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The Volume of Ions and Ion–Solvent Pair Correlation Functions[1]

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In this paper we summarize some of our recent work on the apparent molal volumes of transition metal salts in water. The densities of $NiCl_2$, $Ni(ClO_4)_2$, $CoCl_2$, $Co(ClO_4)_2$, and $Mn(ClO_4)_2$ solutions have been measured from 15 to 140°C. Solutions of $FeCl_2$, $Fe(ClO_4)_2$, $CuCl_2$, $Cu(ClO_4)_2$, $ZnCl_2$, and $Zn(ClO_4)_2$ were measured from 15 to 55°C. The apparent molal volumes at infinite dilution are reported and the effect of temperature is discussed. A new approach to the calculation of ionic volumes from salt volumes is presented. It is shown that the ionic volume is directly related to the direct ion–solvent correlation function. A large ligand field effect on transition metal volumes is noted.

KEY WORDS: density; dilution; ionic volumes; ion–solvent interactions; molal volume; transition elements.

1. INTRODUCTION

Density measurements are an important tool in determining the pressure–volume–temperature (*PVT*) properties of aqueous electrolytes and calculating apparent molal volumes. Investigators [1, 2] have used volume data to evaluate the pressure dependence of equilibrium constants and determine the pressure dependence of chemical potentials. The simplicity of the property has spurred theoreticians to develop models [3, 4] which explain ion–ion and ion–solvent interactions in terms of volume changes.

The volume properties of the first-row transition element divalent ions (Mn^{2+}–Zn^{2+}) are discussed in this paper. In particular, the temperature dependence of the infinite-dilution apparent molal volumes (ϕ_v^0) is dis-

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cussed. Examination of the infinite-dilution apparent molal volumes is a convenient method of evaluating ion–solvent interactions and determining their temperature dependence. The temperature and pressure ranges 15–140°C and 1–300 bars are covered and data are presented for both the chloride and the perchlorate salts of each metal cation.

2. CALCULATIONS

The extrapolation of the apparent molal volumes to infinite dilution has been made using the Redlich–Meyer equation [5].

$$\phi_v = \phi_v^0 + S_v \sqrt{m} + b_v m \tag{1}$$

where ϕ_v^0 is the infinite-dilution apparent molal volume, S_v is the theoretical Debye–Hückel slope, and b_v is an empirical parameter. The theoretical Debye–Hückel slopes have been calculated by Atkinson and Ananthaswamy [6] for temperatures less than 100°C and by Pitzer and Bradley [7] for temperatures exceeding 100°C.

It was necessary to modify Eq. (1) for some salts at high temperatures by adding an additional empirical parameter c,

$$\phi_v = \phi_v^0 + S_v \sqrt{m} + b_v m + c m^{3/2} \tag{2}$$

The dilute solution apparent molal volumes were fitted by either Eq. (1) or Eq. (2) with a weighted nonlinear least-squares fit using a weighting factor of $(1/\sigma_{\phi v})$. Figure 1 shows an extrapolation for $CuCl_2$ at 25°C with $\sigma_{\phi v}$ indicated by the error bars. Table I is a complete listing of

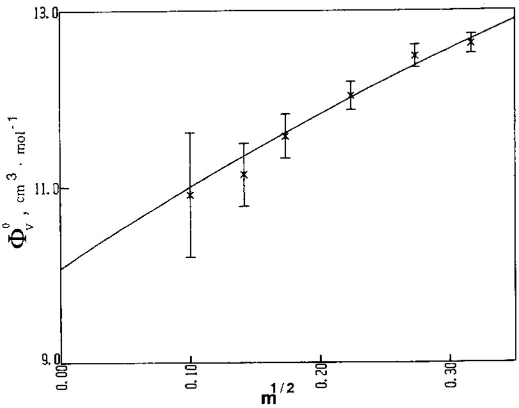

Fig. 1. Illustration of the extrapolation of apparent molal volume data to infinite dilution for $CuCl_2$ at 25°C.

