insertion into the alkyl is greater than the C–H bond ionization. Insertion into the Fe–SiCl$_3$ bond is not as favorable as into the Si(CH$_3$)$_3$ bond, because the Fe–Si bond ionization is much greater, and the stabilization of the metal ionizations by π-back-bonding to SiCl$_3$ would also be lost.

Summary

For a metal to assist a chemical reaction in proceeding at a reasonable rate under reasonable conditions of temperature and pressure, the interactions of the metal with the starting molecules must be sufficiently strong to activate the bonds of interest, but not so strong that subsequent bond-forming and product-elimination processes are significantly hindered. Otherwise the reaction falls into a thermodynamic "hole" which is difficult to escape. Successful catalytic processes involve a fine balance of these forces of interaction and stabilization of intermediates along the reaction pathway. The studies presented here give an indication of the extent that different factors such as the electron richness of the metal, the substitutions on the silyls, and the d-electron count may influence the different steps of the hydrosilation reaction.

It has been shown in this and our previous studies of Si–H bond activation that the substituents on the silicon atom have a large effect on the extent of oxidative addition of the Si–H bond to the metal center. The electronegative chlorine substituents favor oxidative addition over alkyl substituents. The present study shows that if the metal has d electrons which can back-bond to the silyl, this can be an additional factor in the stabilization of the intermediate. The trichlorosilyl ligand is approximately half as effective as a carbonyl ligand at stabilizing the complex through π-back-bonding, and this additional strengthening and shortening of the M–Si bond further favors oxidative addition to form direct metal–silyl and metal–hydride bonds. This factor is not significant for trialkylsilyl ligands, which are negligible as π-back-bonding ligands in these complexes. The Si–H bond of the trialkylailanes does not completely add to the metal in the manganese complexes referred to in this study.

The ionization correlations indicate that ethylene insertion is thermodynamically favored into the metal–silyl bond rather than into the metal-hydride bond in these complexes. This traces primarily to the instability of the metal–silyl σ bond ionization relative to the metal–hydride σ bond ionization. Insertion is favored somewhat more for the trialkylsilyl than for the trichlorosilyl because of the stronger M–Si bond in the latter species due to π-back-bonding and ionic bonding contributions. The final step to product is the reductive elimination of the new alkylsilane. The electronic factors that favor reductive elimination are the reverse of those that favor oxidative addition, and can be influenced by similar changes in ligand and metal substituents and d-electron count.

Acknowledgment. We acknowledge support by the Petroleum Research Fund (PRF No. 20408-AC3) for the study of silyl interactions with metals, U. S. Department of Energy (Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, DE-FG02-86ER13501) for the study of small molecules bound to metals, and the National Science Foundation (CHE8519560) and the Materials Characterization Program, Department of Chemistry, University of Arizona, for assistance in acquiring and maintaining the instrumentation. A. R.-C. would like to acknowledge Dr. Royston Hogan for various discussions and Dr. Mark Jatcko for the new design of the He II source which enabled the collection of high-quality He II data. We also are indebted to T. Don Tilley for providing us with a preliminary review of transition-metal silyl derivatives (ref 16).

Dynamics of Water Protons in Concentrated Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} Aqueous Solutions: A Study Using Incoherent Quasi-Elastic Neutron Scattering

G. John Herdman[†] **and Philip S. Salmon***[,‡]

Contribution from the H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue,
Bristol BS8 1TL, U.K., and the School of Physics, University of East Anglia,
Norwich NR4 7TJ, U.K.
Received August 15, 1990.
Revised Manuscript Received November 28, 1990

