

B. K. Annis, R. L. Hahn, and A. H. Narten

View online: <http://dx.doi.org/10.1063/1.448345>

Published by the [AIP Publishing LLC](#).

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

The image shows a collage of a Physics Today journal cover and a comment on an article. The journal cover features the title "Measured energy in Japan quake" and a comment by Thorne Lay and Hiroo Kanamori. A red arrow points from the journal's title to the comment text.

Hydration of the Dy^{3+} ion in dysprosium chloride solutions determined by neutron diffraction^{a)}

B. K. Annis, R. L. Hahn, and A. H. Narten

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 29 October 1984; accepted 9 November 1984)

The coordination of water molecules about the Dy^{3+} ion in a 2.38 m DyCl_3 in D_2O solution has been determined by neutron scattering. The information was obtained using samples that were identical except for the isotopic species of the Dy^{3+} ions. The experiment yields the distribution of the deuterium and oxygen atoms in the first hydration shell. Each Dy^{3+} ion is surrounded by 7.4 ± 0.5 water molecules. The dysprosium–oxygen separation is 2.37 Å and the dysprosium–deuterium separation is 3.04 Å. The cation–water molecule orientation is closer to planar than that which has generally been observed in other aqueous solutions.

I. INTRODUCTION

In an aqueous solution the spatial correlations between an ion I and the surrounding water molecules are described by two atom pair distribution functions, $g_{\text{IO}}(r)$ and $g_{\text{IH}}(r)$. The functions $g_{\alpha\gamma}(r)$ are defined such that $\rho_\gamma g_{\alpha\gamma}(r)$ is the number of atoms of species γ , in a volume element dV , at a distance r , from an atom of species α , in a solution with a bulk number density ρ_γ , for atoms of species γ . The phenomenon of ionic hydration can be discussed in terms of these atom pair distribution functions which are accessible by a technique that involves neutron diffraction by isotopically substituted samples.

In recent publications,^{1–3} we discussed the hydration of Nd^{3+} and Cl^- ions in 2.85 m aqueous solutions of NdCl_3 , as determined by this technique of neutron scattering from isotopically substituted samples. This work represented the first application of this technique to a 3:1 mixed electrolyte. In particular, we found that the Nd^{3+} cation has a well-defined inner hydration sphere, containing on the average 8.5 water molecules with the oxygens, which point towards the cation, being located at a metal–oxygen distance of 2.48 Å. The hydration number quoted, 8.5, is an absolute number that does not depend on any particular model of the structure of the aqua ion.

Study of the hydration of trivalent lanthanide ions is of interest because of the claims made by Spedding *et al.*⁴ that, as a result of the lanthanide contraction, i.e., the reduction in cationic radius that occurs in going from the light to the heavy rare earths, the hydration number of the heavy lanthanide ions is one unit less than that of the light lanthanide aqua ions. In the present work we have used neutron scattering to study the hydration of the Dy^{3+} ion in 2.38 m solutions of DyCl_3 .

II. EXPERIMENTAL SECTION

A. Preparation of the solutions

So that the precision of the determination of the Dy^{3+} – D_2O correlations would be maximized, identical solutions of DyCl_3 with different enriched Dy isotopes

had to be prepared. In this way, the correlations between other constituents of the solutions, namely, the water–water, Cl–water, and Cl–Cl correlations, would cancel identically when the diffraction pattern from one solution was subtracted from that of another.

To prepare these solutions, we dissolved 10 g samples of enriched Dy_2O_3 (obtained from the USDOE Research Materials Collection) in less than stoichiometric amounts of 9 m DCl in D_2O . Potentiometric titrations of these turbid solutions were performed with dilute DCl to just beyond the equivalence point, to ensure a stoichiometric 3:1 ratio of Dy to Cl. The solutions were allowed to stand for several hours, and the titrations repeated until no perceptible change occurred in “ pD ,” i.e., deuterium ion concentration; this procedure prevented the slow formation of hydrolytic products, such as $\text{Dy}(\text{OD})^{2+}$. To ensure that incoherent neutron scattering from normal hydrogen would be minimized, the water in each solution was removed by evaporation to near dryness, using vacuum and gentle heat, followed by dissolution in D_2O . This procedure was repeated several times under a dry nitrogen atmosphere. Infrared spectroscopy showed that the H_2O content of the resulting stock solutions was ≈ 0.7 wt.%.

