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The Structure of Water in the Vicinity of Complex Ions of Transition Elements in Their Aqueous Solutions as Revealed by the Shift of the Temperature of Maximum Density of Water

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The temperature of the maximum density (TMD) of aqueous solutions was measured for twenty complex ions of transition metals. From the degrees of depression of TMD, Despretz's constant k_D^{ion} and the constant of excess depression of mixing Δk^{ion} were determined. These constants along with B^{ion} coefficient of viscosity give us information on the structure of water in the vicinity of ions. $[Co(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$, and $[Zn(H_2O)_6]^{2+}$ are electrostrictive structure-breakers in the natural order of Irving-Williams, Co(II)<Ni(II)<Cu(II)>Zn(II). Of the complexes $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(pn)_3]^{3+}$, the pn-complex is the strongest hydrophobic structure-maker due to the hydrophobic nature of its aliphatic constituent. Both $[Fe(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$ are fairly strong electrostrictive structure-breakers, while $[Fe(phen)_3]^{2+}$, $[Co(phen)_3]^{2+}$, and $[Co(phen)_3]^{3+}$ are clathrate-like structure-makers. The EDTA and CyDTA complex ions of Co(II), Ni(II), Cu(II), and Zn(II) show no significant difference in k_D^{ion}, the situation being complicated by the hydrophobicity of the ligands and the radius effect of the complex ion. The actions of ions as structure-makers should be classified into three categories; electrostrictive, hydrophobic (iceberg formation), and hydrophobic (clathrate-like structure formation). The characteristic influence of the structure-making nature on k_D^{ion}, Δk^{ion}, and B^{ion} is discussed.

The phenomenon of the maximum density of water occurring at 3.98 °C is interpreted as evidence that water exists as an equilibriating mixture of an ice-like structure (a so-called "iceberg") and a denser one without hydrogen bondings; the iceberg, whose fraction in water diminishes with increasing temperature, gives a smaller coefficient of thermal expansion than that of the denser structure, and the apparent coefficient of thermal expansion of water results in negative values below 3.98 °C.1) Addition of a solute to water generally influences the equilibrium between the two different forms of water causing the shift of the temperature of maximum density (TMD) of water from 3.98 °C. Many simple electrolytes are known to depress the TMD of water, θ, as expressed by the Despretz rule,2)

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

by which it is shown that the degree of depression of TMD, $-\Delta\theta$, is proportional to the mole fraction of a solute, x, at least in low concentration range with the Despretz constant, k_D. The observed data for many simple electrolytes have been published.3)

Since Wada and Umeda4,5) treated the TMD of aqueous solutions of various nonelectrolytes quantitatively in view of water structure, many investigations dealing with this phenomenon as a clue for clarifying the solute-water interactions have been carried out.6—20) Cause of the depression of TMD of an aqueous solution from 3.98 °C ($-\Delta\theta>0$) might be explained as follows. The state of water in the solution at 3.98 °C corresponds to a state of pure water at a temperature higher than 3.98 °C, at which water is composed of the iceberg with a smaller fraction and the denser structure with a larger fraction than at 3.98 °C, the latter being promoted in the close vicinity around the solute added.

The molar volumes of pure water V_1, pure solute V_2, and their mixture V at a given temperature t in centigrade, in a small temperature range close enough to 3.98 °C, can be given by the following equations.

$$V_1 = V_1^*[1+\beta(t-3.98)^2] \tag{2}$$

$$V_2 = V_2^\circ(1+\alpha t), \tag{3}$$

$$V = (1-x)V_1 + xV_2 + \Delta V_x^E, \tag{4}$$

where V_1^* and V_2° are the molar volumes of water at 3.98 °C and of the solute at 0 °C, α and β are the coefficients of thermal expansion of the solute and water ($\beta=7.81\times10^{-6}\ K^{-2}$), and ΔV_x^E is the molar excess volume of mixing at the mole fraction of the solute x. By differentiating V with respect to t and equating the result to zero, the degree of the elevation of TMD, $\Delta\theta$, is given by the following relation.4—6)

$$\Delta\theta = \theta - 3.98$$
$$= -\frac{1}{2(1-x)\beta V_1^*}\left[x\alpha V_2^\circ + \frac{\partial \Delta V_x^E}{\partial t}\right] \tag{5}$$

If ΔV_x^E were either zero in the case of an ideal mixing or constant by chance in the small temperature range around 3.98 °C in a special case, the second term in the bracket on the right-hand side of Eq. 5 would disappear and the Despretz constant k_D would be reduced to k at the limiting dilute concentration.

