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Partial Molal Volumes and Volume Changes for Complex Formation of $[M(phen)_3]Cl_2$ in Aqueous Solutions

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The partial molal volumes, $\bar{V}^\circ$, of $[M(phen)_3]Cl_2$ (M=Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) and 1,10-phenanthroline were determined from density measurements at 25 °C. From the values for $\bar{V}^\circ$ of $[M(phen)_3]^{2+}$, M^{2+} and phen the volume changes for complex formation of $[M(phen)_3]^{2+}$, $\Delta\bar{V}^\circ$, were caluculated. Values for $\bar{V}^\circ$ of $[M(phen)_3]Cl_2$ varied from 445.1 cm³ mol⁻¹ for $[Fe(phen)_3]Cl_2$ to 458.1 cm³ mol⁻¹ for $[Zn(phen)_3]Cl_2$ and were in the order, $[Fe(phen)_3]^{2+} < [Co(phen)_3]^{2+} > [Ni(phen)_3]^{2+} < [Cu(phen)_3]^{2+} < [Zn(phen)_3]^{2+}$. The $\Delta\bar{V}^\circ$ of $[Fe(phen)_3]^{2+}$ was significantly small, 4.7 cm³ mol⁻¹. While those of other metal chelate ions were similar values, *ca.* 20 cm³ mol⁻¹. The smaller $\Delta\bar{V}^\circ$ of $[Fe(phen)_3]^{2+}$ is considered to be due to the spin change from the high-spin aqua ion, $[Fe(OH_2)_6]^{2+}$, to the low-spin complex ion, $[Fe(phen)_3]^{2+}$.

Metal chelate cations such as $[Fe(phen)_3]^{2+}$ are widely used for the determination of a large number of anions by solvent extraction of ion pairs.[1] Extensive studies have been reported to understand the mechanisms of solvent extraction of ion pairs and solute-solvent interactions of metal chelate electrolytes through viscosities,[2] conductivities,[3] solubilities,[4] and salting effects on the solubilities on nonelectrolytes in water.[5] The partial molal volumes and volume changes of complexation are effective in elucidating the solute-solvent interactions, yet few studies have been reported, especially for volume changes of the complex formation reactions of these metal chelates.

In this study, the partial molal volumes of tris(1,10-phenanthroline) complexes of the first transition metal ions (Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) are determined and volume changes on complex formation are estimated. The specific aspect of $[Fe(phen)_3]^{2+}$ has been discussed by the spin change on complexation.

Experimental

The metal chelate electrolytes, $[Fe(phen)_3]Cl_2\cdot 7.5H_2O$, $[Ni(phen)_3]Cl_2\cdot 7.5H_2O$ and $[Co(phen)_3]Cl_2\cdot 7.5H_2O$ were prepared by the literature methods.[2,6,7] $[Cu(phen)_3]Cl_2\cdot 7.5H_2O$ and $[Zn(phen)_3]Cl_2\cdot 7.5H_2O$ were prepared by a method similar to that for the Ni-complex. 1,10-Phenanthroline monohydrate (Hanawa Pure Chemical Industries, Ltd.) was used without further purification. Purity of the products was checked by analysis.

The metal chelate electrolytes were dehydrated by drying to constant weigh under reduced pressure over P_2O_5. All solutions were prepared by weight with deionized and distilled water.

The densities of the sample solutions were measured using a digital densimeter (Shibayama Scientific Co., Ltd. Model SS-D-200) with an external measuring cell which was completely immersed in a water bath controlled to 25.00± 0.002 °C. The system was calibrated with dry air and pure water. The accuracy of the system was checked by measuring the densities of NaCl solutions.[8] The errors in the density measurements were estimated within 3×10^{-6} g cm⁻³.

Results

The apparent molal volumes, ϕ_v, of the solutes have been calculated from the densities of the solutions using the equation:

$$\phi_v = \frac{1000(d^\circ - d)}{md^\circ d} + \frac{M}{d}, \tag{1}$$

where M is the molecular weight of the solute, m is the molality, d° and d are the densities of the solvent and the solution, respectively. The density of pure water at 25 °C was taken from the literature.[9]