The primary method used to assay the concentrations of these D_2O stock solutions was the EDTA titration of Dy^{3+} , using methylene orange as the indicator and acetic acid–sodium acetate solution as the buffer.⁵ The precision of these titrations was better than 0.5%. The densities of the solutions were also measured accurately with calibrated pycnometers as another means of determining their concentrations.⁶

The concentrations of the solutions of the different Dy isotopes were then made identical by dilution, with the D_2O being added precisely by weight. The measured densities of these matched solutions were a further indication that their concentrations were virtually identical. Pertinent data for these solutions are listed in Table I.

B. Neutron data collection and reduction

The neutron experiments were carried out at the Oak Ridge High Flux Isotope Reactor. With the exception of the sample containers, which for the present experiments

^{a)} Research sponsored by the Divisions of Materials Sciences and Chemical Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

TABLE I. Scattering lengths f , number densities ρ , and atom fractions of Dy c for the four 2.38 m solutions of DyCl₃ in D₂O studied by neutron diffraction.^a

Isotope, %	Sample	f (10 ⁻¹² cm)	ρ , Å ⁻³	c
92.3	¹⁶² Dy	-0.0272	0.0970	0.0150
95.9	¹⁶¹ Dy	1.0162	0.0975	0.0149
	^{nat} Dy	1.690	0.0973	0.0150
98.4	¹⁶⁴ Dy	4.869	0.0975	0.0150

^a The scattering lengths (Ref. 12) are averages for the isotopic composition of each sample.

were constructed of Ti-Zr (7 mm o.d., 0.5 mm wall), the diffractometer, counting strategy, and correction procedures were the same as described previously²; only a definition of terms will be given here. The differential scattering cross sections derived from the data are shown in Fig. 1.

To remove the contributions to the differential scattering cross sections from interactions that do not involve the Dy³⁺ ion, the cross section of the ¹⁶²DyCl₃ solution (¹⁶²Dy has the smallest scattering length; see Table I), was subtracted from those of the other three solutions. At this step, the scale factors were adjusted to minimize unphysical features in the Fourier transforms of the difference curves near the origin, as described elsewhere.⁷ The adjusted scale factors were within 3% of the measured values. The resulting differences may be written as

$$\Delta^{\circ}(k) = \Delta(k) + \Delta_s(k), \quad (1)$$

with $\Delta_s(k)$ the self-scattering from uncorrelated atoms, corrected for inelasticity.⁸ Here $k = (4\pi/\lambda)\sin \theta$, λ is the wavelength of the incident neutrons, and 2θ is the scattering angle. The three difference curves $\Delta(k)$ thus derived from the four data sets are shown as points in Fig. 2.

III. DATA ANALYSIS AND RESULTS

The difference functions for the solutions with the nuclides $i = ^{164}\text{Dy}$, ^{nat}Dy , or ^{161}Dy and $j = ^{162}\text{Dy}$ may be written as⁹

$$\Delta_{ij}(k) = \rho[A_{ij}\hat{h}_{\text{DyO}}(k) + B_{ij}\hat{h}_{\text{DyD}}(k) + C_{ij}\hat{h}_{\text{DyCl}}(k) + D_{ij}\hat{h}_{\text{DyDy}}(k)], \quad (2)$$

where ρ is the number density (i.e., the number of nuclei per unit volume) and the constants A_{ij} , B_{ij} , C_{ij} , D_{ij} depend on the concentrations and scattering factors of atoms i and j ; their values are listed in Table II.

The structure functions

$$\hat{h}_{\alpha\gamma}(k) = 4\pi \int_0^\infty r^2 h_{\alpha\gamma}(r) j_0(kr) dr \quad (3)$$

with $j_0(x) = \sin x/x$, contain the desired information on the atom pair distribution functions $g_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) + 1$.

The first three terms in Eq. (2) are linear in the differences of the scattering factors of the Dy isotopes, while the last term is proportional to the difference of their squares. We can therefore write Eq. (2) as the sum of two terms, namely

$$\Delta_{ij}(k) = \rho A_{ij}[\hat{h}_{\text{DyO}}(k) + B'\hat{h}_{\text{DyD}}(k) + C'\hat{h}_{\text{DyCl}}(k)] + \rho D_{ij}\hat{h}_{\text{DyDy}}(k), \quad (4)$$

with $B' = B_{ij}/A_{ij}$ and $C' = C_{ij}/A_{ij}$; the values of these constants are listed in Table II. Equation (4) can be solved for two unknowns, namely the sum $[\hat{h}_{\text{DyO}}(k) + B'\hat{h}_{\text{DyD}}(k) + C'\hat{h}_{\text{DyCl}}(k)]$ and the quantity $\hat{h}_{\text{DyDy}}(k)$. Since we have three difference functions $\Delta_{ij}(k)$, the problem is overdetermined; we have therefore solved the equations by the method of least squares. Because of the ill conditioning of the least-squares matrix to inversion, small errors in $\Delta_{ij}(k)$ will become much larger in the desired results. We have therefore smoothed the functions $\Delta_{ij}(k)$ before the least-squares analysis. The partial structure functions obtained in this way will, in general, not recombine to give the original difference curves to within statistical error, as is shown in the solid curves of Fig. 2.

