Inorganica Chimica Acta, 133 (1987) 331–336

Quantum Chemical Studies on the Hydrated Ions of the Rare Earths

Y.-Q. JIA
Changchun Institute of Applied Chemistry, Academia Sinica, Chanchun, Jilin, China

(Received February 27, 1987)

Abstract

The CNDO/2 quantum chemical method has been used to investigate the hydration of the rare earth ions. The results show that variation of the hydration energy of the first hydration sphere increases monotonically from La to Nd and from Tb to Lu. However, from Nd to Tb this trend is reversed. The fractional hydration numbers of the intermediate rare earth ions (Pm, Sm, Eu and Gd) are evaluated. For Pm, $N = 8.76$; for Sm, $N = 8.53$; for Eu, $N = 8.33$ and for Gd, $N = 8.13$. The more probable configurations for the hydrated ions with different coordination number are presented. The interactions in the first hydration sphere and the secondary hydration sphere, as well as the effect of the secondary sphere on the physical and chemical properties of the aqueous solution, are also discussed.

Introduction

The solvation effect is very important in solution chemistry. It is well known that water is a strong polar solvent; in aqueous solution both anions and cations are solvated. Even the hydrated electron can be formed in aqueous solution. Therefore, the effect of the hydration of ions on various physical and chemical properties of solution is very significant.

But, unfortunately, little is known about the 'structure' of a solution or about ion–solvent interactions in an aqueous solution. Although we know that the effect of hydration on macroscopic and microscopic properties of the solution is very significant, we cannot yet give a precise interpretation of the effect; namely, we do not yet know how the hydration affects the properties of the solution. For example, satisfactory interpretation of some complicated trends in the thermodynamic functions of extraction and complexation for the rare earths cannot yet be given. We believe that this is due to some extent to the fact that we lack detailed knowledge of the structure and composition of the hydrated ions of the rare earths.

The hydration of the rare earth ions and its effect on the physical and chemical properties of aqueous solutions of rare earth salts have been under discussion for many years [1–4]. Over the past few years, Spedding *et al.* have carried out considerable detailed research on various physical and chemical properties of aqueous solutions of the rare earth salts. They have measured the solubilities, equivalent conductances, relative viscosities, free energies, thermal expansions and equilibrium constants [5–7]. The experimental results show that, in general, solutions of rare earth chlorides, perchlorates and nitrates behave as typical strong electrolytes containing ions of high charge. More importantly, they found that a prominent and pervasive feature evident in these macroscopic properties of solutions of the rare earths is an anomaly in the rare earth series between neodymium and terbium. It is as if the light rare earth ions (La to Nd) and the heavy rare earth ions (Tb to Lu) exhibit 'normal' behavior, but the intermediate rare earth ions (Pm to Gd) exhibit 'anomalous' behavior. This 'two series' or 'S-shape' behavior in the thermodynamic and transport properties of aqueous solutions of some rare earth salts from lanthanum to lutetium is often found in solution chemistry of the rare earths.

Spedding *et al.* have established that this phenomenon ('two series' or 'S-shape' behavior) is due to the interactions between the rare earth ions and the water molecules. They have measured the number of water molecules in the first hydration sphere of the hydrated ions across the rare earth series by means of X-ray diffraction [8–10]. The experimental results show that the hydration number varies from lanthanum to lutetium. The hydration number is 9 for the light rare earth ions (La–Nd) and 8 for the heavy rare earth ions (Tb to Lu). But, for the intermediate rare earth ions (Pm, Sm, Eu, and Gd), the hydration number is a fraction between 8 and 9.

X-ray measurements on aqueous solutions of erbium trichloride and erbium triiodide showed that there is a firmly spaced arrangement in the first coordination sphere of the hydrated erbium ion [11].

