.4_8	Pr_4N^+	*3.7_6*[b)]		*3.8_2*[d)]
Rb^+	4.7_7	Bu_4N^+	*8.0_3*[b)]	*9.0_9*[c)]	6.5_2[d)]
Cs^+	5.0_3				
F^-	7.1[d)]	Bu_4P^+	*8.0_2*[e)]		
Cl^-	6.5_5	Bu_3PhP^+	*11.5*[e)]		
Br^-	7.9_5	$Bu_2Ph_2P^+$	*15.1*[e)]		
I^-	10.4[b)]	$BuPh_3P^+$	*18.5*[e)]		
OH^-	9.2_2	Ph_4P^+	*22.1*[e)]		
NO_3^-	12.5_5	$HCOO^-$	6.2_2		
SCN^-	13.1_7[c)]	CH_3COO^-	5.3_9		
BPh_4^-	17.9[f)]	$CH_3CH_2COO^-$	6.0_2		

a) The italicized values are obtained from K_D's which were determined by applying Eq. 6 with the two correction terms, and the others, from K_D's for which only the first correction was applied. The tmd data were taken from; b) Ref. 2, c) Ref. 3, d) Ref. 4, e) Ref. 7, and f) unpublished work.

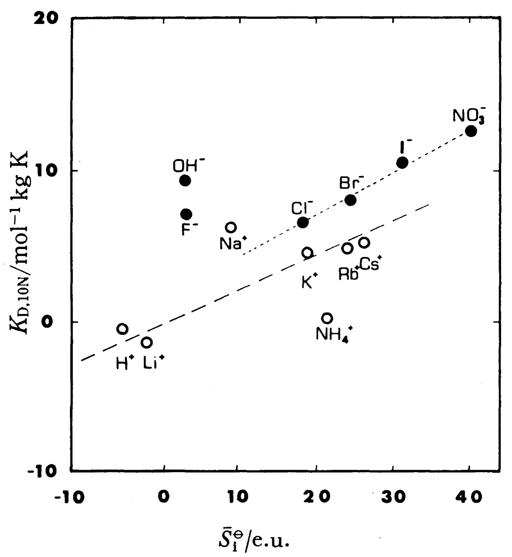

Fig. 1. Ionic Despretz Constants for monovalent ions plotted against the standard partial molal entropy of ion.

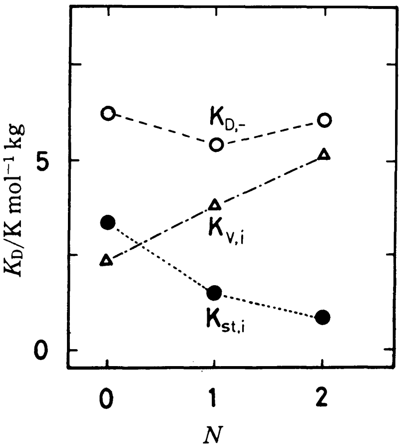

Fig. 2. $K_{D,-}$, $K_{v,i}$, and $K_{st,i}$ for carboxylate ions plotted against the number of carbon atoms (N) in alkyl groups.

The $K_{D,i}$'s for alkali metal ions are in the sequence, $Li^+<K^+<Rb^+<Cs^+<Na^+$ and those for halogenide ions, $Cl^-<F^-<Br^-<I^-$. These orders are, except for Na^+ and F^- ions, consistent with the sequences in the standard partial molal entropies, $\bar{S}_i^\circ$,[25] for each set of the ions at 25 °C (Fig. 1). The $K_{D,-}$ values are somewhat higher than $K_{D,+}$ values when a comparison is made between cations and anions with the same ionic redius, in accordance with the similar trend found in $\bar{S}_i^\circ$'s. The negative $K_{D,+}$ values for H^+ and Li^+ are notable since these ions are known as typical structure-making ions. The $K_{D,+}(NH_4^+)$ is considerably lower (probably negative) than for alkali metal ions (Table 2), suggesting that the ion would be capable of fitting into the partial water structure through hydrogen bonding. These seem to support an intuitive anticipation that the smaller the ionic Despretz constant, the greater is the structure-making ability of the ion.

However, necessity for reexamining in detail the content of $\bar{E}_{ion}^\circ$ and hence that of $K_{D,i}$ for simple ions comes from the disorder for Na^+, OH^-, and F^- ions in the seqiences in $K_{D,i}$. At 25 °C, $\bar{E}_{cation}^\circ$ for alkali metal ions[26] are in the sequence, $Na^+>K^+>Rb^+>Cs^+>Li^+$, which is almost reverse with that at 3.98°, while with anions, $F^-<Cl^-<Br^-<I^-(<NO_3^-)$, which is the same as that at 3.98° except for F^- ion. This fact is thought to reflect the difference in hydration between cation and anion.