$$k = \frac{\alpha V_2^\circ}{2\beta V_1^*} \tag{6}$$

It is clear from Eq. 6 that k is always positive (namely, $-\Delta\theta>0$), since normal substances have positive values for α. Accordingly, the excess depression of TMD of real aqueous solutions at infinitely low concentration is dependent upon the temperature variation of the excess volume of mixing as follows.

$$\Delta k = k_D - k$$
$$= \frac{1}{2\beta V_1^*}\left[\frac{1}{x}\cdot\frac{\partial \Delta V_x^E}{\partial t}\right]_{x\to0} \tag{7}$$

For most simple electrolytes, ΔV_x^E is negative and $\partial\Delta V_x^E/\partial t$ positive due to the electrostriction in the hydration sphere of ions. On the other hand, some alcohols with hydrophobic alkyl radicals such as *t*-butanol exhibit large negative Δk, so large that k_D ($=k+\Delta k$) becomes negative and consequently $\Delta\theta$ positive.4)

In the present investigation, twenty coordinate complexes of some transition elements are adopted as solutes, with ligands of either hydrophilic or hydrophobic nature towards the surrounding water in contact. The observed $\Delta\theta$ might give some clue to the structure of water around the complex ions.

Experimental

Materials. Pure water was made up by treating tap water with ion-exchange resin, followed by double distillation of its alkaline permanganate solution.

For the preparation of aqueous solutions of $[Co(H_2O)_6]Cl_2$, $[Ni(H_2O)_6]Cl_2$, $[Cu(H_2O)_6]Cl_2$, and $[Zn(H_2O)_6]Cl_2$, hydrous salts of $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ of special grade reagents were used without further purification. The concentrations of salts in each solutions were determined by titration with $AgNO_3$ for Co, Ni, and Cu salts and with EDTA for Zn salt. In order to avoid the partial hydrolysis of $ZnCl_2$, HCl was added to the solution of $ZnCl_2$. The TMD values for the solution were obtained by subtracting the value for HCl solution from that for the mixed solute, by virtue of the nature of additivity rule of TMD.[4)]

The crystals of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ were prepared by the usual method. The crystalline $[Co(pn)_3]Cl_3$ (pn: propylenediamine) was obtained by modifying the method for the preparation of $[Co(en)_3]Cl_3$; an aqueous HCl solution of pn containing $CoCl_2$ was oxidized by aeration and the complex was crystallized by addition of hydrochloric ethanol.

The crystals of $K_3[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ were obtained from commercial reagents of special grade.

The crystal of $[Fe(phen)_3]Cl_2 \cdot 7H_2O$ was prepared as follows. An HCl solution saturated with nitrogen gas was mixed with $FeCl_2$ in the presence of iron wire at 60 °C for 20 min in order to reduce Fe(III) which might be present in $FeCl_2$. Stoichiometric amount of 1,10-phenanthroline was added to the mixture for the formation of the Fe(II) complex to which was added NaCl. Then the complex was crystallized by cooling. The crystal of $[Co(phen)_3]Cl_2 \cdot 8H_2O$ was prepared in a similar manner to the case of Fe-complex. $[Co(phen)_3]Cl_3 \cdot 7H_2O$ was made up by passing Cl_2 gas through $[Co(phen)_3]Cl_2$ solution for the purpose of oxidation, the excess amount of Cl_2 being eliminated by vacuum pumping. The concentrations of $[Fe(phen)_3]Cl_2$[21)] and $[Co(phen)_3]Cl_2$[22)] in solution were determined spectrophotometrically.

For the preparation of solutions of EDTA and CyDTA complexes (CyDTA: 1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid), solutions of sodium salts of EDTA and CyDTA were mixed with those of chloride salts of respective metals in equivalent molar quantity. Thus each solution contained $Na_2[M(edta)]+2NaCl$ or $Na_2[M(cydta)]+2NaCl$. The TMD values for pure complex salt solutions were obtained by subtraction of the values for NaCl according to the additivity rule. In the case of Zn complexes, in addition to NaCl, HCl was necessary in their aqueous solutions for the purpose of suppressing the partial hydrolysis of Zn^{2+} ion. The TMD values were determined by also applying the additivity rule to the three kinds of solutes.