Quantum chemical studies on the hydration of ions have been reported [12, 13]. CNDO, INDO and *ab initio* calculation methods have been used to investigate the structure and chemical bond properties of hydrated ions. The calculated results show

0020-1693/87/$3.50

© Elsevier Sequoia/Printed in Switzerland

that in aqueous solution both anions and cations are hydrated, and that the hydration energy of the ions is much higher than the hydrogen bond energy between the water molecules. It is found that in the hydrated ions the interactions between some metal ions and oxygen atoms of the water molecules are not pure ion–dipole electrostatic interactions. For instance, in the hydrated ion of berium, the Be–O bond has some covalent character [13].

Despite much research on the hydration of rare earth ions, quantum chemical studies on the hydrated ions of the rare earths have not been reported. To understand the structure and chemical bonding of the hydrated ions of the rare earths, the present work is a first attempt to apply a quantum chemical method to investigate the hydration of the rare earth ions.

First, we assumed a probable configuration of the first hydration sphere (the primary hydration sphere) for the hydrated ions with coordination number 9 and for the hydrated ions with coordination number 8, respectively. Then, we carried out CNDO quantum chemical calculations for the hydrated ions of all the rare earth ions. From the calculated results, we obtained the 'hydration energy' (ΔE) of the hydrated ion in the first hydration sphere, and then plotted the 'hydration energy' curve across the rare earth series.

The results show that the change in the 'hydration energy' ΔE does exhibit 'two series' or 'S-shape' behavior from lanthanum to lutetium. From the corresponding energy curves, the number of water molecules in the first hydration sphere have been evaluated for the intermediate rare earth ions (Pm, Sm, Eu and Gd). The calculated hydration numbers are in agreement with the experimental results of Spedding *et al.*

Based on the calculated results, translation of two configurations with different hydration numbers into each other is discussed. Some problems about interaction between hydrated ions and the secondary hydration sphere are discussed.

Results

The CNDO/2 quantum chemical method has been used to investigate the hydration of positive rare earth (RE) ions. The atomic orbitals used in the calculation were the 6s, 6p and 5d orbitals for the rare earths; the 2s, 2p orbitals for the oxygen atom; and the 1s orbital for the hydrogen atom.

Geometric parameters (RE–H_2O distance and H_2O–H_2O distance) were taken from Habenschuss and Spedding [8–10].

In the calculation, we assumed that (a) the O–H distance and the H–O–H bond angle are 0.95 Å and 108°, respectively; and (b) the water molecules in the first hydration sphere have axial symmetry about the RE–O bond [14].

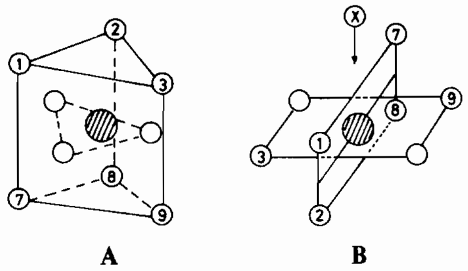

Fig. 1. Two probable configurations for the hydrated ions of rare earths. (A) The configuration of the hydrated ions with nine-coordinated water molecules and D_{3h} symmetry. (B) The configuration of the hydrated ions with eight coordinated water molecules and D_{2h} symmetry: ●: rare earth ion; ○: water molecule; ⊛: water molecule entering into the first hydration sphere. The arrow points to the z-axis of the coordinate of the molecule.

Based on the closest-packed principle and referring to the structures of some hydrated crystals of lanthanide compounds [15], we present two probable configurations for the hydrated ions of the rare earths with different hydration number (Fig. 1). For eight-coordinated hydrated ions, the configuration possesses D_{2h} symmetry (Fig. 1, **B**). For nine-coordinated hydrated ions, the configuration possesses D_{3h} symmetry (Fig. 1, **A**).