The apparent molal volumes of the metal chelate electrolytes were fitted to the Redlich-Mayer equation in order to extrapolate them to infinite dilution:[10]

$$\phi_v = \phi_v{}^\circ + S_vC^{1/2} + b_vC, \tag{2}$$

where $\phi_v{}^\circ$ is the apparent molal volume at infinite dilution (equal to the partial molal volume, $\bar{V}^\circ$), S_v is given by the limiting Debye-Hückel law as 9.706 cm³ dm^3/2 mol^-3/2 for 2:1 electrolytes in water at 25 °C, b_v is a constant and c is the concentration.[10] Equation 2 was rearranged to

$$(\phi_v - S_vC^{1/2}) = \bar{V}^\circ + b_vC, \tag{3}$$

and plots of the left side of Eq. 3 against C are shown in Fig. 1. The parameters, $\bar{V}^\circ$ and b_v, for the molal volumes of $[Fe(phen)_3]Cl_2$ and $[Ni(phen)_3]Cl_2$ are obtained by the least squares method and are given in Table 1. The plots of Eq. 3 for the molal volumes of $[Co(phen)_3]Cl_2$, $[Cu(phen)_3]Cl_2$ and $[Zn(phen)_3]Cl_2$ deviated from linearity at low concentrations due to partial ligand dissociations. However, when measurements were done in 0.01 mol dm⁻³ solutions of 1,10-phenanthroline, the molal volumes showed normal concentration dependences as shown in Fig. 1. Then, by fitting the apparent molal volumes of these chelates in 0.01 mol dm⁻³ solutions of 1,10-phenanthroline to the equation:

$$\phi_v = \bar{V}^\circ + A_vC^{1/2} + B_vC, \tag{4}$$

$\bar{V}^\circ$ and fitting parameters, A_v and B_v, are obtained. These $\bar{V}^\circ$ values are assumed to be those in pure water and are given in Table 1.

The apparent molal volumes of free 1,10-phenanthroline in water were determined at five different concentrations, (1.0×10^{-2}—1.5×10^{-2} mol dm⁻³), which did not show any concentration dependence over the range of experimental errors. Therefore, the mean value of ϕ_v, (142.2±0.1 cm³ mol⁻¹), is regarded as the value at infinite dilution.

The volume changes of the complex formation of

Table 1. Standard partial molal volumes at 25 °C

Solute	$\bar{V}^\circ$ / $cm^3\ mol^{-1}$	b_v a) / $cm^3\ dm^3\ mol^{-2}$	A_v b) / $cm^3\ dm^{3/2}\ mol^{-3/2}$	B_v b) / $cm^3\ dm^3\ mol^{-2}$
$[Fe(phen)_3]Cl_2$	445.1 (443)c)	−21.8		
$[Co(phen)_3]Cl_2$	456.3d)		11.39	−25.2
$[Ni(phen)_3]Cl_2$	454.2	−26.1		
$[Cu(phen)_3]Cl_2$	456.5d)		9.86	−26.8
$[Zn(phen)_3]Cl_2$	458.1d)		7.75	−19.8
phen	142.2			

a) An adjustable parameter of Eq. 2. b) Parameters of Eq. 4. c) Ref. 2. d) $\bar{V}^\circ$ in 0.01 mol dm^{-3} 1,10-phenanthroline solutions.

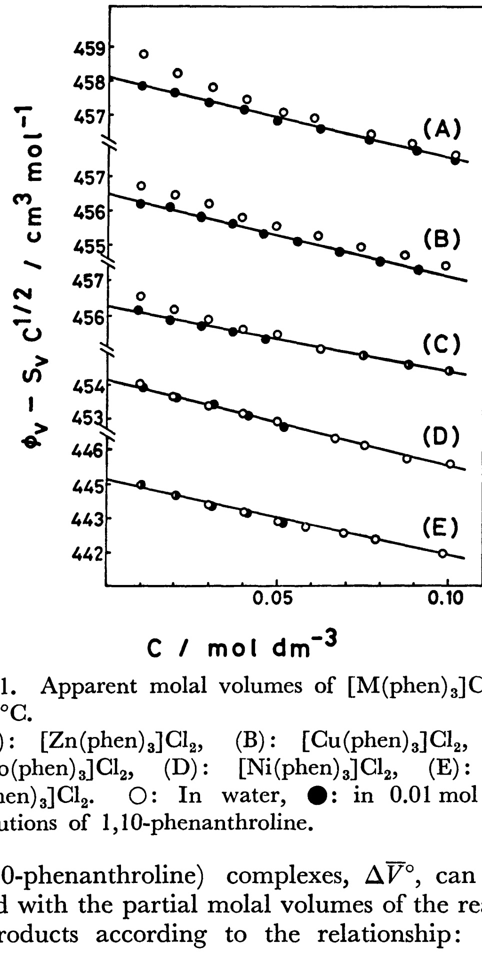

Fig. 1. Apparent molal volumes of $[M(phen)_3]Cl_2$ at 25 °C.
(A): $[Zn(phen)_3]Cl_2$, (B): $[Cu(phen)_3]Cl_2$, (C): $[Co(phen)_3]Cl_2$, (D): $[Ni(phen)_3]Cl_2$, (E): $[Fe(phen)_3]Cl_2$. ○: In water, ●: in 0.01 mol dm^{-3} solutions of 1,10-phenanthroline.