Table I. Infinite-Dilution Apparent Molal Volumes at Temperatures of 15–140°C and Pressure of 1–300 bars

Salt	P (bars)	T (°C)	ϕ_v^0 (cm$^3\cdot$mol^{-1})
$MnCl_2$	1	15	17.19
	1	25	18.11
	1	35	18.13
	1	55	17.70
	1	55	17.69
	20	80	14.88
	20	100	10.91
	20	120	5.10
	20	140	−2.75
	100	80	15.58
	100	100	11.40
	100	120	5.58
	100	140	−1.46
	200	80	16.41
	200	100	12.37
	200	120	6.72
	200	140	0.84
	300	80	16.92
	300	100	14.27
	300	120	8.61
	300	140	1.99
$Mn(ClO_4)_2$	1	15	67.42
	1	25	70.89
	1	35	72.65
	1	45	75.69
	1	55	77.19
	20	80	78.07
	20	100	77.66
	20	120	74.07
	20	140	67.51
	100	80	78.34
	100	100	77.28
	100	120	74.43
	100	140	69.89
	200	80	79.03
	200	100	77.68
	200	120	75.76
	200	140	71.33
	300	80	79.04
	300	100	78.23
	300	120	76.13
	300	140	71.43

Table I. *(Continued)*

Salt	P (bars)	T (°C)	ϕ_v^0 ($cm^3 \cdot mol^{-1}$)
$CoCl_2$	1	15	9.21
	1	25	9.75
	1	35	10.04
	1	45	10.47
	1	55	10.20
	20	80	6.79
	20	100	3.60
	20	120	−3.85
	20	140	−11.10
	100	80	7.72
	100	100	4.04
	100	120	−1.49
	100	140	−9.19
	200	80	8.64
	200	100	5.56
	200	120	−0.22
	200	140	−6.96
	300	80	9.36
	300	100	5.22
	300	120	2.00
	300	140	−5.52
$Co(ClO_4)_2$	1	15	59.09
	1	25	62.44
	1	35	64.93
	1	45	67.57
	1	55	69.18
	20	80	70.26
	20	100	69.50
	20	120	65.82
	20	140	59.94
	100	80	70.38
	100	100	70.53
	100	120	66.92
	100	140	61.64
	200	80	70.83
	200	100	70.72
	200	120	67.45
	200	140	62.06
	300	80	71.17
	300	100	71.51
	300	120	67.58
	300	140	62.65

Table I. *(Continued)*

Salt	P (bars)	T (°C)	ϕ_v^0 (cm^3·mol^{-1})
$NiCl_2$	1	15	5.67
	1	25	6.39
	1	35	6.60
	1	45	6.66
	1	55	5.98
	20	80	4.32
	20	100	−1.25
	20	120	−7.43
	20	140	−14.98
	100	80	4.64
	100	100	0.41
	100	120	−5.42
	100	140	−13.31
	200	80	5.62
	200	100	0.95
	200	120	−4.24
	200	140	−11.74
	300	80	6.74
	300	100	3.15
	300	120	−3.61
	300	140	−9.97
$Ni(ClO_4)_2$	1	15	55.58
	1	25	58.65
	1	35	61.04
	1	45	64.66
	1	55	66.30
	20	80	67.47
	20	100	66.67
	20	120	63.01
	20	140	57.68
	100	80	67.77
	100	100	67.01
	100	120	63.22
	100	140	58.49
	200	80	68.34
	200	100	67.55
	200	120	63.81
	200	140	59.60
	300	80	68.54
	300	100	67.78
	300	120	64.65
	300	140	60.42

Table I. *(Continued)*

Salt	P (bars)	T (°C)	ϕ_v^0 ($cm^3 \cdot mol^{-1}$)
$FeCl_2$	1	15	12.25
	1	25	12.88
	1	35	13.09
	1	45	13.15
$Fe(ClO_4)_2$	1	15	62.19
	1	25	65.77
	1	35	68.28
	1	45	70.95
$CuCl_2$	1	15	8.90
	1	25	10.07
	1	35	10.85
	1	45	11.12
	1	55	10.76
$Cu(ClO_4)_2$	1	15	58.52
	1	25	62.29
	1	35	64.82
	1	45	67.79
	1	55	69.49
$ZnCl_2$	1	15	9.27
	1	25	9.96
	1	35	10.86
	1	45	10.30
	1	55	10.66
$Zn(ClO_4)_2$	1	15	59.31
	1	25	63.14
	1	35	65.66
	1	45	69.20
	1	55	70.71

the ϕ_v^0 values for each salt at all experimental temperatures and pressures. The values of the b_v and c parameters and $\sigma\phi_v$ for the fits can be found in Ref. 8.

