Pulsed Neutron Diffraction Studies on Lanthanide(III) Hydration in Aqueous Perchlorate Solutions

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Z. Naturforsch. **46a**, 84–88 (1991); received August 1, 1990

Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

Pulsed neutron diffraction measurements are reported on 2 molar aqueous solutions of Pr^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Tm^{3+}, and Yb^{3+} in D_2O at room temperature. The first order difference technique on isomorphous ions is used to derive the metal ion pair correlation functions in these systems. The metal-oxygen and metal-deuterium distances and the hydration numbers are determined. The data indicate that the hydration number changes from ~10 for the lighter ions to ~8 for the heavier ones in the series. The water dipole is orientated on the average at an angle of 10~20 degrees to the metal-oxygen vector; these values are significantly smaller than those found for mono- and di-valent ions. The present results are compared with other results from neutron diffraction with isotope substitution, X-ray diffraction, and extended X-ray absorption fine structure.

Key words: Neutron diffraction, Lanthanide(III) ions, Ionic hydration, Structure, Electrolyte solutions.

1. Introduction

Recently the hydration of lanthanide(III) ions in solution has been investigated using X-ray [1–4] and neutron [5, 6] diffraction, extended X-ray absorption spectra (EXAFS) [7], Raman spectra [8], measurements of the glass transition temperature [9], molecular dynamics simulations [10], and quantum mechanical calculations [11, 12].

Generally the results from these investigations indicate that the hydration number changes in going from the lighter to the heavier ions in the series, although some X-ray studies [4] using isomorphous substitution on aqueous lanthanide(III) perchlorate solutions suggested that the hydration number for La^{3+} was 8 as well as for the heavier ions. Neutron diffraction measurements [6] on 0.3 and 1.0 molal aqueous perchlorate and chloride solutions of the Dy^{3+} ion indicated that the hydration number does not depend on the concentration or on the counter ion used. On the other hand, recent molecular dynamics studies [10] gave a concentration dependent hydration number for La^{3+}, being 12 at infinite dilution and decreasing to 10.2 at 2 molal concentration.

In our previous studies [7], using EXAFS on 2 molal lanthanide(III) perchlorate aqueous solutions in the liquid and glassy states, we determined the oxygen coordination of the ions in the series and have found a change in the hydration number from the lighter to the heavier elements. However neutron diffraction is superior to all other methods for obtaining information about the position of hydrogen atoms, and this information leads directly to the orientation of water molecules in the vicinity of the ion. In the present work we have studied the hydration structure of the trivalent lanthanide ions in 2 molar aqueous perchlorate solutions.

All previous neutron first order difference measurements [5, 6] were done with expensive isotopes. For the trivalent lanthanide ions, the 4f orbitals, which vary from $(4f)^1$ for Ce^{3+} to $(4f)^{14}$ for Lu^{3+}, are largely localized inside the filled $(5s)^2(5p)^6$ core and do not participate significantly in bonding. Thus, these ions can practically be regarded as charged spheres with a continuous decrease of the ionic radius in the series; ions with similar ionic radii, like Pr^{3+} and Nd^{3+},

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behave in a similar manner in solution, and thus the corresponding aqueous solutions may be regarded as isomorphous solutions. The neutron first order difference technique with isomorphous pairs has been applied to aqueous divalent transition metal perchlorate solutions to determine the hydration structures of the ions [13]. Unlike the divalent transition metal series, the lanthanide(III) series is more isomorphous. Our second aim was thus to test the applicability of the isomorphous substitution method for aqueous perchlorate solutions of Pr^{3+} and Nd^{3+}, Tb^{3+} and Dy^{3+}, and Tm^{3+} and Yb^{3+} to obtain the pair correlation functions with respect to the metal ions.