Abstract: The method of high-resolution incoherent quasi-elastic neutron scattering (IQENS) is applied to investigate the translational diffusive motion of water protons and the cation to water proton binding time in concentrated Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} aqueous solutions. The IQENS data for the Ga^{3+}, Al^{3+}, and Fe^{3+} solutions are consistent with the model for slow exchange wherein the dynamic hydration number $n_h = 6$. This gives a limit of $\tau_1 \gtrsim 5 \times 10^{-9}$ s for the binding time of protons in the hexa-aquo metal ion species. The IQENS data for the Dy^{3+} aqueous solution show that the water protons are in intermediate or slow exchange, which sets a lower limit of $\tau_1 > 10^{-10}$ s. The second-shell water protons in the Ga^{3+}, Al^{3+}, and Fe^{3+} solutions are not observed to be in slow exchange with the cation which gives a binding time for these protons of $\tau_1^{(2)} < 5 \times 10^{-9}$ s. A reduced limit of $\tau_1^{(2)} \lesssim 10^{-10}$ s is, however, argued for. Although the IQENS data for the Ga^{3+} and Fe^{3+} solutions are, within the experimental uncertainties of the method, consistent with $n_h = 6$, the data are better represented if a degree of hydrolysis is assumed. This gives $n_h < 6$, a lower limit of $\tau_1 \gtrsim 5 \times 10^{-9}$ s for protons in any metal ion hydrolysis products, and an upper limit of $\tau_1 < 5 \times 10^{-9}$ s for any dissociated protons.

1. Introduction

The object of this paper is to present new results on the proton dynamics in concentrated Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} aqueous solutions. The results are obtained by using the method of high-resolution incoherent quasi-elastic neutron scattering (IQENS), which is described by Hewish et al.[1] and Salmon.[2] The merits of the method for the study of ionic solution dynamics are as follows.

---

[*] To whom correspondence should be addressed.

[†] Deceased. Work performed while at the H. H. Wills Physics Laboratory. Last address: Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.

[‡] University of East Anglia.

(1) Hewish, N. A.; Enderby, J. E.; Howells, W. S. *Phys. Rev. Lett.* **1982**, *48*, 756. Hewish, N. A.; Enderby, J. E.; Howells, W. S. *J. Phys. C: Solid State Phys.* **1983**, *16*, 1777.

(2) Salmon, P. S. *J. Phys. C: Solid State Phys.* **1987**, *20*, 1573.

0002-7863/91/1513-2930$02.50/0

The measured spectra are sensitive to the magnitude of the cation to water proton binding time τ_1 such that it is possible to differentiate solutions in fast exchange ($\tau_1 \lesssim 10^{-10}$ s) from those in intermediate (10^{-10} s $< \tau_1 < 5 \times 10^{-9}$ s) or slow ($\tau_1 \gtrsim 5 \times 10^{-9}$ s) exchange on the observation time scale of the method.[2] The binding time of water protons to anions is generally much smaller than their binding time to cations such that the proton population associated with the anions is observed to be in fast exchange on the IQENS observation time scale: IQENS experiments therefore enable limits to be placed on τ_1 in ionic solutions. In particular, the IQENS observation time scale is short compared with that of many other methods used to study kinetic processes. Thus, first-shell solvent molecule species that are observed in fast exchange on the NMR observation time scale may be observed in intermediate or slow exchange when the IQENS method is used. This situation arises, for example, in the case of aqueous neodymium[3,4] and zinc[5] solutions. Furthermore, although the cation to *second-shell* water proton binding time is short, the IQENS method can be used to place limits on its magnitude.[6]

The use of light water solutions and choice of spectrometer parameters ensure that the measured spectra are sensitive only to the classical self-diffusive motion of the water protons, in addition to the magnitude of τ_1. The large incoherent scattering cross section of hydrogen dominates the measured intensities, which makes the spectra dependent only on the self-particle proton motions. The spatial and temporal scales covered in an experiment, which depend on the choice of spectrometer and its setting, are sufficiently large to ensure that macroscopic translational diffusion coefficients are measured. Hence, it is possible to measure self-diffusion coefficients that can be compared with those obtained from techniques such as tracer diffusion or spin-echo NMR. Conversely, results from these techniques can be used as an aid in the analysis of IQENS spectra.