From the quantities $[\hat{h}_{\text{DyO}}(k) + B'\hat{h}_{\text{DyD}}(k) + C'\hat{h}_{\text{DyCl}}(k)]$ and $\hat{h}_{\text{DyDy}}(k)$ thus obtained, a normalized structure function was constructed according to

$$\begin{aligned} H_{\text{Dy}}(k) &= \rho[\hat{h}_{\text{DyO}}(k) + B'\hat{h}_{\text{DyD}}(k) \\ &\quad + C'\hat{h}_{\text{DyCl}}(k)]/[1 + B' + C'] \\ &= \rho[0.283\hat{h}_{\text{DyO}}(k) + 0.650\hat{h}_{\text{DyD}}(k) \\ &\quad + 0.067\hat{h}_{\text{DyCl}}(k)]. \end{aligned} \quad (5)$$

The function $H_{\text{Dy}}(k)$ is shown as the points in Fig. 3, and the values are listed in Table III. Because of the very small values of D_{ij} in Eq. (4) ($D_{ij} \ll A_{ij}$), it is difficult to extract from the data reliable information on the Dy...Dy interactions in the solutions. This will be the subject of a future report.

Fourier inversion of the function $H_{\text{Dy}}(k)$ yields a radial distribution function

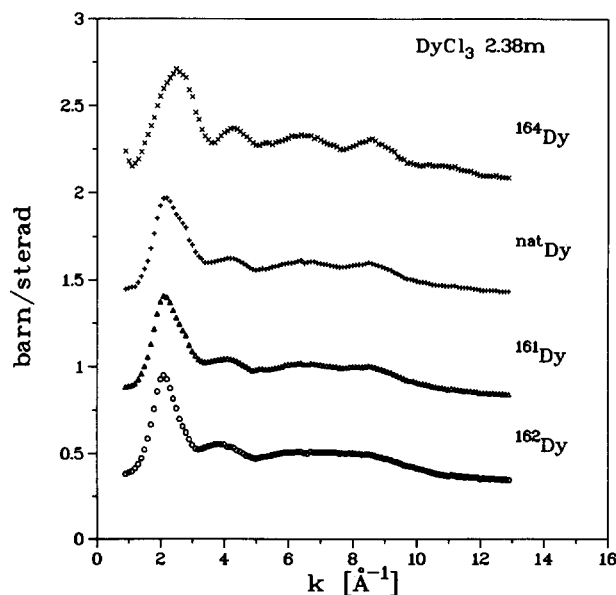


FIG. 1. Neutron scattering cross sections of 2.38 m DyCl₃ solutions, identical in every respect except for the isotopic state of the Cl ions. The statistical error of an average data point is $< \pm 0.001$.

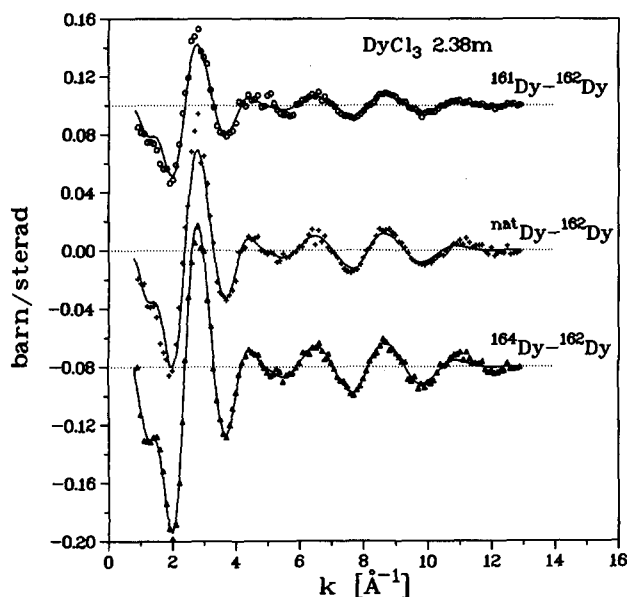


FIG. 2. Difference curves $\Delta(k)$ derived from the cross sections shown in Fig. 1. The curves for ^{164}Dy - ^{162}Dy have been divided by 2 to fit the figure. The solid curves show recombination of partial structure factors derived from smoothed $\Delta_{ij}(k)$.

$$G_{\text{Dy}}(r) = 1 + (2\pi^2\rho r)^{-1} \int_0^\infty k H_{\text{Dy}}(k) \sin(kr) dk$$

$$= 0.283g_{\text{DyO}}(r) + 0.650g_{\text{DyD}}(r) + 0.067g_{\text{DyCl}}(r) \quad (6)$$

which is shown in Fig. 4.