3. RESULTS

The general temperature dependence of ϕ_v^0 values for a limited number of electrolytes has been established [9–11]. The transition metal electrolytes discussed in this paper reveal temperature trends in ϕ_v^0 similar to those established in pevious work. Figure 2 is a typical example of the shape for a ϕ_v^0 vs T plot for strong electrolyte systems. The plot is for $NiCl_2$. The plot goes through a maximum at approximately 40°C. Each salt investigated has a maximum in its volume–temperature curve. The temperature at which this maximum occurs yields important information about solute–solvent interactions.

The volume–temperature plots are fitted with a simple polynomial,

$$\phi_v^0 = a + bt + ct^2 \tag{3}$$

where a, b, and c are empirical parameters. A second-degree plynomial was found to represent the ϕ_v^0 data with maximum deviations less than $\pm 0.5\ \mathrm{cm^3 \cdot mol^{-1}}$, which is in good agreement with experimental uncertainties. The temperature at which the maximum ϕ_v^0 value occurs is found by differentiating Eq. (3) and setting the result equal to zero,

$$t_{\max} = \frac{-b}{2c} \tag{4}$$

The values for $t_{\max}$, a, b, and c are listed in Table II. The $t_{\max}$ values for the chloride salts fall within a small temperature range ±5.0°C. This might be expected due to the very similar size and charge densities of the cations. It is worth noting that the perchlorate salts have a signiticantly higher $t_{\max}$ then the chlorides. Yet no significant trend can be established within perchlorate salts themselves.

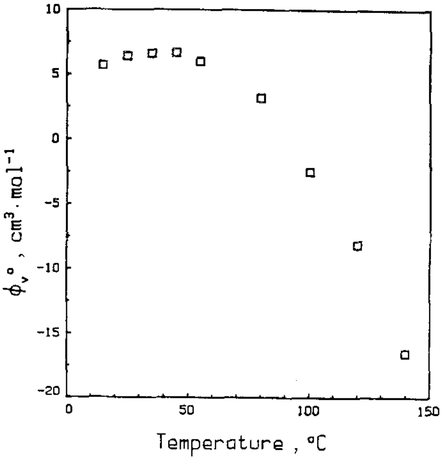

Fig. 2. Plot of ϕ_v^0 as a function of temperature for $NiCl_2$.

Table II. ϕ_v^0 Temperature Parameters for Eq. (3)

Electrolyte	a ($cm^3 \cdot mol^{-1}$)	b ($cm^3 \cdot mol^{-1} \cdot deg^{-1}$)	$10^3 c$ ($cm^3 \cdot mol^{-1} \cdot deg^{-2}$)	σ ($cm^3 \cdot mol^{-1}$)	t_{max} (°C)
$MnCl_2$	15.16	0.159	−2.04	0.28	39.0
$FeCl_2$	10.87	0.115	−1.42	0.06	40.3
$CoCl_2$	6.69	0.183	−2.21	0.46	41.4
$NiCl_2$	3.28	0.178	−2.21	0.46	40.3
$CuCl_2$	6.06	0.226	−2.55	0.05	44.3
$ZnCl_2$	7.57	0.137	−1.51	0.37	45.4
$Mn(ClO_4)_2$	61.30	0.442	−2.83	0.18	78.1
$Fe(ClO_4)_2$	56.40	0.424	−2.28	0.26	93.0
$Co(ClO_4)_2$	53.01	0.447	−2.83	0.22	79.0
$Ni(ClO_4)_2$	49.05	0.464	−2.88	0.46	80.6
$Cu(ClO_4)_2$	52.27	0.459	−2.64	0.28	86.9
$Zn(ClO_4)_2$	52.85	0.470	−2.59	0.48	90.7
HCl	15.71	0.118	−1.48	0.06	45.4
$HClO_4$	39.62	0.197	−0.92	0.20	90.7

The shape of the electrolyte volume–temperature curve and its corresponding maximum can be qualitatively explained using ionic hydration concepts. Bulk water has a relatively open molecular structure which becomes even more open with increasing temperature. When ions are added to solution they electrostatically compress the surrounding water molecules, causing a negative volume contribution which is counteracted by a positive volume contribution due to the ion's physical size and disordered secondary hydration effects. The slope of the volume–temperature curve and the temperature of the volume maximum are dependent upon whether the electrostriction or positive volume contribution dominates.