The $\bar{E}_{ion}^\circ$ for simple ions can be decomposed into components corresponding to the decomposition of $\bar{V}_{ion}^\circ$. Applying a semiempirical equation, Millero[19,27] divided $\bar{V}_{ion}^\circ$ into three terms, the crystal partial molal volume $\bar{V}_{cryst}^\circ$, the electrostriction partial molal volume $\bar{V}_{elect}^\circ$, and the disordered or void-space partial molal volume $\bar{V}_{disord}^\circ$. Since $\bar{V}_{cryst}^\circ$ is hardly affected by temperature change, the corresponding expansibility can be ignored. He showed that $\bar{V}_{elect}^\circ$ goes through a minimum at a point near room temperature which depends on the ionic radius while $\bar{V}_{disord}^\circ$ increases with increasing temperature. The $\bar{E}_{elect}^\circ$, therefore, changes sign from positive to negative with rising temperature while the $\bar{E}_{disord}^\circ$ is always positive. The sign of the ionic charge would affect both the temperature at which the $\bar{E}_{elect}^\circ$ changes its sign and the magnitude of the $\bar{E}_{disord}^\circ$ through the effect of ionic charge on the orientation of water dipoles. This would be responsible for the difference between cation and anion in the ionic-radius dependence of the sequences in $\bar{E}_{ion}^\circ$ at the two temperatures.

More satisfactory knowledge is required to explain the irregularity for Na^+, OH^-, and F^- ions found in the magnitudes for $\bar{E}_{ion}^\circ$.

Organic Ions. Here, extraction of $K_{st,i}$ from $K_{D,i}$ for some organic ions is examined.

The first example is the carboxylate ion. The nitroalkanes RNO_2, having the same alkyl groups as those of carboxylate ions, may serve as model compounds in estimating $K_{v,i}$'s for the anions, which require expansibilities of the hypothetical liquids composed of hypothetical chargeless molecules, RCOO. The results for three carboxylate ions are shown in Fig. 2, where $K_{D,i}$, $K_{v,i}$, and $K_{st,i}$ are plotted against the number of carbon atoms in the alkyl groups. In the estimation for $K_{v,i}$ for the formate ion, V_2° and α_2 of formic acid were used, since no data are available for liquid HNO_2. This may be allowed as a first approximation, as expected from the following: The molal expansibility E° of nitromethane at 4 °C is 0.064 cm^3 mol^{-1} K^{-1}, comparable to that of super-cooled acetic acid, 0.060, which was estimated by extrapolation. E° of nitroethane, 0.079, is very close to E° of propionic acid, 0.078. These E°'s were calculated from volumetric data compiled by Riddick and Bunger.[28]

Although no regularity is found in $K_{D,i}$ with respect to the alkyl-chain length, a marked tendency is found in the order of $K_{st,i}$ which agrees with our anticipation that since alkyl groups would promote the water structures in their vicinity, the $K_{st,i}$ would decrease with increasing the alkyl-chain length. The results seem to indicate that the charged group, $-COO^-$, contributes positively to $K_{st,i}$ and hence may be regarded as a structure-breaking group.

Some alkanes of the type, R_4C, may permit us to estimate E°'s for the hypothetical liquids corresponding to neutral compounds, R_4N's. The estimated value for $K_V(Me_4C)$ is 13.7 K mol^{-1} kg, with $\alpha_2=1.8\times10^{-3}$ K^{-1} and $V^{\circ}(4\ ^{\circ}C)=118.6$ cm^3 mol^{-1}.[28] Substitution of this value in Eq. 10 gives a large negative value for $K_{st,i}$, of about -11 K mol^{-1} kg. However, it may be reasonable to regard this value as the lower limit for $K_{st,i}(Me_4N^+)$, since no allowance was made for electrostriction of the ion itself which would lead to a lower $K_{v,i}$ value. Although no data are available for estimating E°'s of higher homologs, Pr_4C and $(n\text{-}Bu)_4C$, E°'s of four n-alkanes, C_5, C_9, C_{13}, and C_{17}, are available, that is, 0.175, 0.189,[28] 0.24 and 0.28 cm^3 mol^{-1} K^{-1}, respectively. The last two were estimated by Gunn and Yamada's method,[29] which gives the values 0.169, and 0.195 for the first two members. Employing tentatively, in place of $K_{v,i}$'s, the K_V's calculated from these E°'s, 11.2, 12.1, 15.1, and 17.8 K mol^{-1} kg, we obtain large negative values, around -10 K mol^{-1} kg, for $K_{st,i}$ for all R_4N^+ ions.