Of the features in the function $G_{\text{Dy}}(r)$, the peaks at 2.4 and 3.0 Å can be interpreted by the following procedure. The integral

$$N(r) = 4\pi\rho \int r^2 G_{\text{Dy}}(r) dr \quad (7)$$

evaluated from 2.0 Å to the first minimum at 2.70 Å has a value $N_1 = 7.10$. The integral of Eq. (7) over the second peak from 2.70 to 3.50 Å has a value $N_2 = 14.52$. From the definition of the atom pair distribution functions the number of γ atoms with atom fraction c_γ around an α atom is

$$n = 4\pi c_\gamma \rho \int r^2 g_{\alpha\gamma}(r) dr. \quad (8)$$

If we combine Eqs. (7) and (8) and tentatively assign the peaks at 2.4 and 3.0 Å, respectively, to the $\text{Dy} \cdots \text{O}$ and $\text{Dy} \cdots \text{D}$ interactions, we find that $n_1 = 7.87$, $n_2 = 13.9$, and $n_2/n_1 = 1.8$. This ratio is in reasonable agreement with the expected value of $n_2/n_1 = 2$ for D_2O , and the principal source of this discrepancy is the poor area definition due to the substantial overlap of the peaks in

the vicinity of 2.7 Å. In the case of NdCl_3 in $\text{D}_2\text{O}^{1,2}$ the first peak was considerably narrower than in the case for the dysprosium solution, and a value of $n_2/n_1 = 1.9$ was obtained. An estimate of the hydration number of water molecules around a dysprosium ion can be obtained from the average quantity $(n_1 + n_2/2)/2$. In this manner we found a hydration number of 7.4 ± 0.5 .

A more refined analysis of the function $G_{\text{Dy}}(r)$ could be readily made by assuming some functional form for the peaks corresponding to the $\text{Dy} \cdots \text{O}$ and $\text{Dy} \cdots \text{D}$ distributions and performing a least-squares fit. However, $G_{\text{Dy}}(r)$ is a calculated quantity which to some extent is influenced by the truncation of the Fourier integral in Eq. (6) at $k_{\text{max}} = 12.8 \text{ Å}^{-1}$, the maximum value accessible in our experiments. This is evidenced by the oscillations around zero for $r < 2.0 \text{ Å}$ in $G_{\text{Dy}}(r)$ as shown in Fig. 4 (dashed curve). In order to remove the effects of this truncation and to better facilitate a separation of the contributions of the two atom-atom distributions, we now turn to an analysis of the structure function $H_{\text{Dy}}(k)$ shown in Fig. 3.

The function $H_{\text{Dy}}(k)$ is almost completely determined by the near-neighbor $\text{Dy} \cdots \text{O}$ and $\text{Dy} \cdots \text{D}$ interactions beyond the first maximum near 2.7 Å^{-1} . We write this part of the structure function as the sum of two terms, namely

$$H_{\text{Dy}}(k) = 0.283w\hat{w}_{\text{DyO}}(k) + 0.650w\hat{w}_{\text{DyD}}(k), \quad (9)$$

with $\hat{w}_{\alpha\gamma}(k) = j_0(kR_{\alpha\gamma})\exp(-l_{\alpha\gamma}^2 k^2/2)$. This leads to a function $G_{\text{Dy}}(r)$ for which [apart from correction terms of order $(l_{\alpha\gamma}/R_{\alpha\gamma})^2$], $R_{\alpha\gamma}$ is the peak position, and $2.35l_{\alpha\gamma}$ is the full width at half-maximum of the distribution for the separation of atoms α and γ in the first coordination sphere of a dysprosium ion. The quantity w is the total number of water molecules in this sphere. The desired values of w , l , and R for the $\text{Dy} \cdots \text{O}$ and $\text{Dy} \cdots \text{D}$ interactions were then obtained by least squares fitting of the experimental function $H_{\text{Dy}}(k)$ for values of $k > 2.7 \text{ Å}^{-1}$. A comparison of the calculated curve thus obtained and the points obtained from experiment is shown in Fig. 3. The resulting distances R_{DyO} and R_{DyD} are 2.37 and 3.04 Å, respectively, and the least-squares value of the hydration number w is 7.4 ± 0.1 which is identical to that obtained in the analysis of the function $G_{\text{Dy}}(r)$. The overall uncertainty of the hydration number is estimated to be ± 0.5 . The parameters obtained from this analysis of the function $H_{\text{Dy}}(k)$ are listed in Table IV. A previous x-ray diffraction study⁵ of DyCl_3 at 3.3 m gave values of 7.93 and 2.37 Å for the hydration number and $\text{Dy} \cdots \text{O}$ distance, respectively, in good agreement with the present results.