The hydration reaction can be represented as follows:

$$RE^{3+} + nH_2O \rightleftharpoons [RE(H_2O)_n]^{3+}$$

To evaluate the hydration energy, first, the total energy E_1 of the hydrated ion $[RE(H_2O)_n]^{3+}$ ($n = 8$ or 9) is calculated, then the total energy E_2 of the cluster of water molecules $(H_2O)_n$ ($n = 8$ or 9) in the first hydration sphere is calculated. This is regarded as a cavernous hydration sphere without the central rare earth ion. We may regard the energy difference ΔE ($\Delta E = E_1 - E_2$) as the 'hydration energy'. We must point out that it is only an approximation, because: (i) CNDO is a semi-empirical calculation method; (ii) the extra energy must be needed to form the cavernous hydration sphere from the continuous medium; and (iii) the effect of the hydrogen bond is also omitted. Unfortunately, we must make such an approximation because of lack of knowledge of the structure of the liquid. However, this approximation may only cause a systematic error for the calculation of the hydration energy, and perhaps it may be permissible for comparison of the same series of compounds.

The hydration energy curves are shown in Fig. 2. In Fig. 2, curve 1 is for the nine-coordinated hydrated ions, and curve 2 is for the eight-coordinated hydrated ions.

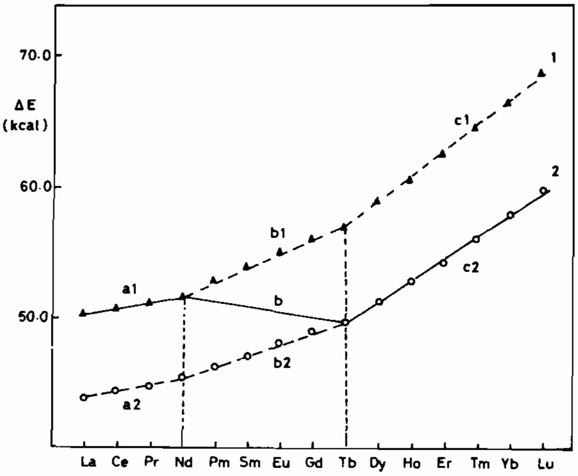

Fig. 2. The hydration energy curves across the rare earth series. Curve 1: the hydrated ions with nine coordinated water molecules, $[RE(H_2O)_9]^{3+}$. Curve 2: the hydrated ions with eight coordinated water molecules $[RE(H_2O)_8]^{3+}$.

As Fig. 2 shows, curves 1 and 2 are both composed of three segments: $a1$-$b1$-$c1$ and $a2$-$b2$-$c2$, respectively. Each segment of the curves is nearly a straight line.

It is very interesting that the two break points both on curve 1 and on curve 2 are just at neodymium and at terbium, respectively. If the break point on curve 1, which corresponds to neodymium, connects with the break point on curve 2, which corresponds to terbium, the straight line b can be obtained.

If the segment $b1$ of curve 1 were regarded as the hydration energy curve of Pm, Sm, Eu, and Gd when these ions had a coordination number of 9 in the first hydration sphere, and the segment $b2$ of curve 2 were regarded as the hydration energy curve of Pm, Sm, Eu, and Gd when these ions had coordination number of 8 in the first coordination sphere, the segment b could be regarded as the hydration energy curve of Pm, Sm, Eu, and Gd when these ions possess fractional coordination numbers. Therefore, the energy difference ΔE_{12} $(\Delta E_1 - \Delta E_2)$ can be regarded as the monohydration energy, which must be needed if a water molecule is moved from the first hydration sphere with nine-coordinated water molecules. From the curve $b1$ and $b2$, we can evaluate the energy difference ΔE_{1b} $(\Delta E_{1b} = \Delta E_{b1} - \Delta E_b)$ and ΔE_{2b} $(\Delta E_{2b} = \Delta E_b - \Delta E_{b2})$ for Pm, Sm, Eu and Gd, respectively. If we let $\Delta n_1 = \Delta E_{1b}/\Delta E_{12}$ and $\Delta n_2 = \Delta_{2b}/\Delta E_{12}$, we can evaluate the practical hydration number in the first hydration sphere for Pm, Sm, Eu and Gd from the corresponding Δn_1 and Δn_2. Namely, the practical hydration number (N) should be either $N = 9 - \Delta n_1$ or $N = 8 + \Delta n_2$.