If a solution is in fast exchange, only a single proton population is observed and the corresponding averaged translational diffusion coefficient, $\bar{D}$, of the entire proton population is obtained from the measured IQENS spectra, which are described by a single-Lorentzian scattering law given by

$$\tilde{S}(Q,\omega) = \frac{1}{\pi\hbar}\frac{\bar{D}Q^2}{(\bar{D}Q^2)^2 + \omega^2} \tag{1}$$

where $\hbar Q$ and $\hbar\omega$ ($\equiv \Delta E$) are the momentum and energy transfers, respectively. If a solution is in slow exchange, however, two proton populations will be observed and the measured IQENS spectra are then described by a scattering law that is given by the sum of two weighted Lorentzians:

$$\tilde{S}(Q,\omega) = \frac{1}{\pi\hbar}\left[c_1\frac{D_1Q^2}{(D_1Q^2)^2 + \omega^2} + (1 - c_1)\frac{D_2Q^2}{(D_2Q^2)^2 + \omega^2}\right] \tag{2}$$

In eq 2, D_1 is the translational diffusion coefficient of protons bound to the cation for a time τ_1 ($\gtrsim 5 \times 10^{-9}$ s), c_1 is the atomic fraction of these protons, and D_2 is the translational diffusion coefficient of the remaining protons in solution. The average diffusion coefficient of the protons in the system is given by the expression

$$\bar{D} = c_1D_1 + (1 - c_1)D_2 \tag{3}$$

The value of c_1 in eq 2 and 3 is determined as follows. Of the water protons initially surrounding a cation, consider only those that remain bound to the cation for a time that is sufficiently long for them to acquire the cation self-diffusion coefficient D_{ion}.[2] Let the initial average number of water molecules containing these protons be denoted by $n_h(t = 0)$.[7] Then the average number of water protons will be $2n_h(0)$, and this value can include protons in the second and subsequent hydration shells of the cation. The value of $n_h(t)$ will decrease with respect to time, owing to water proton exchange, according to the expression

$$n_h(t) = n_h(0)e^{-t/\tau_1}$$

where $n_h(t)$ is usually abbreviated to n_h. If $\tau_1 \lesssim 10^{-10}$ s, the proton exchange is fast on the IQENS observation time scale and the observed $n_h = 0$ such that eq 2 reduces to eq 1. If $\tau_1 \gtrsim 5 \times 10^{-9}$ s, however, $n_h > 0$ and its value is used to fix c_1. n_h is termed a *dynamic* hydration number since it is associated with an explicit time scale, i.e., that required for a water proton to acquire a self-diffusion coefficient $D_1 = D_{\mathrm{ion}}$. It is not identical with the (static) hydration number since the latter refers to the average number of water molecules in the first coordination shell of the cation, a description that does not involve the adoption of any particular cation-water binding time.[8,9] Hence, the IQENS method gives information on D_1 ($=D_{\mathrm{ion}}$) and n_h for solutions that are observed to be in the slow-exchange limit.

The IQENS method was brought to bear on Ga^{3+}, Al^{3+}, Fe^{3+}, and Dy^{3+} aqueous solutions to determine the exchange regime for both the first- and second-shell cation-bound water protons, to estimate the dynamic hydration number n_h, and to test whether reliable values for D_{ion} can be measured for those trivalent metal ion solutions observed to be in slow exchange. The solution concentrations were chosen to satisfy two conflicting requirements. First, the concentrations must be high enough to ensure that the first Lorentzian in eq 2 is given a substantial weighting through the factor c_1, the fraction of the total proton population bound to the cation. Conversely, the concentrations cannot be too high, else most of the solvent molecules will be shared and the concept of distinct hydration environments will lose its validity.

The experimental procedure and data analysis will first be described. The results will then be presented and discussed both in terms of the potentialities of the IQENS method for the investigation of trivalent metal ion solutions and in terms of their relevance to the field of ionic solution dynamics. The Ga^{3+} results will be considered prior to those for Al^{3+} owing to a more complete knowledge of the solution dynamics from tracer diffusion experiments.

2. Experimental Procedure

The IQENS experiments were made by using the back-scattering spectrometer IN10 at the Institut Laue-Langevin, Grenoble. Generally, spectra were measured at six equally spaced Q values in the range 0.11 $\text{Å}^{-1} \leqslant Q \leqslant 0.31$ Å^{-1} in an energy-transfer window of about ±15 μeV with an energy resolution function having half-width at half-maximum (HWHM) ≈1 μeV. The Q resolution, $\Delta Q = \pm 0.017$ Å^{-1} at each Q value, was poor as maximum detected flux was desired.