2. Experimental

Aqueous lanthanide(III) perchlorate solutions were prepared by dissolving the corresponding metal oxides (99.99%, Shin-etsu Chemicals) in a stoichiometric amount of deuterated perchloric acid, which had been obtained by repeated substitution of reagent grade perchloric acid (70%) with heavy water. The content of light water in the solutions was checked by ^{1}H-NMR and infrared spectroscopy to be less than 1%. A small amount of the deuterated perchloric acid was added to the solutions to prevent hydrolysis of the ions. The sample solutions of isomorphous pairs, Pr^{3+}–Nd^{3+}, Tb^{3+}–Dy^{3+}, and Tm^{3+}–Yb^{3+}, were prepared so that the concentrations of the constituents are the same in the two solutions. The concentration of metal ions was determined by titration with EDTA. The amount of perchlorate ions was estimated by a cation exchange resin. The content of free deuterium ions was calculated from the stoichiometry: $[D^+] = [ClO_4^-] - 3[M^{3+}]$. The densities of the sample solutions were measured on a Paar DMA 35 densitometer. The compositions and important parameters of the sample solutions are summarized in Table 1.

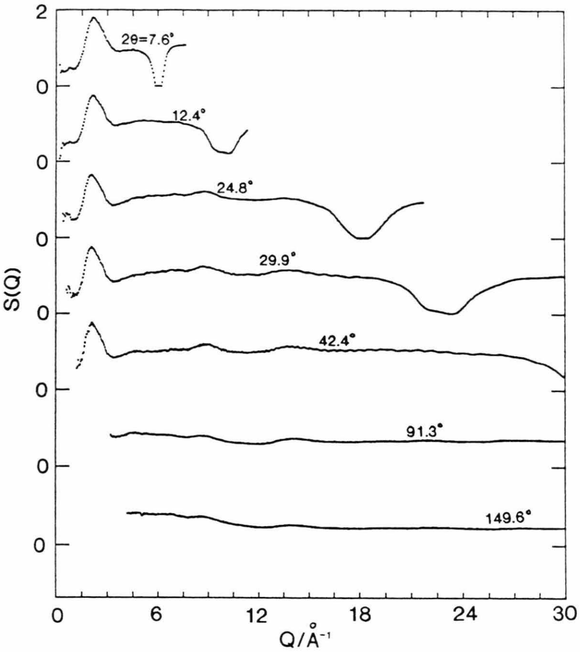

Fig. 1. Total structure factor $S(Q)$ for 2.5 molar aqueous perchlorate solution in D_2O of Tm(III) ion for several scattering angles.

Table 1. The compositions and important parameters for the sample solutions investigated. b, r, and ϱ_0 are the neutron scattering length, the ionic radius, and the number density of the solutions, respectively.

Solutions	Pr	Nd	Tb	Dy	Tm	Yb
b (10^{-12} cm)	0.445	0.769	0.738	1.69	0.705	1.24
r (Å)	1.09	1.08	1.00	0.99	0.95	0.94
Concentrations (mol dm^{-3})						
M^{3+}	2.56	2.51	1.98	1.98	2.56	2.54
D^+	0.0788	0.0753	3.03	3.04	0.0773	0.0776
ClO_4^-	7.76	7.61	8.97	8.98	7.76	7.70
D_2O	37.4	36.4	36.5	36.6	40.0	39.7
ϱ_0 (atoms Å^{-3})	0.0926	0.0903	0.0956	0.0962	0.0972	0.0964

Neutron diffraction measurements for the solutions of Pr^{3+} and Nd^{3+} ions were performed on an LAD instrument at a pulsed neutron facility (ISIS) of Rutherford Appleton Laboratory, while those for the other solutions were made at a pulsed neutron facility (KENS) of National Laboratory for High Energy Physics (KEK) on the HIT instrument. The details of LAD [14] and HIT [15] have been described elsewhere. The sample solution was kept at room temperature in a cell made of Ti–Zr null matrix alloy (8 mm in inner diameter, 0.3 mm in wall thickness, and 85 mm in height) during the measurements. Neutron scattering measurements were also made for a vanadium rod of 8 mm diameter, the empty cell, and background. The data measured were corrected for background, absorption [16] and multiple scattering [17] in the sample and the cell, and then normalized to absolute units by use of the data from the vanadium rod.