For the intermediate rare earth ions (Pm, Sm, Eu and Gd), the calculated hydration numbers in the first hydration sphere are listed in Table I. As Table I shows, the calculated hydration numbers of Pm, Sm, Eu and Gd are in good agreement with the hydration numbers Habenschuss and Spedding presented from experimental results [10].

TABLE I. The Calculated Number of Water Molecules in the First Hydration Sphere for the Intermediate Rare Earth Ions $[RE(H_2O)_n]^{3+}$

Rare earth ion	Pm	Sm	Eu	Gd
ΔE_{12}	6.7	6.8	7.1	7.1
ΔE_{1b}	1.6	3.2	4.8	6.2
ΔE_{2b}	5.1	3.6	2.3	0.9
Δn_1	0.24	0.47	0.67	0.87
Δn_2	0.76	0.53	0.33	0.13
$N = 9 - \Delta n_1$	8.76	8.53	8.33	8.13
$N = 8 + \Delta n_2$	8.76	8.53	8.33	8.13
N [10]		8.6–8.7	8.4	

From the above mentioned results, we can regard the curve ($a1$-b-$c2$) in Fig. 2 as the practical hydration energy curve across the rare earth series. The segment $a1$ represents the hydration energy curve of the hydrated ions with a coordination number of 9; the segment $c2$ represents the hydration energy curve of the hydrated ions with a coordination number of 8; the segment b represents the hydration energy curve of the hydrated ions with a coordination number between 8 and 9.

The calculated results show that the components of the occupied molecular orbitals of the hydrated ions include the valence orbitals of the central rare earth ion. Besides, the energies of some occupied molecular orbitals in the hydrated ions decrease slightly in comparison with the energies of the corresponding occupied molecular orbitals of the water molecule cluster without the central rare earth ion. This means that covalent bonds between the rare earth ions and the oxygen atom of the coordinated water molecules in the hydrated ion are formed, although they are weaker.

We have noted that the main components of the lowest unoccupied molecular orbital (LUMO) in the eight-coordinated hydrated ions are the $5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals of the rare earths.

Besides, we must also point out that the hydration energies of the hydrated ions with a coordination number of 9 are always higher than that of the hydrated ion with a coordination number of 8 for the same rare earth ion.

These results will help us to understand interaction in the hydrated ions as well as the transition between the two different configurations of the hydrated ions.

Discussion

From the foregoing results, we know that the change in the hydration energy ΔE across the rare earths (the curve *a*1-*b*-*c*2 in Fig. 2) exhibits the 'two series' or 'S-shape' behavior. This corresponds with the phenomena Spedding *et al.* have observed in measurement of physical and chemical properties of some rare earth salt solutions. The calculated hydration numbers of Pm ($N = 8.7$), Sm ($N = 8.53$), Eu ($N = 8.33$), and for Gd ($N = 8.13$) are in agreement with the average coordination numbers Habenschuss and Spedding obtained from the experimental results for Sm ($N = 8.6$–8.7) and Eu ($N = 8.4$) [10]. This agreement shows that our calculated results are reasonable.

Now let us discuss the configurations of the hydrated ions of the intermediate rare earth ions. In practice, this is a problem about the transition of the hydrated ion configuration from the configuration with a coordination number of 8 to the configuration with a coordination number of 9.

Mioduski and Siekierski have discussed the probable configurations of the hydrated ions of the rare earths on the basis of the 'double–double' effect of the rare earth compounds [4]. We believe that the configuration **A** in Fig. 1 is the most probable configuration for the hydrated ion $[RE(H_2O)_9]^{3+}$. This configuration is often observed in the hydrate crystals of some rare earth salts, for example in the $RE(C_2H_5SO_4)_3 \cdot 9(H_2O)$ crystal [15]. In our opinion, the configuration **B** in Fig. 1 may be the most probable configuration for the hydrated ion $[RE(H_2O)_8]^{3+}$.