The section of the volume–temperature curve before the maximum is dominated by the positive volume contribution, thus ϕ_v^0 increases with temperature. As the temperature continues to increase, the electrostriction term becomes much larger until it balances the positive volume contributions (temperature of maximum volume). Beyond this temperature the electrostriction term continues to increase and begins to dominate the volume–temperature curve, causing a decrease in ϕ_v^0. If temperatures become high enough, the ϕ_v^0 values for the chloride salts become negative, indicating an overall volume constriction of the solution upon addition of the electrolyte.

Figure 3 shows plots of the volume–temperature curve for $NiCl_2$ and $Ni(ClO_4)_2$. These nickel systems reveal the same trends as those found in each of the salt systems studied. The volume maximum occurs at a higher temperature for the perchlorate salt. The cause if this shift must lie in the

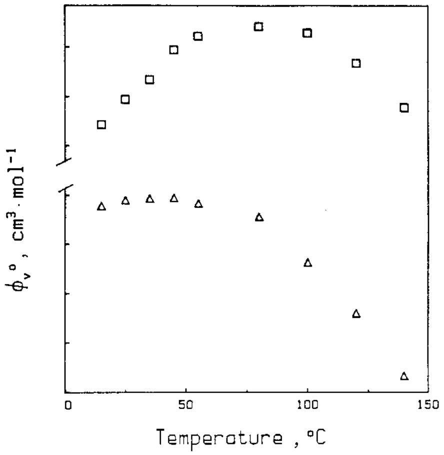

Fig. 3. Plot of the temperature dependence of ϕ_v^0 for $NiCl_2$ and $Ni(ClO_4)_2$.

anion properties since the salts have a common cation. The shift can best be explained by referring to the electrostriction caused by the anions present in each solution. Enderby et al. [12] have established that the chloride ion is hydrated in aqueous solution similar to the transition metal cations. It exists as a six-coordinate species with an octahedral structure. The primary hydration shell is not as well defined or as stable as the primary hydration shell of a cation but is significantly electrostricted. The perchlorate ion is a very large ion with a low charge density which exhibits negligible hydration and consequently causes much less electrostriction of the solvent.

The result is that the chloride salts receive electrostriction contributions from all three ions present, while the perchlorate salts receive an electrostriction contribution primarily from the cation. Thus, the magnitude of the electrostriction term increases much more rapidly for the chloride salts, causing the volume maximum to occur at a lower temperature.

Analysis of the electrolyte volume maximums as a function of cation, by comparing salts with common anions, yields little significant information. Comparison of the chloride and perchlorate salts indicates that interchange of a transition metal ion has little effect upon the temperature at which the volume maximum occurs. Again, the temperature at which the salt volume maximum occurs is highly dependent upon the electrostriction properties of the individual ions as a function of temperature. Since all the divalent transition metal ions have very similar electrostriction properties, especially at elevated temperatures, interchanging the cations has a negligible effect on the overall salt volume maxima.

The infinite-dilution apparent molal volumes are a linear function of pressure over the experimental pressure range investigated. This relation holds for each electrolyte studied. It was found that the chloride salts have a greater pressure dependence than the corresponding perchlorate salts, which means higher compressibilities. The differences in the behavior of the chloride and perchlorate salts with common cations, with respect to their temperature and pressure properties, indicate a substantial anion dependence. It now becomes desirable to calculate ionic volumes using a semiempirical approach which preserves ion-specific trends.

3.1. Ionic Volumes

An important property of the infinite-dilution apparent molal volume occurs via application of the ionic volume additivity principle. Standard procedure has been to use the convention of setting the proton volume $\bar{V}^0(H^+)=0$ at all temperatures and pressures. The additivity principle now allows calculation of any desired ionic volume from pure salt data. When this convention is used, much of the information about ion–solvent interactions is obscured because the temperature and pressure effects on the proton volume are ignored. The convention, with its obvious inadequuacy, exists only because of the difficulties involved in calculating ionic volumes using theoretically rigorous methods. We now seek to develop a method to relate cation and anion volumes while preserving, independently, the effects of temperature and pressure on the cation and anion.