The total structure factor $S(Q)$ may be defined as

$$S(Q) = (\sum c_i b_i)^{-2} \sum \sum c_i c_j b_i b_j (s_{ij}(Q) - 1), \qquad (1)$$

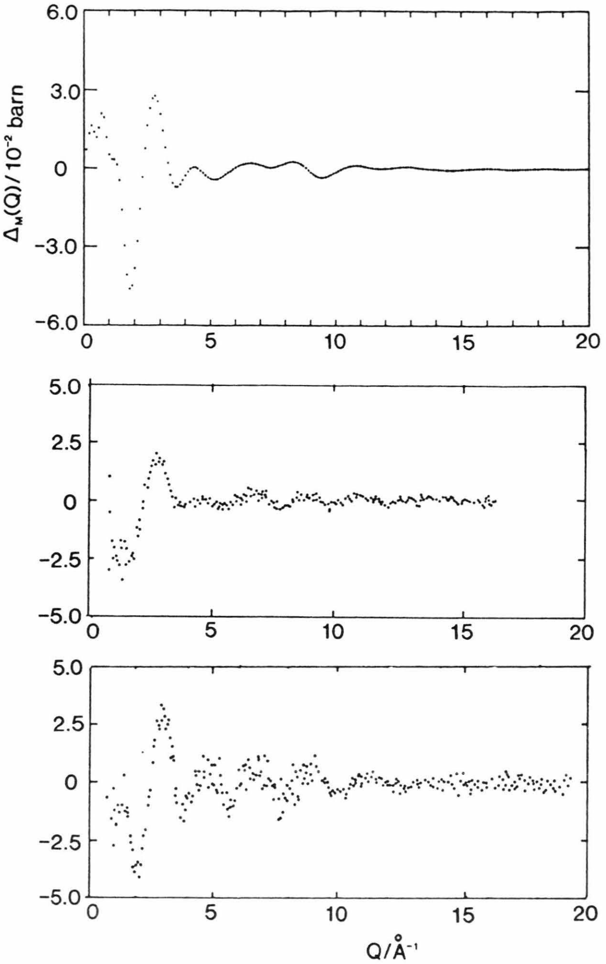

Fig. 2. Combined difference functions $\Delta_M(Q)$ for aqueous solutions of isomorphous Nd(III) and Pr(III) ions (top), Tb(III) and Dy(III) ions (middle), and Tm(III) and Yb(III) ions (bottom).

Table 2. The coefficients (in 10^{-27} cm^{-2}) in (2) and (3) in the text for the sample solutions.

	A	*B*	*C*	*D*	*E*
Pr^{3+}–Nd^{3+}	3.50	2.81	0.528	0.110	6.94
Tb^{3+}–Dy^{3+}	7.42	6.24	1.28	0.357	15.3
Tm^{3+}–Yb^{3+}	5.58	4.34	0.781	0.262	11.0

where the momentum transfer Q is given by $(4\pi \sin \theta)/\lambda$ with θ half the scattering angle and λ the wavelength. $I(Q)$ is the normalized corrected intensity, and c_i and b_i are, respectively, the atomic fraction and the coherent scattering length of the i-th particle. $s_{ij}(Q)$ is the partial structure factor of i–j pairs in the system. The scattering lengths and all parameter values necessary for the correction procedures were taken from [18]. Figure 1 shows a typical set of diffraction patterns vs. scattering angle.

The difference function $\Delta(Q)$ between the two total structure factors for isomorphous ions is given by

$$\Delta_M(Q) = A(s_{MO}(Q)-1) + B(s_{MD}(Q)-1) + C(s_{MCl}(Q)-1) + D(s_{MM}(Q)-1), \quad (2)$$

$$A = 2c_M c_O b_O (b_M - b_{M'}), \quad B = 2c_M c_D b_D (b_M - b_{M'}),$$
$$C = 2c_M c_{Cl} b_{Cl} (b_M - b_{M'}), \quad D = c_M^2 (b_M^2 - b_{M'}^2).$$

Experimentally obtained difference functions $\Delta_M(Q)$ are given in Fig. 2 for isomorphous solutions of Pr^{3+}–Nd^{3+}, of Tb^{3+}–Dy^{3+}, and of Tm^{3+}–Yb^{3+} ions. It should be noted that resonance absorption is observed in the Q region of interest for sample solutions containing Tm, Tb, and Dy (see Figure 1). However, the data at different scattering angles were successfully combined, leaving out the region near the resonance, to give a single experimental difference function over the whole Q region. The data for aqueous solutions of Pr^{3+} and Nd^{3+} ions were analysed as to pair correlation function by the maximum entropy method.