It is well known that the decrease in the $RE–H_2O$ distance across the rare earth series is due to the decreasing size of the rare earth ions from La to Lu, and that the change in the number of coordinated water molecules in the first hydration sphere is due to crowding of the ligands as the central rare earth ion becomes smaller. So, the hydrated ions of the heavy rare earths (Tb to Lu) possess eight coordnated water molecules and take the configuration **B**; the configuration has D_{2h} symmetry. The hydrated ions of the light rare earths (La to Nd) possess nine coordinated water molecules and take the configuration A; the configuration has D_{3h} symmetry. As for the hydrated ions of the intermediate rare earths (Pm to Gd), we believe that they may take a transitional configuration between configuration **A** and configuration **B**.

From terbium to gadolinium, the ionic radius becomes larger and larger. The first hydration sphere is not so crowded that one of the water molecules in the secondary hydration sphere can partly enter into the first hydration sphere. As mentioned above, for the hydrated ions with eight coordinated water molecules, the components of the lowest unoccupied molecular orbital are mainly composed of the $5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals of the central rare earth ion. If we regard the lowest unoccupied molecular orbital as the 'valence orbital' of the hydrated ion, this orbital is mainly in the direction of the z-axis in the coordinate of the molecule.

If one of the water molecules in the secondary hydration sphere wants to enter into the first hydration sphere, chemical bond formation may be most favorable when the water molecule is close to the central rare earth ion along the z-axis, because the lone-pair electrons of the oxygen atom of the entering water molecule can interact with the 'valence orbital' of the hydrated ion. The entering water molecule will be closer to the rare earth ion as the size of the rare earth ion becomes larger. When the size of the rare earth ion is large enough to overcome the steric hindrance, the water molecule in the secondary hydration sphere finally enters into the first hydration sphere. When the entering water molecule approaches the rare earth ion along the z-axis (see Fig. 1, **B**), the first hydration sphere will be distorted. The water molecules 1, 2, 3 and 7, 8, 9 in configuration **B** will gradually move to the corresponding positions of the water molecules 1, 2, 3 and 7, 8, 9 in configuration **A**. Therefore, we suggest that the hydrated ions of the intermediate rare earths might take a transitional configuration between **A** and **B**, namely a distorted configuration **A** or a distorted configuration **B**.

Spedding, Pikal and Ayers have suggested that there are both eight-coordinated hydrated ions and nine-coordinated hydrated ions in the aqueous solution at one time, and that there exists an equilibrium between the two coordination species for the intermediate rare earths [2]. We know that the hydration reaction is also a complexation reaction in practice. Of course, we cannot rule out the possibility that two kinds of hydrated ions exist in equilibrium in solution. If this is true, we can evaluate the ratio of the components of the two hydrated ions from the average coordination number.

Pm ($N = 8.76$) $[RE(H_2O)_9]^{3+}:[RE(H_2O)_8]^{3+} = 0.76:0.24$

Sm ($N = 8.53$) $[RE(H_2O)_9]^{3+}:[Re(H_2O)_8]^{3+} = 0.53:0.47$

Eu ($N = 8.33$) $[RE(H_2O)_9]^{3+}:[RE(H_2O)_8]^{3+} = 0.33:0.67$

Gd ($N = 8.13$) $[RE(H_2O)_9]^{3+}:[RE(H_2O)_8]^{3+} = 0.13:0.87$

As the above results show, if there were two hydrated ions in the aqueous solution at one time, the difference between the magnitudes of the two hydrated species may not be very large. Therefore, the two sets of structure parameters could be obtained by means of X-ray diffraction. Of course, the difference between these structural parameters might be very small, perhaps only a more precise method could check whether the two hydration species exist in aqueous solution.

However, we know that thermodynamic and transport data on the aqueous solutions of rare earth salts show that variation in some physical and chemical properties of the solution (for example, free energy) occurs gradually, not abruptly, from lanthanum to lutetium. So, we believe that the alternative explanation about the transitional configuration based on the quantum chemical calculation may be more reasonable.