Determination of TMD. For the determination of TMD, a specially designed dilatometer was used.[4)]

Determination of Coefficients of Thermal Expansion of Solutes. For the determination of α for various solutes, a specific gravity bottle of ordinary shape was used. Details of procedure have been reported.[4)] Determination of α was not necessarily performed for all the complexes adopted in the present investigation, because of the difficulty in obtaining some complexes in pure form and not in the form of aqueous solution. It was found that the contribution of k to k_D was not large enough for the order of Δk in the respective series of homologues of complexes to be altered when k_D itself was adopted instead. Thus, theoretical considerations will be made by a comparison of either k or Δk_D.

Determination of B-Coefficients of Aqueous Solutions. The viscosity of the aqueous solutions of $K_3[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ at 25 °C was determined with an Ostwald-type viscometer. It took 164.5 s for water to flow down at 25 °C. Accoding to the Jones-Dole equation,[23)]

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC, \qquad (8)$$

B-coefficient can be obtained from the slope of the linear plot of $[(\eta/\eta_0)-1]/\sqrt{C}$ against $\sqrt{C}$, in which η and η_0 denote viscosity of solution and of pure water, respectively, and C concentration of the solute.

Results and Discussion

The linear relationships of the shift of TMD, $\Delta\theta$, against the mole fraction of solutes, x, following Eq. 1, can be seen from the straight lines for some examples given in Fig. 1. The case for the solution of mixed

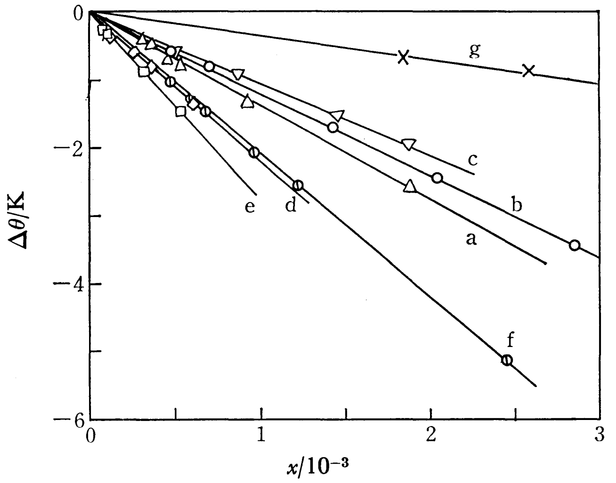

Fig. 1. Proportional relationship between shift of TMD, $\Delta\theta$, and mole fraction of solutes, x.
a: $[Co(NH_3)_6]Cl_3$, b: $[Co(en)_3]Cl_3$, c: $[Co(pn)_3]Cl_3$, d: $[Fe(phen)_3]Cl_2$, e: $[Co(phen)_3]Cl_2$, f: $K_3[Co(CN)_6]$, g: HCl.

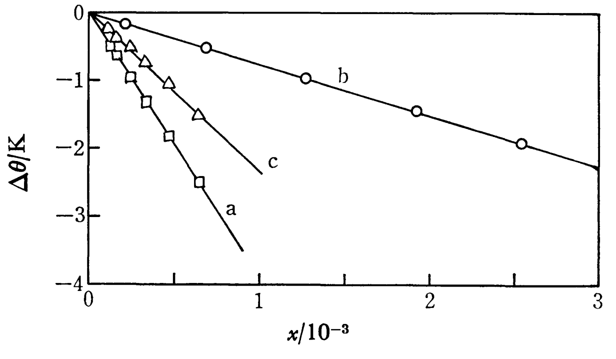

Fig. 2. $\Delta\theta$ *vs.* x plot for $Na_2[Co(edta)]$ obtained from the additivity rule.
a: $Na_2[Co(edta)]+2NaCl$, b: NaCl, c: $Na_2[Co(edta)]$.

TABLE 1. DESPRETZ CONSTANT k_D, THE COEFFICIENT OF THERMAL EXPANSION α, MOLAR VOLUME AT 0 °C V_2° OF VARIOUS SOLUTES, AND CONSTANT FOR IDEAL MIXING k AND THE EXCESS OF THE COASTANT Δk