It is impossible at this stage to judge whether or not the absolute values for "true" $K_{st,i}$ increase with lengthening the alkyl-chain length because any corrections have not been made for the electrostriction effect as already noted and the $K_{v,i}$'s used are tentative. We may at least state that the sign of $K_{st,i}$'s for the higher members of R_4N^+ ions would be negative. The negative sign assigned for lower members, Me_4N^+ and Et_4N^+, seems to be inconsistent with the view that Me_4N^+ ion is a structure breaker and that the Et_4N^+ ion hardly affects the water structure.

Generally it is assumed[25] that there are two contradictory factors that are responsible for the states of cosphere water around R_4N^+ ions, one is a weak electric field exerted by the ions which is important with Me_4N^+ ion and makes the ion a structure-breaker. The other is the structure-making ability of the alkyl groups. As the ion gets larger, from Me_4N^+ through Et_4N^+ and Pr_4N^+, the former effect becomes less important and the two effects balance near the Et_4N^+ ion. There are many criteria[25,30] indicating the Me_4N^+ ion to be a structure breaker, however, other facts have also been found. As revealed by the dielectric relaxation study by Haggis *et al.*,[31] the water relaxation time is lengthened by the presence of Me_4NBr, Me_4NI, and Et_4NCl, while it is shortened by the presence of inorganic salts. Pottel and Lossen[32] showed that the molal change of relaxation time of water in R_4NBr solutions with respect to the relaxation time of pure water is positive for all the R_4NBr examined. However the relative relaxation time change per mole of CH_2 group per kg water increases with the alkyl chain length from Me_4NBr to Et_4NBr and to Pr_4NBr. At this point it reaches a constant value equal to that for aliphatic hydrocarbons with an arbitrary number of CH_2 groups. On the other hand, a negative value was found for NH_4Br. Using the Samoilov equation, Uedaira[33] determined the activation energies of the exchange of the nearest water molecules next to an ion and found them to be positive for four R_4NBr's, from Me_4NBr to Bu_4NBr, *i.e.*, the water molecules close to the non-polar group are less mobile than in pure water. Wen and Hung[34] determined the standard molal free energy of transfer (ΔF°_{tr}) of hydrocarbons (methane, ethane, propane, and butane) from water to 0.1 mol kg^{-1} solutions of R_4NBr at four temperatures. They found that the ΔF°_{tr} values are all negative except for methane in Me_4NBr solution at 5 °C and with NH_4Br solution they are positive. All these results seem to indicate that the Me_4N^+ ion is different from some simple ions known as structure breakers, such as Cs^+ and I^-. It displays, though weakly and partially, the effect on the water structure inherent to aliphatic hydrocarbons.

Comparison of K_D in D_2O for a given salt with that in H_2O seems to be of interest, since D_2O is known to possess more structure than H_2O and the structure-influencing ability of salt should be stronger in D_2O than in H_2O, while $K_{v,i}$ for any ion should be common to two solvents. The K_D's of R_4NBr's in D_2O were obtained by Conway and Laliberte[4] as well as those in H_2O. In spite of the anticipation that K_D for Me_4NBr would be larger in D_2O than in H_2O and the reverse would be true for Bu_4NBr, all the K_D's in D_2O are smaller by some 2 K mol^{-1} kg, including Me_4NBr, indicating that there would be some factor which is reflected in $K_{st,i}$ but not in other probes.[37] In this respect, Wen's comment[25] about the difference in volumetric property between two structure breakers, Cs^+ and Me_4N^+ ions, seems to be suggestive. The excess heats of mixing ($\Delta_m H^{ex}$) in the systems, Pr_4NBr–$CsBr$ and Pr_4NBr–Me_4NBr, are negative whereas the excess volume of mixing ($\Delta_m V^{ex}$) in the Pr_4NBr–$CsBr$ system is considerably larger than that in Pr_4NBr–KBr system, while $\Delta_m V^{ex}$ in Pr_4NBr–Me_4NBr system is comparable to that in Pr_4NBr–KBr system. He pointed out that $\Delta_m H^{ex}$ is largely a measure of change in the number of hydrogen bonds of water in the solution, whereas $\Delta_m V^{ex}$ is a measure of the change in the geometric arrangement of water and ions. This comment may be valid also in the present case, since K_D is essentially a volumetric property.

From the above, we may conclude that $K_{st,i}$ for the Me_4N^+ ion can be negative in spite of being a net structure breaker. This means that classification of ions into the structure maker and structure breaker based on the sign and magnitude of $K_{st,i}$ is not always consistent with that based on different probes. The situation may be more or less common to all classification criteria because our knowledge about the structures of water and the so-called hydrophobic hydration are far from complete.

For a series of phosphonin salts, $(n\text{-}Bu)_{4-n}Ph_nPX(n=0\text{—}4)$, new values for K_D's are assigned in this work because the preceding values[7] had not been corrected for the temperature dependence of the b_V-coefficients. As seen from Table 2, the present conclusion is essentially the same as the preceding, the $K_{st,i}$ would increase with increase in the number of phenyl groups in agreement with information obtained from other probes[35,36] that the water structures around the cations decrease with n.