tris(1,10-phenanthroline) complexes, $\Delta\bar{V}^\circ$, can be estimated with the partial molal volumes of the reactants and products according to the relationship:

$$\Delta\bar{V}^\circ = \bar{V}^\circ([M(phen)_3]^{2+}) + 6\bar{V}^\circ(H_2O) - \bar{V}^\circ([M(OH_2)_6]^{2+}) - 3\bar{V}^\circ(phen), \quad (5)$$

where $\bar{V}^\circ([M(phen)_3]^{2+})$, $\bar{V}^\circ(H_2O)$, $\bar{V}^\circ([M(OH_2)_6]^{2+})$, and $\bar{V}^\circ(phen)$ are the partial molal volumes of metal chelate ions, water, aqua ions and 1,10-phenanthroline, respectively. The partial molal volumes of the hexaaqua complex ions can be estimated in good approximation by the equation:

$$\bar{V}^\circ([M(OH_2)_6]^{2+}) = \bar{V}^\circ(M^{2+}) + 6\bar{V}^\circ(H_2O), \quad (6)$$

where $\bar{V}^\circ(M^{2+})$ is the partial molal volume of the transition metal cation, which is generally obtained in the literature. By substituting Eq. 6 into Eq. 5, we obtain a simpler relation:

$$\Delta\bar{V}^\circ = \bar{V}^\circ([M(phen)_3]^{2+}) - \bar{V}^\circ(M^{2+}) - 3\bar{V}^\circ(phen), \quad (7)$$

Table 2. Ionic partial molal volumes and volume changes for the formation of $[M(phen)_3]^{2+}$ a)

M(II)	$\bar{V}^\circ(M^{2+})$ / $cm^3\ mol^{-1}$	$\bar{V}^\circ([M(phen)_3]^{2+})$ / $cm^3\ mol^{-1}$	$\Delta\bar{V}^\circ$ / $cm^3\ mol^{-1}$
Fe(II)	−32.6b)	398.7	4.7
Co(II)	−36.2c)	409.9	19.5
Ni(II)	−39.2c)	407.8	20.4
Cu(II)	−35.9d)	410.1	19.4
Zn(II)	−35.5c)	411.7	20.6

a) Estimated values using $\bar{V}^\circ(Cl^-) = 23.2$ $cm^3\ mol^{-1}$ and $\bar{V}^\circ(ClO_4^-) = 49.5$ $cm^3\ mol^{-1}$. b) Ref. 11. c) Ref. 13. d) Ref. 12.

which means that $\Delta\bar{V}^\circ$ can be estimated from the partial molal volumes of metal chelate ions, transition metal cations and 1,10-phenanthroline. The partial molal volumes of the transition metal cations were estimated from the literature values for $FeCl_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $Zn(ClO_4)_2$ using the additivity principle with $\bar{V}^\circ(Cl^-) = 23.2$ and $\bar{V}^\circ(ClO_4^-) = 49.5$ $cm^3\ mol^{-1}$.[11–13] The ionic partial molal volumes are given in Table 2.

Discussion

Partial Molal Volumes and the Solvation of the $[M(phen)_3]^{2+}$ *Ions.* The $\bar{V}^\circ$ of the aqua ions are in a sequence, $[Fe(OH_2)_6]^{2+} > [Co(OH_2)_6]^{2+} > [Ni(OH_2)_6]^{2+} < [Cu(OH_2)_6]^{2+} < [Zn(OH_2)_6]^{2+}$. The molal volumes of the chelate cations are in the same sequence except for the molal volume of $[Fe(phen)_3]^{2+}$, that is, $[Fe(phen)_3]^{2+} < [Co(phen)_3]^{2+} > [Ni(phen)_3]^{2+} < [Cu(phen)_3]^{2+} < [Zn(phen)_3]^{2+}$. From the results of X-ray analysis, the bond lengths of M–N are 1.97 Å and 2.09 Å in $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$, respectively.[14,15] The Cu–N distances in $[Cu(phen)_3]^{2+}$ are 2.04 Å and 2.33 Å in the equatrial position and in the axial position, respectively.[16] From the M–N bond lengths, the molal volumes of these chelate cations are expected in the order, $[Fe(phen)_3]^{2+} < [Ni(phen)_3]^{2+} < [Cu(phen)_3]^{2+}$, which is in agreement with the observed sequence of the molal volumes of these chelate cations. However the M–N bond lengths could not be a direct measure of the molal volumes of these chelate ions. That is, if one assumes a rigid sphere for these chelates, then the radius of $[M(phen)_3]^{2+}$ is estimated about 5.5 Å from its molal volume. For such a sphere, a difference of 0.1 Å in radius due to the M–N bond length yields a difference about 20 to 25 cm^3 mol^{-1} in the molal volume, which is about one order larger than the observed differences of these complexes except for $[Fe(phen)_3]^{2+}$.