Complex	k_D / 10^3 K	α / 10^{-4} K^{-1}	V_2° / cm^3·mol^{-1}	k / 10^3 K	Δk / 10^3 K
$[Co(H_2O)_6]Cl_2$	0.899				
$[Ni(H_2O)_6]Cl_2$	0.914				
$[Cu(H_2O_6)]Cl_2$	0.964				
$[Zn(H_2O)_6]Cl_2$	0.883				
$[Co(NH_3)_6]Cl_3$	1.344	4.14	155.67	0.229	1.115
$[Co(en)_3]Cl_3$	1.130	5.18	233.62	0.431	0.699
$[Co(pn)_3]Cl_3$	1.035	6.00	276.49	0.590	0.445
$[Fe(phen)_3]Cl_2$	2.207	1.26[a)]	573.73[a)]	0.514	1.693
$[Co(phen)_3]Cl_2$	2.727	0.60[b)]	572.04[b)]	0.244	2.483
$[Co(phen)_3]Cl_3$	2.224				
$K_3[Fe(CN)_6]$	2.150	3.87	173.36	0.223	1.927
$K_3[Co(CN)_6]$	2.105	5.19	172.31	0.318	1.787
$Na_2[Co(edta)]$	2.26				
$Na_2[Ni(edta)]$	2.30				
$Na_2[Cu(edta)]$	2.26				
$Na_2[Zn(edta)]$	2.32				
$Na_2[Co(cydta)]$	2.52				
$Na_2[Ni(cydta)]$	2.27				
$Na_2[Cu(cydta)]$	2.26				
$Na_2[Zn(cydta)]$	2.31				
HCl	0.354				
NaCl	0.740				
KCl	0.644	1.01	37.09	0.013	0.631

a) $7H_2O$ hydrate. b) $8H_2O$ hydrate.

solute, $Na_2[Co(edta)]+2NaCl$, is shown in Fig. 2. Subtraction of the slope of the straight line independently observed for NaCl from that observed for the mixed solute gives the slope for $Na_2[Co(edta)]$ only.

Thus, the values of $\Delta\theta$ obtained for various solutes at various x give values of k_D for each solute. They are given in Table 1, along with the observed data of α and $V_2°$ and the calculated values of k and Δk. On the simple assumption that the individual contributions of K^+ and Cl^- ions to the total KCl value of k_D, k, and Δk are equal to each other, these constants for all salts can be divided into each component ion, k_D^{ion}, k^{ion}, and Δk^{ion}, using values of $k_D^{ion}(K^+)=k_D^{ion}(Cl^-)=0.322\times10^3$ K, $k^{ion}(K^+)=k^{ion}(Cl^-)=0.007\times10^3$ K, and $\Delta k^{ion}(K^+)=\Delta k^{ion}(Cl^-)=0.315\times10^3$ K. The values of the ionic constants for complex ions thus obtained are given in Table 2, ionic values of B-coefficient also being given, on the basis of $B^{ion}(Cl^-)=-0.00_7$ at 25 °C.[28)] The constants assigned for individual ions can be compared with each other only among ions of the same electric charges. However, it is meaningless to compare them between ions of opposite signs or different charges.

(i) $[Co(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$, *and* $[Zn(H_2O)_6]^{2+}$. As regards alkaline earth metal ions, the value of k_D^{ion} increases in the order Mg^{2+} (0.10×10^3) < $Sr^{2+}(0.56\times10^3)$ < $Ba^{2+}(0.66\times10^3)$.[3)] It seems that the stronger electrostrictive structure-breaker the ion, the greater its k_D^{ion} value. The aqua complexes of transition metal ions are comparatively weak electrostrictive structure-breakers in the order Co(II) < Ni(II) < Cu(II) > Zn(II) as is seen in Table 2. Such an order is frequently recognized in the chemical properties of complexes of high spins, the so-called Irving-Williams' natural order[29)] based on the crystal field stabilization energies and ionic radii. This indicates that the aqua complex of copper(II) displays the largest electrostrictive structure-breaking, probably due to Jahn-Teller's distortion, and that the structure of water in contact with the coordinated shell might be destroyed to the greatest extent in the case of copper(II).

(ii) $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, *and* $[Co(pn)_3]^{3+}$. The value of both k_D^{ion} and Δk^{ion} of these cobalt(III) complexes decreases in the order NH_3-complex > en-complex > pn-complex (Table 2). The outer layers of these complex ions are covered with many hydrogen atoms; $[Co(NH_3)_6]^{3+}$ has 18 H-atoms, which are all bonded with 6 N-atoms; $[Co(en)_3]^{3+}$ has 24 H-atoms, 12 of which are bonded with 6 N-atoms and the other 12 with 6 C-atoms; $[Co(pn)_3]^{3+}$ has 30 H-atoms, 12 of which are bonded with 6 N-atoms and 18 with 9 C-atoms. Due to the difference in the electronegativity of N and C atoms, an H-atom bonded with a C-atom is more hydrophobic than one bonded with an N-atom. Part of the positive charges on cobalt(III) is rather scattered on H-atoms bonded with N-atoms, in the manner $\overset{\curvearrowleft}{\mathrm{Co{-}}}\overset{\curvearrowleft}{\mathrm{N{-}}}\mathrm{H^{\delta+}}$, making the ammine complex to