The complete experiment required spectra to be taken of the solution in its container, the empty container, the background (measured with the solution present and the spectrometer analyzer crystals shielded by cadmium) and, to give the energy resolution function, a vanadium disk of 2-mm thickness.

The data were analyzed by first correcting the measured solution spectra for background and container scattering. Using a least-squares algorithm, the resultant intensities $I(Q,\omega)$ at each Q value were then compared with the scattering law corresponding to either fast exchange (eq 1) or slow exchange (eq 2) by using the function

$$\tilde{I}(Q,\omega) = \alpha(Q)\int\frac{\tilde{S}(Q,\omega)R(Q,\omega - \omega')}{R_1^*(Q,\omega')}\,d\omega' \tag{4}$$

where $\alpha(Q)$ is a normalization factor, $R(Q,\omega)$ is the measured resolution

---

(3) Salmon, P. S.; Howells, W. S.; Mills, R. *J. Phys. C: Solid State Phys.* **1987**, *20*, 5727.

(4) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1973.

(5) Salmon, P. S.; Bellissent-Funel, M-C.; Herdman, G. J. *J. Phys: Condens. Matter* **1990**, *2*, 4297.

(6) Salmon, P. S.; Herdman, G. J.; Lindgren, J.; Read, M. C.; Sandström, M. *J. Phys: Condens. Matter* **1989**, *1*, 3459.

(7) Although the IQENS method is *proton* sensitive, the first IQENS experiments were made on systems in which significant hydrolysis products were not expected. Therefore, to retain continuity of notation, $n_h(0)$ will refer to the average number of water molecules; that is, the average number of protons is given by twice this value.

(8) Lincoln, S. F. *Coord. Chem. Rev.* **1971**, *6*, 309.

(9) Impey, R. W.; Madden, P. A.; McDonald, I. R. *J. Phys. Chem.* **1983**, *87*, 5071.

Table I. Experimental Details of the Solutions Used for the IQENS Experiments[a]

solute	[solute], molal	[acid], molal	$I^{1/2}$,[b] molar$^{1/2}$	pH[c]	T, °C	mass density, g cm^{-3}	water molecule no. density, Å^{-3}	effective scattering cross section per water molecule, barn	effective absorption cross section per water molecule, barn
$Ga(ClO_4)_3$	2.357 (6)		3.35		28 (1)	1.479	0.0265	202	18
$Al(ClO_4)_3$	2.000 (7)	0.02	3.15	−0.7	19.0 (5)	1.369	0.0277	201	15
$Fe(ClO_4)_3$	2.00	1.11[d]	3.39	−1.8	28 (2)	1.493	0.0263	205	19
$Fe(NO_3)_3$	2.00	1.07[e]	3.44	−1.0	19.0 (5)	1.351	0.0285	203	4
$Dy(ClO_4)_3$	1.45 (6)		2.74		26 (1)	1.45	0.0290	203	106
	1.45 (6)		2.74		38 (1)	1.44	0.0288	203	106

[a] The cross sections refer to the experimental wavelength of 6.271 Å. The solute concentration is the number of moles of solute per 1000 g of solvent (acid and water). The acid concentration is the number of moles of acid per 1000 g of water. [b] At 25 °C and evaluated by assuming the absence of any hydrolysis products. [c] Measured by using a standard pH meter with electrodes adapted for strongly acidic conditions by the use of PTFE seals. [d] Acid is $HClO_4$. [e] Acid is HNO_3.

function, and $R_1^*(Q,\omega)$ is the correction for multiple scattering and attenuation of the neutron beam in the sample. The minimized quantity at each Q value in the fitting procedure was χ^2, given by

$$\chi^2 = \sum_{j=i}^{N} \frac{[\bar{I}(Q,\omega_j) - I(Q,\omega_j)]^2}{\sigma_j^2} \qquad (5)$$

where j labels the energy-transfer channel, N (≈121) is the total number of channels, and σ_j is the statistical error on $I(Q,\omega_j)$. A measure of the overall goodness of fit is given by the average $\bar{\chi}^2$ of the χ^2 over all measured Q values. Further details of the correction procedure have been reported by Salmon.[2]