The radius of the circumscribed sphere of $[Fe(phen)_3]^{2+}$ was estimated as 7 Å,[17] with the volume of 865 cm^3 mol^{-1}.[5] However, the molal volumes are in the range from 398.7 cm^3 mol^{-1} for $[Fe(phen)_3]^{2+}$ to 411.7 cm^3 mol^{-1} for $[Zn(phen)_3]^{2+}$, which are about 4 to 6% smaller than the three times of the molal volume of the free 1,10-phenanthroline, (426.6 cm^3 mol^{-1}). These facts indicate that water creates a solvation cage closely surrounding the three-bladed propeller of 1,10-phenanthroline, each moiety around each 1,10-phenanthroline is almost the same as the solvation cage of the free 1,10-phenanthroline molecule except around the nitrogen atoms. Such a closely surrounding solvation cage is consistent with a fact that, in aqueous solutions of the complex $[Cr(phen)_3]^{2+}$, water molecules can enter into the pockets between the ligands, penetrating the radius about 7 Å of the complex by about 2 Å.[18]

Volume Changes on Complexation. The partial molal volumes in the present work allow one to estimate the volume changes, $\Delta\overline{V}^\circ$, on the complex formation of,

$$[M(OH_2)_6]^{2+} + 3\text{phen} \rightarrow [M(\text{phen})_3]^{2+} + 6H_2O.$$

As shown in Table 2, the $\Delta\overline{V}^\circ$ values are almost equal except for the very small $\Delta\overline{V}^\circ$ of $[Fe(phen)_3]^{2+}$.

The exceptionally small $\overline{V}^\circ$ and the resultant small $\Delta\overline{V}^\circ$ of $[Fe(phen)_3]^{2+}$ can be related to the contraction of the volume due to the spin change from high to low on the complex formation. Such an effect of spin change on complex formation was also observed for the entropy change.[19] That is, the formation of $[Fe(phen)_3]^{2+}$ at 20 °C is accompanied by a negative change in the entropy but for the other chelate cations the changes are positive.

On complexation of alkali or alkaline earth ions with crown ethers or criptands, the $\Delta\overline{V}^\circ$ values vary in a wide range from 0 to 28 cm^3 mol^{-1} depending on the sizes of the ions and ligands.[20,21] In these complexes, metal ions have more than one water molecule and the charges are not completely screened from the water.[20]

For the complexation of Ni^{2+} with EDTA and MIDA, $\Delta\overline{V}^\circ$ are 25.5 and 26.8 cm^3 mol^{-1}, respectively.[22] These rather larger values are attributed to the partial neutralization of charges on complexation and to the delocalization of the residual charges on the chelate complexes.[22]

A volume change due to the electrostriction for a 2:2 electrolyte can be estimated from $\Delta\overline{V}^\circ$ on an ion pair formation. The $\Delta\overline{V}^\circ$ for $CaSO_4$ is 25.2 cm^3 mol^{-1},[23] but $\Delta\overline{V}^\circ$ of $MgSO_4$ is less than 10 cm^3 mol^{-1},[24] where the former is known to form a contact ion pair, but the latter, predominantly an outer sphere one.

In the present system, though charges are not neutralized, they are delocalized in the large aromatic ligands, which is responsible for the hydrophobic character on these complexes.[2,5] The volume changes of the present reaction, which are comparable to those of the contact ion pair formation and the complexation of Ni–EDTA or Ni–MIDA, may be due to the volume changes of water molecules released from the electronic fields of the central metal ions.

The Change of the Hydration Number on Complexation. On complexation, it may be assumed that the ligand hydration is almost the same for the free and coordinated ligand and only the hydration water of the aqua ions are released to the bulk. By using a simple model for the electrostriction of the ions the change of the hydration number, Δn_H, accompanied on the complexation can be estimated through an equation:[23–26]

$$\Delta n_H = \Delta\overline{V}^\circ/(\overline{V}^\circ_B - \overline{V}^\circ_E), \tag{8}$$

where $\overline{V}^\circ_B$ and $\overline{V}^\circ_E$ are partial molal volumes of the bulk and electrostricted water, respectively. Using Padova's estimation,[25] $\overline{V}^\circ_E - \overline{V}^\circ_B = -2.1$ cm^3 mol^{-1}, Δn_H of about 10 is obtained for these chelates except for $[Fe(phen)_3]^{2+}$. Of course this calculation depends on the estimation of the molal volume of the electrostricted water, and the number of released water molecules is not absolute. However the present estimation of Δn_H of 10 seems reasonable in comparison with the hydration number of the transition metal cations. That is, most of these were found in the range of 8 to 12,[27–29] except for the value of 6 estimated for coordinated water from NMR[30] and adiabatic compressibility[31] measurements.

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