By the Fourier transform of $\Delta_M(Q)$ one obtains the radial distribution function, $\Delta G_M(r)$, represented as

$$\Delta G_M(r) = A\,g_{MO}(r) + B\,g_{MD}(r) + C\,g_{MCl}(r) + D\,g_{MM}(r) + E,$$
$$E = -(A+B+C+D). \quad (3)$$

The coefficients A, B, C, D, and E for the sample solutions are given in Table 2. Figure 3 shows the radial distribution functions $\Delta G_M(r)$ obtained for the corresponding isomorphous perchlorate solutions.

3. Results and Discussion

As seen in Fig. 3, in all the $\Delta G_M(r)$ two prominent peaks are observed in the range 2–4 Å, which are ascribed to the metal-oxygen and the metal-deuterium interactions within hydrated lanthanide(III) ions, respectively. The broad third peak centered around 4.3 Å arises from the second neighbour interactions related to the central metal ion. The first and second peaks are not as sharp as in the results obtained with isotope substitution [5, 6]. This may be partly due to inadequacies in the assumption of chemical equivalence in the isomorphous substitution method.

In order to analyze the individual peaks quantitatively, we employed a least squares fitting procedure using a Gaussian function to represent each peak.

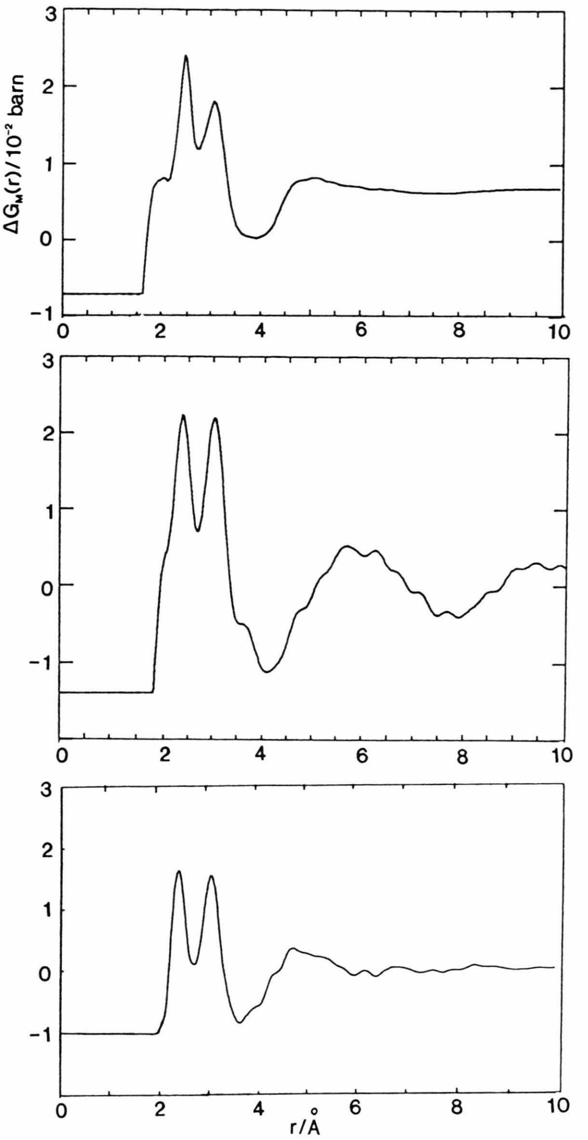

Fig. 3. Radial distribution functions $\Delta G_M(r)$ obtained from the $\Delta_M(Q)$ data of Figure 2. Same sequence as Figure 2.

Table 3. Structural parameters for the lanthanide(III) hydration obtained in the present work, together with previous results from neutron isotopic substitution [5, 6], X-ray diffraction [2, 4], and X-ray absorption studies [7]. r, N, and θ are the interatomic distance, the hydration number, and the tilt angle, respectively.