The Ga^{3+} solution was held in a planar container made from two tantalum windows of 0.1-mm thickness and 1.6-mm spacing. The other solutions were also held in a planar container, but the window material was changed to sapphire of 0.5-mm thickness and the spacing was reduced to 1.2 (Al^{3+} solution), 1.2 [$Fe(NO_3)_3$ solution], 0.88 [$Fe(ClO_4)_3$ solution], or 0.9 mm (Dy^{3+} solution). In view of different solution thicknesses, which affect the shape of the measured $I(Q,\omega)$ through the multiple scattering term in eq 4, and the use of different container materials, example spectra will be given for at least the Ga^{3+} and $Fe(ClO_4)_3$ solutions.

A 2.00 molal (mol kg^{-1}) $Al(ClO_4)_3$ solution was prepared by adding perchloric acid to aluminum hydroxide which had been precipitated by reducing the chloride with excess sodium carbonate. The aluminum and perchlorate concentrations were measured, respectively, by EDTA back titration with Solochrome Black indicator[10] and by titrating a diluted solution against sodium hydroxide with bromothymol blue indicator. The chloride concentration was less than 0.3% of the perchlorate concentration and the solution was slightly acidic, giving an Al^{3+} to ClO_4^- ratio of 1:3.01.

A 2.357 molal $Ga(ClO_4)_3$ solution was prepared by dissolving gallium oxide in perchloric acid. The $Fe(ClO_4)_3$ (Fluka, AG) and $Fe(NO_3)_3$ (Analar, BDH) solutions were prepared by dissolving nonahydrate crystals in dilute acid solution. The pH was less than zero to suppress hydrolysis.[11] A 1.45 molal $Dy(ClO_4)_3$ solution was prepared by dissolving dysprosium oxide in perchloric acid. The Dy^{3+} solution concentration was lower than the others described herein because of the large absorption cross section of dysprosium (Table I). The container during the Dy^{3+} solution experiments gave problems which resulted in sample loss during the course of the experiment and hence an uncertainty in the concentration of ±0.06 molal. Further sample details are given in Table I.

3. Results

3.1. The Cation Diffusion Coefficient D_{ion}. It is useful to have values of D_{ion} from other techniques for the solutions investigated by the IQENS method.[12] For example, if the cation–proton binding time τ_1 is desired from an IQENS experiment, then D_{ion} can be used to fix D_1 such that both the fast-exchange (eq 1) and the slow-exchange (eq 2) scattering laws have, for a given n_h value, the *same* number of fitted parameters. The IQENS data can then be readily compared on an equal footing with the two models. Values of D_{ion} are also useful when the accuracy of the D_1 values measured for solutions in slow exchange is tested.

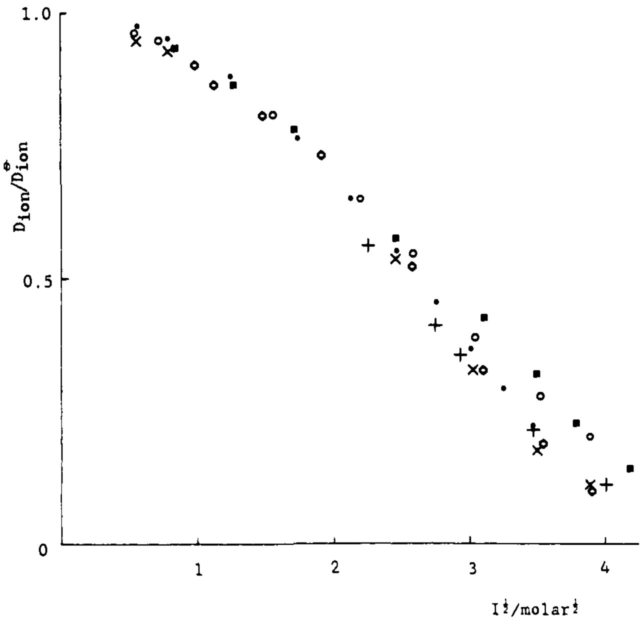

Figure 1. Relative diffusion coefficients of cations for a number of polyvalent metal salt aqueous solutions plotted against $I^{1/2}$. If C_i is the concentration of the ith charged species in molar (moles per liter) and Z_i the charge on that species, then $I \equiv 0.5\sum C_iZ_i^2$. (×) $Cr(ClO_4)_3$; (◇) $Fe(ClO_4)_3$; (+) $AlCl_3$; (○) $CrCl_3$; (■) $LaCl_3$; (●) $NiCl_2$.