TABLE 2. IONIC VALUES OF k_D^{ion}, k^{ion}, Δk^{ion}, AND B^{ion}

Complex ion		k_D^{ion} 10^3 K	k^{ion} 10^3 K	Δk^{ion} 10^3 K	B^{ion} mol^{-1}
(i)	$[Co(H_2O)_6]^{2+}$	0.255			0.38[24] 0.36[25]
	$[Ni(H_2O)_6]^{2+}$	0.270			
	$[Cu(H_2O)_6]^{2+}$	0.320			
	$[Zn(H_2O)_6]^{2+}$	0.239			
(ii)	$[Co(NH_3)_6]^{3+}$	0.378	0.209	0.170	0.17[24]
	$[Co(en)_3]^{3+}$	0.164	0.411	−0.246	0.56[24]
	$[Co(pn)_3]^{3+}$	0.069	0.570	−0.500	0.88[24]
(iii)	$[Fe(phen)_3]^{2+}$	1.563	0.501	1.063	
	$[Co(phen)_3]^{2+}$	2.082	0.231	1.853	1.61[24]
	$[Co(phen)_3]^{3+}$	1.258			1.53[24]
(iv)	$[Fe(CN)_6]^{3-}$	1.184	0.203	0.982	0.27
	$[Co(CN)_6]^{3-}$	1.139	0.298	0.842	0.29
(v)	$[Co(edta)]^{2-}$	1.42			0.88[26]
	$[Ni(edta)]^{2-}$	1.46			0.86[26]
	$[Cu(edta)]^{2-}$	1.42			0.82[26]
	$[Zn(edta)]^{2-}$	1.48			0.86[26]
(vi)	$[Co(cydta)]^{2-}$	1.68			1.03[27]
	$[Ni(cydta)]^{2-}$	1.43			1.01[27]
	$[Cu(cydta)]^{2-}$	1.42			0.92[27]
	$[Zn(cydta)]^{2-}$	1.47			0.98[27]
	H^+	0.032			
	Na^+	0.418			
	Cl^-	0.322	0.007	0.315	0.007[28]

be very hydrophilic. Thus, the outer layer of the coordinate sphere of the complex ions is more hydrophobic in the reverse order of k_D^{ion} and Δk^{ion}, namely NH_3-complex < en-complex < pn-complex. Probably, the icelike structure with hydrogen bondings might be promoted in the vicinity of $[Co(pn)_3]^{3+}$ in spite of its electrostrictive structure-breaking effect caused by the electric charge on the central metal ion. It seems that the stronger hydrophobic structure-maker a complex ion, the smaller both Δk_D^{ion} and k^{ion} values. A similar trend has been noticed in the series of hydrophobic alcohols.[4]

The values of B-coefficients from viscosity of their aqueous solutions are in the order NH_3-complex<en-complex<pn-complex,[24] in line with the expectation from the physical interpretation of B-coefficient.

(iii) $[Fe(phen)_3]^{2+}$, $[Co(phen)_3]^{2+}$, *and* $[Fe(phen)_3]^{3+}$. These 1,10-phenanthroline-complexes have very large values of k_D^{ion}, Δk^{ion}, and B^{ion} as compared with other cations with the same electric charges, but it is clear that they are of hydrophobic nature on account of phen molecules surrounding the central metal ions. The hydrophobicity of phen-complex ions of iron and cobalt is well accounted for by the fact that R_f-value of thin layer chromatography with aqueous solutions is 1.0 for $[Co(NH_3)_6]^{3+}$, while it is zero for phen-complexes.[30] The abnormally large values of k_D^{ion} and Δk^{ion} might arise not from iceberg promotion but from the occurrence of a clathrate-like structure of water formed around the phen-complex ions. This is deduced by the fact that a similar phenomenon has been found in the case of tetrabutylammonium ion where k_D^{ion} value is outstandingly large as compared with other homologous tetraalkylammonium ions, since only $(n\text{-}C_4H_9)_4N^+$ is of suitable shape and size to fit in a clathrate-like cage structure of water.[9] Of the three complexes, $[Co(phen)_3]^{2+}$ may have the most favored conditions[31] for the clathrate-like cage to wrap the complex ion in, although only the dimension of $[Fe(phen)_3]^{2+}$ is known.[32]

On the other hand, the large value of B^{ion} [24] indicates that the formation of clathrate-like structure would interfere with smooth flow of the aqueous solution; this may be easily understood by taking the steric framework of hydrogen bondings in clathrate structure into consideration.