TABLE II. Stoichiometric factors for the three difference curves derived from the four neutron data sets see Eq. (2).

$i-j$	$10^2 A_{ij}$	$10^2 B_{ij}$	$10^2 C_{ij}$	$10^2 D_{ij}$	B'	C'
161-162	0.5676	1.305	0.1341	0.023 07		
nat-162	0.9368	2.154	0.2220	0.064 24	2.299	0.2365
164-162	2.663	6.123	0.6291	0.530 0		

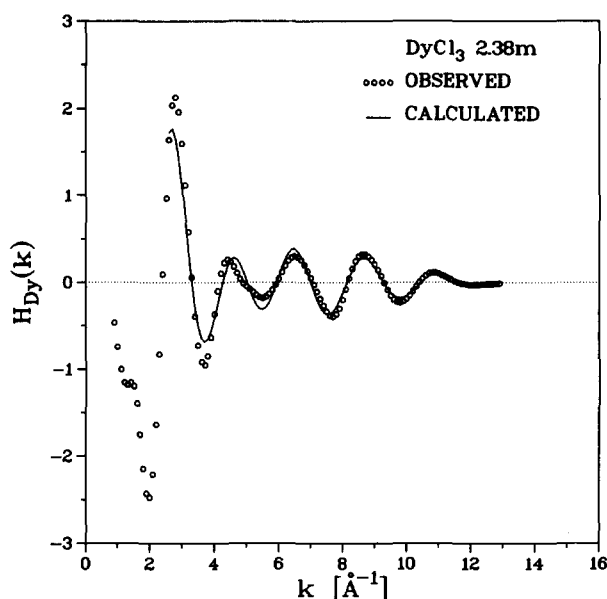


FIG. 3. Structure functions for dysprosium derived from the three difference curves shown in Fig. 2 (circles) and calculated from the least-squares parameters in Table IV with Eq. (10) solid line.

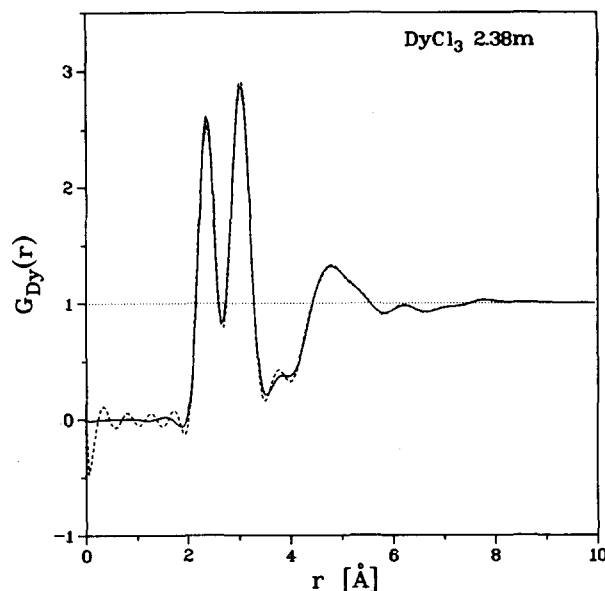


FIG. 4. Radial distribution function, $G_{Dy}(r)$ obtained from the truncated data (dashed curve) and from the extrapolated data solid curve.

In principle the $Dy \cdots Cl$ interaction can make a small contribution to $G_{Dy}(r)$. The best way to assess this possibility is to include a term $\hat{\omega}_{DyCl}$ in Eq. (9) and

attempt to improve the least-squares fit. A physically reasonable lower limit on the $Dy \cdots Cl$ distance is provided by an x-ray diffraction study¹⁰ of crystalline $DyCl_3 \cdot 6H_2O$ which yielded a value of 2.750 Å. This