From Fig. 2, we know that the 'hydration energy' ΔE of the nine-coordinated hydrated ions is always larger than that of the eight-coordinated hydrated ions. This means that the central rare earth ion would prefer to bond with more water molecules if there were no steric hindrance. In practice, all the hydration numbers of the rare earths are not 9. This shows that the coordination number in the first hydration sphere should be mainly governed by the size of the central rare earth ion. However, it is arguable as to whether it is dictated by the strength of the ion–dipole interaction [8].

Mioduski and Siekierski have discussed the chemical bond in hydrated ions of rare earths based on the 'double–double' effect and the nephelauxetic effect and proposed that there are some degrees of covalency in rare earth hydrates [4].

Some quantum chemical calculations show that the interaction in some hydrated ions is not pure ion–dipole electrostatic interaction. *Ab initio* calculations show that the Be–O bond in the hydrated ion of berium has some covalent character [13]. Our calculated results also show that partial covalent bonds in the hydrated ions of the rare earths are formed, although this bond is weaker. Based on the quantum chemical calculation, we obtained the hydration energy curve and the coordination numbers of the intermediate rare earths. These results are in agreement with experimental data. Although the calculated hydration energy curve exhibits an 'S-shape' behavior, in general, the hydration energy increases as the atomic number increases, except between Pm and Tb.

Goldman and Morse [16] have carried out semi-empirical calculations on the hydration enthalpies for all the rare earth ions based on the electrostatic model. In their calculations, the primary hydration number N is an adjustable parameter in order to fit the calculation to the experimental data. They have obtained satisfactory results by means of this fitting method [16]. However, the hydration number used in their calculations is 5.6 for all the hydrated ions of the rare earths. It is very different from the hydration number which is determined experimentally. Because the primary hydration number used in their calculations is adjustable, this 'hydration number' N can absorb some systematic errors in the model. However, the difference between the 'hydration number' they used in the calculations and the real hydration number determined experimentally is so large that we suspect that the interaction in the hydrated ions of the rare earths cannot be purely electrostatic interaction. At least, the interaction in the first hydration sphere may not necessarily be a pure electrostatic interaction.

Because the hydration enthalpy determined experimentally increases monotonically across the rare earth series [16], we expect that the hydration energy should increase monotonically across the rare earth series. However, why does the calculated hydration energy curve (Fig. 2, curve *a*1-*b*-*c*2) not increase monotonically from La to Lu?

We must point out that the calculated hydration energy curve is only for the first hydration sphere. We feel that the thermodynamic data determined experimentally can only include the final results, in which the hydration energy of the first hydration sphere and the hydration energy of the secondary hydration sphere cannot be distinguished.

As Fig. 2 shows, although the curve *a*1-*b*-*c*2 exhibits an 'S-shape', the hydration energies of the first hydration sphere of the intermediate rare earths do not decrease too much. The hydration energy of the dysprosium ion is larger than that of the praseodymium ion and only slightly smaller than that of the neodymium ion. We believe that it is very possible that the hydration energy of the secondary hydration sphere of the light rare earth ions is different from that of the secondary hydration sphere of the heavy rare earth ions, because all the rare earth ions are tripositive, and the size of the first hydration sphere of the heavy rare earth ions with a coordination number of 8 is smaller than that of the first hydration sphere of the light rare earth ions with a coordination number of 9. The charge–radius ratio of the former must be larger than that of the latter. Although the interaction in the first hydration sphere may not be purely electrostatic, the interaction in the secondary hydration sphere will be electrostatic. According to the electrostatic model, the interaction energy between the water molecules in the secondary hydration sphere and the hydrated ion with the first hydration sphere will be in direct proportion to the charge–radius ratio of the first hydration sphere. So, we can expect that the hydration energy of the secondary hydration sphere of the heavy rare earths must be larger than the hydration energy of the secondary hydration sphere of the light rare earths. The difference between them cannot only compensate for the slight difference between the hydration energy of the first hydration sphere of the light rare earths and the hydration energy of the heavy rare earths, but it should also make the total hydration energy curve increase monotonically from La to Lu. Perhaps this can be verified experimentally.