As a conclusive remark, it can be said that although $K_{D,i}$ for simple inorganic ions and $K_{st,i}$ for organic ions can be regarded as parameters indicating structure-influencing ability of ions, it may not always be the case. Particularly, $K_{\mathrm{st,i}}$'s for R_4N^+ ions are inconclusive, and more elaborate studies are required.

References

1) H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940).

2) A. J. Darnell and J. Greyson, *J. Phys. Chem.*, **72**, 3021; 3032 (1968).

3) G. Wada and M. Miura, *Bull. Chem. Soc. Jpn.*, **42**, 2498 (1969).

4) B. E. Conway and L. H. Laliberte, *Trans. Faraday Soc.*, **66**, 3032 (1970).

5) J. R. Kuppers, *J. Phys. Chem.*, **78**, 1041 (1974).

6) G. Wada, E. Nagao, N. Kawamura, and K. Kinumoto, *Bull. Chem. Soc. Jpn.*, **51**, 1937 (1978).

7) K. Takaizumi and T. Wakabayashi, *Bull. Chem. Soc. Jpn.*, **55**, 2239 (1982).

8) G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn.*, **35**, 646, 1797 (1962).

9) F. Franks and B. Watson, *Trans. Faraday Soc.*, **63**, 329 (1967).

10) D. A. Armitage, M. J. Blandamer, K. W. Morcom, and N. C. Treloar, *Nature*, **219**, 718 (1968).

11) D. D. MacDonald, M. D. Smith, and J. B. Hyne, *Can. J. Chem.*, **49**, 2815 (1971).

12) M. Sakurai, T. Komatsu, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **45**, 1038 (1972).

13) S. V. Subrahmanyan and N. M. Moorthy, *Z. Phys. Chem. Neue Folge*, **88**, 116 (1974).

14) a) D. D. MacDonald and J. B. Hyne, *Can. J. Chem.*, **54**, 3073 (1976); b) D. D. Macdonald, *ibid.*, **55**, 800 (1977).

15) J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, **74**, 658 (1970).

16) J. R. Kuppers, *J. Phys. Chem.*, **79**, 2105 (1975).

17) J. R. Kuppers, *Can. J. Chem.*, **55**, 798 (1977).

18) O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964). The original equation is referred to the concentration scale, mol dm^{-3}, but in this study the difference between the scale and the molality scale is ignored for dilute solutions.

19) F. J. Millero, "The Partial Molal Volumes of Electrolytes in Aqueous Solutions," in "Water and Aqueous Solutions," ed by R. A. Horne, Wiley-Interscience, New York (1972), Chap. 13.

20) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publication, Inc., New York (1964), Chap. 8.

21) "International Critical Tables," ed by E. W. Washburn, McGraw Hill Book Co., Inc., New York (1933), Vol. 3.

22) G. Perron, N. Desrosiers, and J. E. Desnoyers, *Can. J. Chem.*, **54**, 2163 (1976).

23) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 2738 (1966).

24) F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, **72**, 1758 (1968).

25) H. L. Friedman and C. V. Krishnan, "Thermodynamics of Ion Hydration," in "Water," ed by F. Franks, Plenum Press, New York (1973), Vol. 3, Chap. 1.

26) F. J. Millero, *J. Phys. Chem.*, **72**, 4589 (1968).

27) F. J. Millero, *J. Phys. Chem.*, **73**, 2417 (1969).

28) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York (1970).

29) R. D. Gunn and T. Yamada, *AIChE J.*, **17**, 1341 (1971).

30) W. Y. Wen, "Aqueous Solutions of Symmetrical Tetraalkylammonium Salts," in "Water and Aqueous Solutions," ed by R. A. Horne, Wiley-Interscience, New York (1972), Chap. 15.

31) G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).

32) R. Pottel and O. Lossen, *Ber. Bunsenges. Phys. Chem.*, **71**, 135 (1967).

33) H. Uedaira, *Zh. Fiz. Khim.*, **42**, 3024 (1968); *Chem. Abstr.*, **70**, 77184r (1969).

34) W.-Y. Wen and J. H. Hung, *J. Phys. Chem.*, **74**, 170 (1970).

35) K. Takaizumi and T. Wakabayashi, *J. Solution Chem.*, **9**, 809, 819 (1980).

36) T. Wakabayashi and K. Takaizumi, *J. Solution Chem.*, in press.

37) Some differences are found, as recognized by Perron *et al.*,[22] between $\phi_2{}^{\circ}$'s for Pr_4NBr and Bu_4NBr in D_2O obtained by Conway and Laliberte[4] and those by Perron *et al.*,[22] and the K_D's in D_2O for the two salts might be inconclusive. Reexamination may be required.