TABLE III. Structure function $H_{Dy}(k)$ defined in Eq. (6) and shown in Fig. 3 as points.*

k	$H_{Dy}(k)$	k	$H_{Dy}(k)$	k	$H_{Dy}(k)$	k	$H_{Dy}(k)$
0.80	-0.150	3.80	-0.895	6.80	0.193	9.80	-0.254
0.90	-0.356	3.90	-0.678	6.90	0.121	9.90	-0.245
1.00	-0.636	4.00	-0.403	7.00	0.042	10.00	-0.219
1.10	-0.895	4.10	-0.133	7.10	-0.037	10.10	-0.180
1.20	-1.049	4.20	0.079	7.20	-0.114	10.20	-0.132
1.30	-1.079	4.30	0.207	7.30	-0.193	10.30	-0.079
1.40	-1.058	4.40	0.252	7.40	-0.270	10.40	-0.029
1.50	-1.108	4.50	0.235	7.50	-0.336	10.50	0.015
1.60	-1.317	4.60	0.182	7.60	-0.380	10.60	0.051
1.70	-1.677	4.70	0.115	7.70	-0.384	10.70	0.076
1.80	-2.079	4.80	0.053	7.80	-0.358	10.80	0.089
1.90	-2.373	4.90	0.006	7.90	-0.288	10.90	0.091
2.00	-2.427	5.00	-0.026	8.00	-0.185	11.00	0.084
2.10	-2.172	5.10	-0.052	8.10	-0.062	11.10	0.072
2.20	-1.610	5.20	-0.082	8.20	0.065	11.20	0.058
2.30	-0.810	5.30	-0.116	8.30	0.178	11.30	0.045
2.40	0.101	5.40	-0.143	8.40	0.265	11.40	0.033
2.50	0.964	5.50	-0.151	8.50	0.321	11.50	0.021
2.60	1.632	5.60	-0.138	8.60	0.345	11.60	0.011
2.70	2.017	5.70	-0.107	8.70	0.342	11.70	0.002
2.80	2.100	5.80	-0.064	8.80	0.316	11.80	-0.004
2.90	1.924	5.90	-0.009	8.90	0.273	11.90	-0.008
3.00	1.556	6.00	0.057	9.00	0.218	12.00	-0.009
3.10	1.069	6.10	0.129	9.10	0.151	12.10	-0.008
3.20	0.529	6.20	0.198	9.20	0.076	12.20	-0.006
3.30	0.003	6.30	0.253	9.30	-0.006	12.30	-0.003
3.40	-0.449	6.40	0.286	9.40	-0.088	12.40	-0.002
3.50	-0.782	6.50	0.297	9.50	-0.160	12.50	0.000
3.60	-0.968	6.60	0.285	9.60	-0.213	12.60	0.000
3.70	-1.002	6.70	0.250	9.70	-0.244	12.70	0.000
						12.80	0.000

* The rms error of an average data point (from counting statistics only) is ± 0.001 .

TABLE IV. Parameters^a from least-squares fit of Eq. (9).

<i>n</i>	<i>R</i> _{DyO} , Å	<i>l</i> _{DyO} , Å	<i>R</i> _{DyD} , Å	<i>l</i> _{DyD} , Å
7.4 (1)	2.370 (3)	0.152 (3)	3.042 (3)	0.188 (3)

^a The numbers in parentheses are the standard errors σ in the last decimal digit from the least-squares analysis of the structure function $H_{Dy}(k)$ shown in Fig. 3. The variance $\sigma^2 = a_{ii} \Sigma (H_{\text{obsd}} - H_{\text{calcd}})^2$, where the a_{ii} are the diagonal terms of the inverse least-squares matrix.

distance is equivalent to the sum of the ionic radii of Dy³⁺ and Cl[−]. We found that improved least-squares fits occurred only for Dy···Cl distances that were less than 2.75 Å; we therefore conclude that Cl[−] ions do not contribute significantly to the first hydration sphere of the Dy³⁺ ion in aqueous solution.

The curve calculated from these least-squares parameters with Eq. (9) can be used to extrapolate the function $H_{Dy}(k)$ derived from the data to large values of k . Fourier transformation of the extrapolated curve according to Eq. (6) yields the solid curve in Fig. 4 (listed in Table V), which is seen to be free of the spurious oscillations in the dashed curve derived from the truncated data. In the region of interest for hydration, the shape of the radial distribution function is not significantly changed, and the total area between $r = 2.0$ and 3.5 Å differs by less than

TABLE V. Radial distribution function $G_{Dy}(r)$ obtained from the extrapolated data as shown in Fig. 4 (solid line).