	r_{MO}/Å	r_{MD}/Å	N	$\theta/^\circ$	Method	Ref.
Pr^{3+}/Nd^{3+}	2.48	3.14	10 ± 1	22	Neutron	this work
Pr^{3+}	2.539		9.2		X-ray	[5a]
Nd^{3+}	2.48	3.13	8.5	25	Neutron	[5a]
Nd^{3+}	2.513		8.9		X-ray	[2b]
Nd^{3+}	2.51		9.5		EXAFS	[7]
Tb^{3+}/Dy^{3+}	2.39	3.08	9 ± 1	10	Neutron	this work
Tb^{3+}	2.409		8.2		X-ray	[2a]
Tb^{3+}	2.400		8.0		X-ray	[4]
Dy^{3+}	2.37	3.04	7.4	19	Neutron	[5a]
Dy^{3+}	2.39	3.03	7.9	29	Neutron	[6]
Dy^{3+}	2.396		7.9		X-ray	[2a]
Tm^{3+}/Yb^{3+}	2.33	3.02	8 ± 1	12	Neutron	this work
Tm^{3+}	2.358		8.1		X-ray	[2a]
Tm^{3+}	2.33		8.0		EXAFS	[7]
Yb^{3+}	2.32	2.98	7.8	24	Neutron	[6]

The interatomic distances and the hydration numbers were estimated from the positions and the areas of the individual Gaussian finally obtained. The tilt angle θ of water molecules bound to the metal ions was calculated using the M–O and M–D distances and the molecular parameters of D_2O ($r_{OD} = 0.98$ Å, D–O–D angle 104.5°). The final results are summarized in Table 3, together with those obtained by the neutron diffraction with the isotopic replacement method [5, 6], X-ray diffraction [1–4], and X-ray absorption measurements [7].

As seen in Table 3, the M–O and M–D interatomic distances obtained by the present isomorphous substitution technique are in good agreement within the uncertainties (±0.03 Å) with the values found by the neutron isotopic replacement method. The present M–O bond lengths also agree with the findings from X-ray diffraction and X-ray absorption measurements.

The hydration number obtained by the present pulsed neutron diffraction method is less accurate than the bond lengths; this originates from uncertainties associated in the correction procedures such as absorption and multiple scatterings for neutrons of various energies (white neutrons) and in joining the data of individual detectors. However, the present results indicate that the hydration number of the lanthanide(III) ions changes from ~10 for the light ions to ~8 for the heavy ions in the series. This conclusion is consistent with the findings in X-ray absorption studies [7] of aqueous lanthanide(III) perchlorate solutions and X-ray diffraction measurements [2] of aqueous lanthanide(III) chloride solutions.

The tilt angles of bound water molecules around the lanthanide(III) ions found in the present studies fall within the θ range 10–20° in the series. The values for the trivalent lanthanide(III) ions are significantly smaller than those found for monovalent ions like

Ag^+ (45°) [19] and Li^+ (40 ~ 52°) [20], and for divalent ions like Ni^{2+} (42°) [21] and Ca^{2+} (34 ~ 38°) [22] in aqueous solutions of similar salt concentrations as used here. Since the valence electrons in 4f orbitals of the trivalent lanthanide ions are shielded by the $(5s)^2(5p)^6$ core and are not involved significantly in chemical bonding, the interaction between the lanthanide(III) ion and water molecules is mainly electrostatic. The average tilt angle of hydrated water molecules is defined by the minimum of the combined potential surfaces of the electrostatic metal-water interactions, of the water-water repulsion in the first hydration shell, and of the hydrogen-bonding interactions between the inner sphere water molecules and water molecules or perchlorate ions present in the second sphere. The significant decrease in the tilt angle from the mono- or divalent ions to the trivalent ions is thus ascribed to much larger metal-water electrostatic interactions for the trivalent ions.

4. Conclusions

The first order difference method combined with the isomorphous substitution was applied to 2 molar aqueous perchlorate solutions in D_2O of Pr^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Tm^{3+}, and Yb^{3+} ions. A comparison of the present results with those from the isotopic substitution method has shown that the present pairs of solutions are practically isomorphic. The neutron diffraction data indicate a change in the hydration number from ~ 10 for the light lanthanide(III) ions to ~ 8 for the heavy ones in the series, consistent with findings from X-ray diffraction and X-ray absorption fine structure studies. The orientation of water molecules bound to the ions is not significantly different in the series, however the tilt angles for the trivalent ions are significantly smaller than the values found previously for lower valent ions. This reflects the larger metal-water electrostatic interactions for the tripositive ions.

Acknowledgements

The present work was supported in part by the Grant-in-Aid for Scientific Research on Priority Area of "Molecular Approaches to Non-equilibrium Processes in Solutions" from the Ministry of Education, Science and Culture, Japan and by the United Kingdom Science and Engineering Research Council.

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