For the present solutions, results for D_{Ga}[13] and D_{Fe}[14] are available from tracer diffusion studies. In the case of the $Fe(ClO_4)_3$ solution the Fe^{3+}:$HClO_4$:H_2O ratios were different between the IQENS and tracer diffusion solutions. However, Easteal et al.[14] observed that plots of $D_{ion}/D_{ion}^{\ominus}$ for a number of polyvalent cations (M^{n+}), where $D_{ion}^{\ominus}$ is the cation diffusion coefficient at infinite dilution, against the square root of the ionic strength (I) show a similarity for the different M^{n+} species even at high I values. As shown in Figure 1 the reduced data for D_{Ni} in $NiCl_2$,[3,15] D_{Cr} in $Cr(ClO_4)_3$,[16,17] and D_{Al} in $AlCl_3$[18] are very similar to those for D_{Fe} in $Fe(ClO_4)_3$. On the other hand, the reduced data for D_{La} in $LaCl_3$[19] and D_{Cr} in $CrCl_3$,[17] while similar to each other, are distinct from the other data at high ionic strengths. In the case of $CrCl_3$ the departure in the plots was attributed by Easteal et al.[14] to the occurrence of inner-sphere complexing of Cl^- by Cr^{3+}, and it was conjectured that the departure for $LaCl_3$ may be accounted for by an inner-sphere complexing effect. In aqueous perchlorate solutions inner-sphere complexing of the anion by the

---

(10) Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd ed.; Longman: London, 1961.

(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

(12) Salmon, P. S. *Physica B* **1989**, *156/157*, 129.

(13) Price, W. E.; Woolf, L. A. Unpublished results.

(14) Easteal, A. J.; Price, W. E.; Woolf, L. A. *J. Phys. Chem.* **1989**, *93*, 7517; private communication.

(15) Stokes, R. H.; Phang, S.; Mills, R. *J. Solution Chem.* **1979**, *8*, 489.

(16) Easteal, A. J.; Edge, A. V. J.; Woolf, L. A. *J. Phys. Chem.* **1988**, *92*, 2716.

(17) Easteal, A. J.; Mills, R.; Woolf, L. A. *J. Phys. Chem.* **1989**, *93*, 4968.

(18) Van der Maarel, J. R. C.; de Bleijser, J. *Chem. Phys. Lett.* **1987**, *141*, 251.

(19) Weingärtner, H.; Braun, B. M.; Schmoll, J. M. *J. Phys. Chem.* **1987**, *91*, 979.

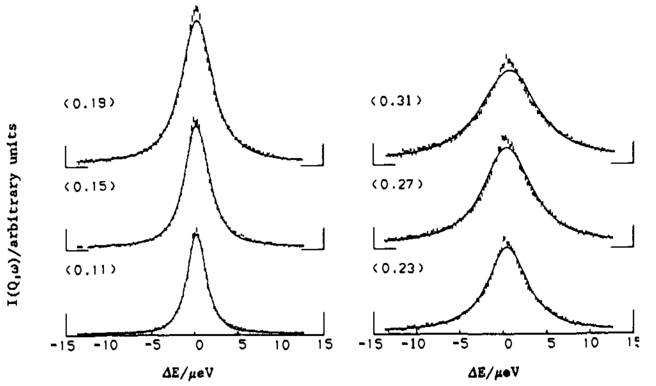

Figure 2. Attempt to fit the IQENS data for the 2.357 molal $Ga(ClO_4)_3$ solution using the single-Lorentzian scattering law for fast exchange (eq 1). The vertical lines give the statistical error on $I(Q,\omega)$, while the full curve gives the fitted function. The Q values are given in parentheses (in $Å^{-1}$).