The extent of development of clathrate-like structure is thus supposed to be in the order $[Fe(phen)_3]^{2+} < [Co(phen)_3]^{2+} > [Co(phen)_3]^{3+}$.

(iv) $[Fe(CN)_6]^{3-}$ *and* $[Co(CN)_6]^{3-}$. The value of both k_D^{ion} and Δk^{ion} of cyano complexes which are of hydrophilic nature lies in the order Fe(III)-complex>Co(III)-complex but that of B-coefficient lies in the reverse order. This is consistent, indicating that $[Fe(CN)_6]^{3-}$ ion is a stronger electrostrictive structure-breaker than $[Co(CN)_6]^{3-}$ ion. Since both are of low spin complexes, Fe(III)-complex has a smaller crystal field stabilization energy with a ionic radius longer than that of Co(III)-complex, thus being a weaker electrostrictive structure-maker or a stronger electrostrictive structure-breaker.

(v) EDTA and CyDTA Complexes of Co(II), Ni(II), Cu(II), and Zn(II). The values of k_D^{ion} and B^{ion} [26,27] do not significantly differ from each other among these complex ions, with the exception of k_D^{ion} of $[Co(cydta)]^{2-}$ ion. CyDTA has a cyclohexane ring in its molecule, which is very hydrophobic and is large in dimension. Consequently, the stronger hydrophobicity of CyDTA, which would make the value of k_D^{ion} smaller as a hydrophobic structure-maker, might cancel the effect of the larger ionic radius of cydta-complex ion, making the value of k_D^{ion} larger as an electrostrictive structure-breaker, as compared with the cases of edta-complex ions. This might be due to the fact that almost no difference is seen between the edta- and cydta-complexes. According to Yasuda,[24,27] divalent metal chelates of EDTA and CyDTA are supposed to be partly present in penta-coordinated structure in aqueous solution. The various forms of these complexes make the systematic differences caused by the crystal field theory ambiguous. A similar result is also noticed in the values of B^{ion}.

Up to the present time, ions in aqueous solution have often been simply classified into two types, the structure-maker and the structure-breaker on the basis of the interactions between ions and water molecules as solvent. In view of the present considerations, however, the simple classification seems to be no longer sufficient for understanding the behavior of complex ions. The structure-making or -breaking nature can be divided into more detailed categories as shown in Table 3.

There are two causes for structure formation of water around ions; "electrostrictive" and "hydrophobic", the

Table 3. General trends of variation of Δk^{ion} (or $k_{\mathrm{D}}^{\mathrm{ion}}$) and B^{ion} caused by a structure-maker
In case of a structure-breaker, the trends should be reversed.

	Δk^{ion} or $k_{\mathrm{D}}^{\mathrm{ion}}$	B^{ion}	Examples
Electrostrictive	Decrease	Increase	Simple ion (alkali and alkaline earth metals) Aqua ion
Hydrophobic			
Iceberg	Decrease	Increase	$[\mathrm{Co(pn)_3}]^{3+}$
Clathrate-like	Increase	Increase	$[\mathrm{Co(phen)_3}]^{2+}$ $(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}^+$

latter being further divided into "iceberg" formation and "clathrate-like" formation. They give rise not necessarily to similar behavior but in quite opposite direction on the variation of Δk^{ion} or $k_{\mathrm{D}}^{\mathrm{ion}}$, according to their kind and type of hydrophobicity, while B^{ion} shows always the same tendency of variation, irrespective of the sort of structure formation. Hydrophobic structure formation is usually promoted by the presence of alkyl radicals, giving rise to icelike structure or so-called icebergs in the vicinity of the ions. If the shape, size, and certain other unknown conditions are satisfied for any hydrophobic ions by chance, water molecules would come together, wrapping ions in clathrate-like polyhedral cages connected with each other by hydrogen bondings. This structure makes the solution more viscous.

The partial molar entropy of the solution for an ion of a structure-maker also always shows a nagative value, being useless, as well as B^{ion}, for identifying the cause of structure formation. The measurement of TMD thus affords one convenient and effective method for finding the water structure in the close range outside the complex ions.

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