<i>r</i>	<i>G</i> _{Dy} (<i>r</i>)	<i>r</i>	<i>G</i> _{Dy} (<i>r</i>)	<i>r</i>	<i>G</i> _{Dy} (<i>r</i>)	<i>r</i>	<i>G</i> _{Dy} (<i>r</i>)
0.00	0.000	2.50	1.798	5.00	1.259	7.500	0.998
0.05	−0.013	2.55	1.340	5.05	1.236	7.550	1.005
0.10	−0.011	2.60	0.992	5.10	1.212	7.600	1.012
0.15	−0.010	2.65	0.822	5.15	1.189	7.650	1.018
0.20	−0.008	2.70	0.853	5.20	1.167	7.700	1.023
0.25	−0.005	2.75	1.068	5.25	1.145	7.750	1.025
0.30	−0.003	2.80	1.425	5.30	1.123	7.800	1.027
0.35	−0.002	2.85	1.862	5.35	1.100	7.850	1.026
0.40	−0.001	2.90	2.300	5.40	1.077	7.900	1.024
0.45	0.000	2.95	2.658	5.45	1.052	7.950	1.022
0.50	0.000	3.00	2.861	5.50	1.026	8.000	1.018
0.55	0.000	3.05	2.864	5.55	1.000	8.050	1.015
0.60	0.000	3.10	2.664	5.60	0.975	8.100	1.012
0.65	0.001	3.15	2.300	5.65	0.953	8.150	1.010
0.70	0.001	3.20	1.841	5.70	0.934	8.200	1.008
0.75	0.002	3.25	1.365	5.75	0.922	8.250	1.006
0.80	0.003	3.30	0.939	5.80	0.915	8.300	1.006
0.85	0.003	3.35	0.606	5.85	0.915	8.350	1.005
0.90	0.003	3.40	0.382	5.90	0.920	8.400	1.005
0.95	0.002	3.45	0.257	5.95	0.930	8.450	1.005
1.00	0.000	3.50	0.212	6.00	0.942	8.500	1.005
1.05	−0.003	3.55	0.219	6.05	0.955	8.550	1.005
1.10	−0.006	3.60	0.254	6.10	0.966	8.600	1.004
1.15	−0.008	3.65	0.298	6.15	0.975	8.650	1.004
1.20	−0.009	3.70	0.336	6.20	0.980	8.700	1.004
1.25	−0.009	3.75	0.363	6.25	0.980	8.750	1.004
1.30	−0.006	3.80	0.376	6.30	0.976	8.800	1.004
1.35	0.000	3.85	0.378	6.35	0.969	8.850	1.004
1.40	0.006	3.90	0.375	6.40	0.960	8.900	1.004
1.45	0.013	3.95	0.372	6.45	0.950	8.950	1.004
1.50	0.019	4.00	0.378	6.50	0.940	9.000	1.004
1.55	0.021	4.05	0.398	6.55	0.933	9.050	1.004
1.60	0.018	4.10	0.435	6.60	0.928	9.100	1.004
1.65	0.010	4.15	0.491	6.65	0.926	9.150	1.003
1.70	−0.004	4.20	0.564	6.70	0.927	9.200	1.003
1.75	−0.023	4.25	0.652	6.75	0.931	9.250	1.002
1.80	−0.043	4.30	0.748	6.80	0.937	9.300	1.002
1.85	−0.058	4.35	0.848	6.85	0.944	9.350	1.002
1.90	−0.060	4.40	0.946	6.90	0.950	9.400	1.002
1.95	−0.071	4.45	1.038	6.95	0.957	9.450	1.002
2.00	0.052	4.50	1.118	7.00	0.962	9.500	1.002
2.05	0.222	4.55	1.186	7.05	0.966	9.550	1.002
2.10	0.510	4.60	1.240	7.10	0.969	9.600	1.002
2.15	0.926	4.65	1.279	7.15	0.971	9.650	1.002
2.20	1.441	4.70	1.305	7.20	0.972	9.700	1.002
2.25	1.973	4.75	1.318	7.25	0.974	9.750	1.002
2.30	2.402	4.80	1.320	7.30	0.977	9.800	1.002
2.35	2.615	4.85	1.313	7.35	0.981	9.850	1.001
2.40	2.554	4.90	1.300	7.40	0.985	9.900	1.001
2.45	2.247	4.95	1.281	7.45	0.991	9.950	1.001

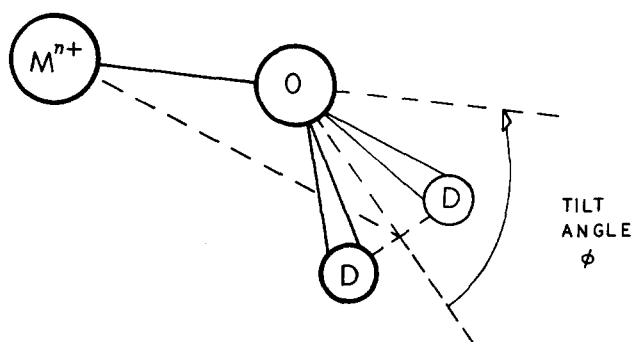


FIG. 5. Orientation of a water molecule in the first hydration sphere of Dy³⁺ in 2.38 m DyCl₃ aqueous solution. There are 7.4 water molecules in the first hydration sphere around Dy³⁺, and the tilt angle is 17° ± 3°.