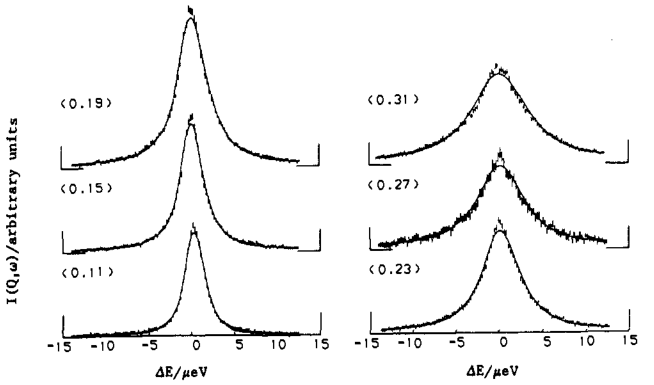

Figure 3. As Figure 2 but for a 2 molal acidified $Fe(ClO_4)_3$ solution.

cation is not thought to occur.[20] The observation of an apparent similarity in the cation diffusion coefficients for perchlorate solutions was therefore used as an aid in the analysis of the present IQENS solution data.

The estimate $D_{ion} = (0.163 \pm 0.007) \times 10^{-9}$ m² s⁻¹ was obtained for the Ga^{3+} solution from tracer diffusion studies[13] at 25 °C by assuming an Arrhenius temperature dependence with an activation energy obtained from D_{Ga} measurements made at a concentration of 2.373 molal and at temperatures of 25 and 30 °C. This value of D_{Ga} at the IQENS solution temperature compares with a value of $(0.169 \pm 0.007) \times 10^{-9}$ m² s⁻¹ estimated by using an activation energy equal to that of pure water. The agreement, within experimental error, between these two values gives credence to an approach adopted for estimating the temperature dependence of D_{ion} values in previous aqueous solution IQENS data analyses[3,5,6] and in the other analyses described herein.

For the Al^{3+} solution $D_{Al} = (0.14 \pm 0.01) \times 10^{-9}$ m² s⁻¹ was estimated by using the lower branch of the perchlorate solution data in Figure 1. This value compares with $D_{Al} = 0.11 \times 10^{-9}$ m² s⁻¹ in an aqueous $AlCl_3$ solution of the same concentration and at the IQENS experiment temperature.[18]

D_{Fe} for the acidified perchlorate solution was taken as $(0.15 \pm 0.01) \times 10^{-9}$ m² s⁻¹, i.e., as equal to the tracer diffusion value for Fe^{3+} in an acidified $Fe(ClO_4)_3$ solution of the same ionic strength.[14] For the acidified nitrate solution D_{Fe} was estimated as $(0.12 \pm 0.01) \times 10^{-9}$ m² s⁻¹ by using the tracer diffusion value of 0.144×10^{-9} m² s⁻¹ for D_{Fe} at 25 °C in an acidified $Fe(NO_3)_3$ solution with $[Fe(NO_3)_3] = 2.011$ molal and $[HNO_3] = 1.075$ molal,[14] i.e., at a concentration close to that of the IQENS solution (Table I).

D_{Dy} values were taken from both the lower and upper branches of Figure 1 and were, respectively, $(0.29 \pm 0.02) \times 10^{-9}$ and $(0.31 \pm 0.02) \times 10^{-9}$ m² s⁻¹ for the solution at 26 °C and (0.35 ± 0.02)

Table II. Results Obtained from Fitting the IQENS Data for the $Ga(ClO_4)_3$ Aqueous Solution Described in Table I[a]

T, °C	n_h	c_1	D_1	D_2	$\bar{D}$	$\overline{\chi^2}$
28 (1)	0				0.60 (3)	276
	3	0.1274	0.163 (fixed)	0.70 (2)	0.64 (2)	175
	3.5	0.1486		0.73 (2)	0.64 (2)	165
	4	0.1698		0.75 (2)	0.65 (2)	158
	4.5	0.1911		0.78 (2)	0.66 (2)	155
	5	0.2123		0.81 (2)	0.67 (2)	156
	5.5	0.2335		0.85 (2)	0.69 (2)	161
	6	0.2548		0.88 (3)	0.70 (3)	172
	6.5	0.2760		0.92 (2)	0.71 (3)	190
	7	0.2972		0.96 (3)	0.72 (3)	214
	8	0.3397		1.05 (3)	0.75 (3)	289
	9	0.3822		1.14 (4)	0.77 (4)	400
	10	0.4246		1.24 (4)	0.78 (4)	551
	6	0.2548	0.147 (fixed)[b]	0.90 (3)	0.71 (3)	191
			0.179 (fixed)[b]	0.87 (3)	0.69 (3)	161
	4.5	0.1911	0.158 (10) (fitted)	0.78 (2)	0.66 (2)	149
	5	0.2123	0.175 (9) (fitted)	0.80 (2)	0.67 (2)	149
	5.5	0.2335	0.191 (8) (fitted)	0.82 (2)	0.67 (2)	149
	6	0.2548	0.206 (8) (fitted)	0.84 (2)	0.68 (2)	150