An ionic volume, $\bar{V}_i^0$ can be written as the sum of three contributions,

$$\bar{V}_i^0 = \bar{V}^0(\text{intr}) + \bar{V}^0(\text{ele}) + \bar{V}^0(r) \qquad (5)$$

where $\bar{V}^0(\text{intr})$ is a combination of the crystallographic and cavity volume contributions, $\bar{V}^0(\text{ele})$ is the electrostiction volume resulting from electrostatic compression of the solvent, and $\bar{V}^0(r)$ is a local solvent response term which is associated with secondary hydration properties.

We have modified [8, 13] the semiempirical treatment present by Millero [14]. The resulting equations for ionic volume are presented below:

$$\bar{V}_+^0 = A_+ r_+^3 - \frac{B_+}{r_+} + A_T \frac{r_+^4}{r_-^2} \qquad (6)$$

$$\bar{V}_-^0 = A_- r_-^3 - \frac{B_-}{r_-} + A_T r_-^2 \qquad (7)$$

$$\bar{V}_2^0 = \bar{V}_+^0 + \bar{V}_-^0 = A_+ r_+^3 + A_- r_-^3 - \frac{B_+}{r_+} - \frac{B_-}{r_-} + A_T\left(\frac{r_+^4}{r_-^2} + r_-^2\right) \qquad (8)$$

where r_i is the Pauling crystallographic radius, A and B are the pressure-independent parameters, and A_T is a parameter which includes the pressure dependence of the ionic volume. The only unknown in Eqs. (6)–(8) is A_T. Using Eq. (8), the NaCl data reviewed by Pitzer and Rogers [9] and the Pauling radii [15], values for A_T as a function of temperature and pressure were determined and the volumes $\bar{V}^0(\text{Na}^+)$ and $\bar{V}^0(\text{Cl}^-)$ were calculated.

Figure 4 compares the temperature dependence of the total ionic volume for Na^+ and Cl^- with the salt volume. The cation volume has a maximum at 47°C, the anion maximum occurs at 76°C, and the maximum salt volume is at 63°C. The cation volume was expected to peak at a temperature below that if the salt due to the effect of electrostriction. The cation has a much greater electrostricted volume, which increases with temperature at a more rapid rate than the corresponding anion volume. The anion volume maximum is at a temperature greater than that of the salt as a result of its smaller electrostriction effects.

The consistency of this empirical theory for predicting ionic volumes can be checked by comparing the value of $\phi_v^0(\text{H}^+)$ calculated from this approach with the values determined by a variety of statistical mechanical and empirical theories. There are numerous estimates for the ionic partial molal volume of the proton at 25°C. Zana and Yeager [16] reported a value of $\phi_v^0(\text{H}^+) = -5.4\ \text{cm}^3 \cdot \text{mol}^{-1}$, determined from ionic vibration-potential measurements, which has been widely used as a reference. The value of $\phi_v^0(\text{H}^+)$ at 25°C determined from the chloride volume calculated from Eq. (6) is $-3.92\ \text{cm}^3 \cdot \text{mol}^{-1}$. This number deviates $1.4\ \text{cm}^3 \cdot \text{mol}^{-1}$ from the work of Zana and Yeager but is within the range of previously

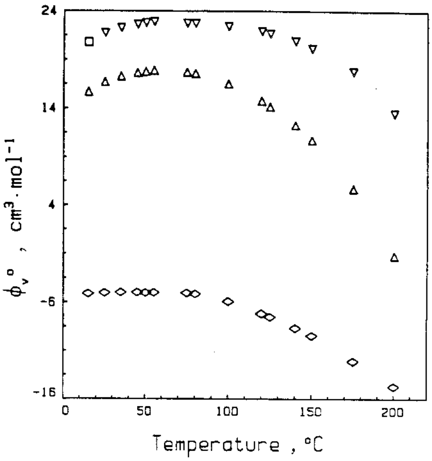

Fig. 4. Plot of $\phi_v^0(\text{NaCl})$, $\phi_v^0(\text{Cl}^-)$, and $\phi_v^0(\text{Na}^+)$ as a function of temperature.

reported literature values [17–19]. Proton volume values calculated at other temperatures show consistent temperature trends which are of a reasonable magnitude.