1% from that obtained from Eq. (6). Consequently the experimentally accessible range of k is adequate for the determination of the inner coordination sphere.

IV. DISCUSSION

The radial distribution function (Fig. 4) establishes that the first hydration sphere of water molecules around a dysprosium ion is well defined. Since the peaks in the distribution function are quite well separated and could be unambiguously identified with the O and D atoms of the coordinated water molecules, it is possible to make an estimate of the orientation or "tilt" of the water molecules about the ionic core. Since there is only one Dy-D peak in $G_{Dy}(r)$, with an FWHM of 0.44 Å, we conclude the deuterium atoms are equidistant from Dy³⁺; then the known geometry of the water molecules in the liquid and our measured values of the ion-atom distances permit calculation of the angle between the plane containing the water molecule and the Dy³⁺···O axis (see Fig. 5). A tilt angle of 0° corresponds to the dipole moment of the water molecule pointing away from the ionic core while an angle of 55° implies that one of the "lone pair" orbitals points toward the core. In the case of DyCl₃ a value of 17° ± 3° was obtained. This is quite similar to that of 24° ± 4° found in a 2.85 m NdCl₃ aqueous solution. (The tilt angle for the NdCl₃ solution was erroneously reported earlier² as 55°.) These angles are somewhat smaller than those so far found for mono and divalent ions at similar concentrations.¹¹

The decrease in coordination number from 8.5 to 7.4 for Nd³⁺ and Dy³⁺, respectively, is in good agreement with results derived from x-ray diffraction.⁴ We note that the estimated uncertainty of 0.5 in each of these numbers is probably optimistic. However, since the peaks in the radial distribution function for Dy³⁺ were found to be located at smaller distances than those for Nd³⁺, the effective volume of the hydration shell is smaller for Dy³⁺ than for Nd³⁺, and a reduction in the hydration number is to be expected. The hydration numbers found in our studies are not integers; they represent average values

from which local and instantaneous deviations occur in the liquid. Also, the information on cationic hydration presented is valid only for the relatively concentrated solutions, and the results may not be representative of the more dilute regime.

We finally note that the data contain no apparent evidence for direct ion pairing, or contact pairs, a result also found for NdCl₃ solutions. However, a definitive statement about ion pairing will come from a knowledge of $G_{\text{DyCl}}(r)$ which requires further experiments on DyCl₃ in which the isotopic states of both Dy and Cl have been changed.

¹ A. H. Narten and R. L. Hahn, *Science* **217**, 1249 (1982).

² A. H. Narten and R. L. Hahn, *J. Phys. Chem.* **87**, 3193 (1983).

³ S. Biggin, J. E. Enderby, R. L. Hahn, and A. H. Narten, *J. Phys. Chem.* **88**, 3634 (1984).

⁴ A. Habenschuss and F. H. Spedding, *J. Chem. Phys.* **73**, 442 (1980).

⁵ A. Habenschuss and F. H. Spedding, *J. Chem. Phys.* **70**, 2797 (1979).

⁶ F. H. Spedding, V. W. Saeger, K. A. Gray, P. K. Boneau, M. A. Brown, C. W. DeKock, J. L. Baker, L. E. Shiers, H. Weber, and A. Habenschuss, *J. Chem. Eng. Data* **20**, 72 (1975).

⁷ W. E. Thiessen and A. H. Narten, *J. Chem. Phys.* **77**, 2656 (1982).

⁸ L. Blum and A. H. Narten, *Adv. Chem. Phys.* **34**, 203 (1976).

⁹ J. E. Enderby and G. W. Neilson, *Rep. Prog. Phys.* **44**, 593 (1981).

¹⁰ A. Habenschuss (private communication).

¹¹ J. E. Enderby, *Annu. Rev. Phys. Chem.* **34**, 155 (1983).

¹² L. Koester, H. Rauch, M. Herkers, and K. Schröder, Summary of Neutron Scattering Lengths, *Berichte der Kernforschungsanlage Jülich GmbH*, Jül-1755, December 1981.