As mentioned above, not only the first hydration sphere but also the secondary hydration sphere affects the physical and chemical properties of the aqueous solution. We know that the water molecules in the secondary hydration sphere can exchange rapidly with non-coordinated solvent molecules or with other anions in the aqueous solution, for example Cl^- or NO_3^-. So, all the components in the secondary hydration sphere may not necessarily be the water molecules, except in very dilute solution. We believe that the effect of the hydration of ions on the physical and chemical properties of aqueous concentrated solutions must be different from the effect in dilute solutions. Perhaps it can help us understand why the trends in the variations in the equivalent conductance curves and in the relative viscosity curves in the different concentrations are different [5, 6]. Since the anions in the solution may enter into the secondary hydration sphere, this can also be used to explain why the effect of the hydration of ions is slightly different in the different solutions of the rare earth salts.

Conclusions

The CNDO quantum chemical method has been used to investigate the hydration of the rare earth ions. The calculated results show that the change in the hydration energy increases monotonically from La to Nd and from Tb and Lu. But this trend is reversed suddenly between Nd and Tb. From the corresponding ΔE curves, the fractional hydration numbers for Pm, Sm, Eu and Gd have been evaluated. These results are in agreement with the results of Spedding *et al.*, obtained from experiments.

Based on the quantum chemical calculated results, the more probable configurations for the first hydration sphere of the hydrated ions with different coordination number have been discussed. The results show that the interaction in the hydrated ions of the rare earths may not necessarily be purely electrostatic interaction, and that the chemical bond in the hydrated ions has some covalent character.

We believe that not only the first hydration sphere but also the secondary hydration sphere will affect the physical and chemical properties of the solution. The interaction in the secondary hydration sphere may be an electrostatic interaction. Because of the exchange reaction, other anions in the aqueous solution may enter into the secondary sphere. This can help us to understand why the trends in the variations in some physical and chemical properties of the solution are different in different solutions.

Acknowledgments

The author thanks Prof. S. H. Lin and Prof. Moeller, Department of Chemistry, Arizona State University, for their support and suggestions.

References

1 I. Grenthe, *Acta Chem. Scand., 18*, 293 (1964).
2 F. H. Spedding, M. J. Pikal and B. O. Ayers, *J. Phys. Chem., 70*, 2440 (1966).
3 R. H. Betts and R. H. Voss, *Can. J. Chem., 51*, 538 (1973).
4 T. Moiduski and S. Siekierski, *J. Inorg. Nucl. Chem., 37*, 1647 (1975).
5 F. H. Spedding and J. A. Rard, *J. Phys. Chem., 78*, 1435 (1974).
6 F. H. Spedding, L. E. Shiers and J. A. Rard, *J. Chem. Eng. Data, 20*, 66 (1975).
7 J. A. Rard, H. O. Weter and F. H. Spedding, *J. Chem. Eng. Data, 22*, 187 (1977).
8 A. Habenschuss and F. H. Spedding, *J. Chem. Phys., 70*, 2797 (1979).
9 A. Habenschuss and F. H. Spedding, *J. Chem. Phys., 70*, 3758 (1979).
10 A. Habenschuss and F. H. Spedding, *J. Chem. Phys., 73*, 442 (1980).
11 G. W. Brady, *J. Chem. Phys., 33*, 1079 (1960).
12 P. Russegger, H. Lischka and P. Schuster, *Theoret. Chim. Acta, 24*, 191 (1972).
13 P. Schuster and H. W. Preuss, *Chem. Phys. Lett., 11*, 35 (1971).
14 L. O. Morgan, *J. Chem. Phys., 38*, 2788 (1963).
15 J. Albertsson and I. Elding, *Acta Crystallogr., Sect. B, 33*, 1460 (1977).
16 S. Goldman and L. R. Morse, *Can. J. Chem., 53*, 2695 (1975).