The cation volumes calculated using the $\phi_v^0(\mathrm{Cl}^-)$ values determined from Eq. (8) are listed in Table III. Analysis of Table III indicates that the cation volumes calculated from the theoretically determined Cl_ volumes reflect the appropriate temperature dependence—they become more negative with increasing temperature. Additionally, the cation volumes exhibit the expected systematic pressure dependence. The volumes increase with increased pressure.

Several trends exist in the cation volumes invesigated. First, electrostriction effects are important in determining the cation temperature dependence in aqueous solutions. The cation volume becomes increasingly negative with temperature. Second, the cation volumes have been found to show trends which parallel their CFSEs. Additionally, the hydration of the chloride ion and lack of hydration of the perchlorate ion were found to make important contributions to the hydration properties of the electrolyte.

Table III. Infinite-Dilution Ionic Volumes ($\mathrm{cm^3 \cdot mol^{-1}}$) at 1 bar

T (°C)	$\mathrm{Mn^{2+}}$	$\mathrm{Fe^{2+}}$	$\mathrm{Co^{2+}}$	$\mathrm{Ni^{2+}}$	$\mathrm{Cu^{2+}}$	$\mathrm{Zn^{2+}}$	$\mathrm{H^+}$
Values determined using $\mathrm{Cl^-}$ volumes calculated from Eq. (7)							
15	−24.4	−29.3	−32.4	−35.9	−32.7	−32.3	−3.7
25	−25.3	−30.6	−33.7	−37.1	−33.4	−33.5	−3.9
35	−26.4	−31.4	−34.5	−37.9	−33.7	−33.7	−4.3
45	−27.5	−32.1	−34.8	−38.6	−34.1	−34.9	−4.6
55	−28.1		−35.6	−39.8	−35.0	−35.1	−5.1
80	−30.5		−38.6	−41.1			−5.4
100	−33.9		−41.2	−46.1			−6.4
120	−38.7		−47.6	−51.2			−7.5
140	−44.6		−52.9	−56.8			−8.5
Conventional ionic volumes							
15	−17.0	−2.11	−25.2	−28.7	−25.6	−25.0	0.00
25	−17.4	−22.6	−25.8	−29.4	−25.7	−25.3	0.00
35	−18.1	−22.8	−25.6	−29.7	−25.7	−25.3	0.00
45	−17.9	−23.3	−25.6	−28.9	−25.2	−24.9	0.00
55	−17.9		−25.6	−29.2	−25.2	−24.6	0.00
80	−20.2		−28.2	−30.8			0.00
100	−22.0		−29.8	−33.6			0.00
120	−24.6		−33.2	−36.4			0.00
140	−29.3		−37.2	−40.3			0.00

Another interesting application of this work occurs when a comparison with the theoretical work of Patey and Kusalik [4] is made. Their expression for the infinite dilutation partial molecular volume is

$$\bar{V}_2^0 = \nu kTX_T^0 - \rho_s kTX_T^0(\nu_+ C_{+s}^0 + \nu_- C_{-s}^0) \qquad (9)$$

where k is Boltzman's constant, T is temperature, X_T^0 is the solvent compressibility, ρ_s is the solvent molecular density, v_i is the number of ions i per mole of electrolyte, and $C_{\alpha\beta}$ is the direct ion–solvent correlation function. The ionic split of the volume is clear. Note that the expression consists of a solvent term (solute effects excluded) and a solute–solvent interaction term. This is in good agreement with the ionic volume approach we have used. The data presented here could be a valuable tool in analyzing and determining the nature of the ion–solvent correlation functions. Great insight could be gained into the actual properties of ionic behavior through examination of the ion–solvent correlation functions.

4. CONCLUSIONS

An important development of this work was the formulation of a consistent semiempirical method to calculate ionic volumes independent of the standard convention which sets $\phi_v^0(H^+) = 0$ at all temperatures and pressures. The model successfully calculated ionic volumes utilizing a small number of temperature and pressure parameters. Additionally, the proton volumes calculated with this method are in good agreement with the best values reported in the literature.

Finally, these volume results tell us that transition element hydration properties are quite complex. Although the change in cation radius in the transition metal series is small, the ionic volume change from Mn^{2+} to Ni^{2+} is almost 50%. It is clear that a quantitative theory for transition metal hydration must include ligand field effects in addition to common electrostatics.

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