[a] In the analyses the data were compared with the fast-exchange scattering law (eq 1), corresponding to $n_h = 0$, and with the slow-exchange scattering law (eq 2) with c_1 fixed, D_2 fitted, and D_1 treated as either a fixed or a fitted parameter. $\bar{D}$ is the average diffusion coefficient of all water protons in solution and either is obtained directly from the fitted spectra ($n_h = 0$) or is evaluated by using eq 3. $\bar{D}_{tracer} = 0.65$ (2) is the same quantity but is obtained from tracer diffusion studies. $D_0 = 2.44$ (7) is the diffusion coefficient of pure water at the IQENS solution temperature. All diffusion coefficients are quoted in units of 10^{-9} m² s⁻¹. [b] $D_1 = D_{Ga}$ (1 ± 0.1).

Table III. As Table II but for the $Al(ClO_4)_3$ Solution of Table I with $D_0 = 1.98$ (3) and with $\bar{D}_{tracer} = 0.53$ (2), the Value for an $AlCl_3$ Aqueous Solution of the Same Concentration (2.000 molal) and at the Same Temperature (19 °C)[18]

T, °C	n_h	c_1	D_1	D_2	$\bar{D}$	$\overline{\chi^2}$
19.0 (5)	0				0.54 (2)	252
	3	0.1081	0.14 (fixed)	0.62 (2)	0.57 (2)	192
	4	0.1441		0.65 (2)	0.58 (2)	178
	5	0.1802		0.69 (2)	0.59 (2)	169
	5.5	0.1982		0.71 (2)	0.60 (2)	167
	6	0.2162		0.73 (2)	0.60 (2)	166
	6.5	0.2342		0.75 (2)	0.61 (2)	168
	7	0.2522		0.78 (2)	0.62 (2)	174
	8	0.2882		0.83 (2)	0.63 (2)	189
	9	0.3243		0.89 (3)	0.65 (3)	219
	12	0.4324		1.11 (5)	0.69 (5)	416
	6	0.2162	0.13 (fixed)	0.74 (2)	0.61 (2)	167
			0.15 (fixed)	0.72 (2)	0.60 (2)	166
			0.11 (fixed)	0.75 (2)	0.61 (2)	173
	5	0.1802	0.115 (9) (fitted)	0.70 (2)	0.59 (2)	163
	5.5	0.1982	0.131 (8) (fitted)	0.71 (2)	0.59 (2)	163
	6	0.2162	0.146 (7) (fitted)	0.72 (2)	0.60 (2)	163

Table IV. As Table II but for the $Fe(ClO_4)_3$ Solution of Table I with $\bar{D}_{tracer} = 0.68$ (4) and $D_0 = 2.43$ (12)

T, °C	n_h	c_1	D_1	D_2	$\bar{D}$	$\overline{\chi^2}$
28 (2)	0				0.55 (1)	131
	3	0.1190	0.15 (fixed)	0.65 (1)	0.59 (1)	86
	4	0.1586		0.69 (1)	0.60 (1)	77
	4.5	0.1785		0.71 (1)	0.61 (1)	75
	5	0.1983		0.74 (1)	0.62 (1)	74
	5.5	0.2181		0.76 (1)	0.63 (1)	74
	6	0.2380		0.79 (1)	0.64 (1)	77
	7	0.2776		0.86 (1)	0.66 (1)	91
	8	0.3173		0.93 (1)	0.68 (1)	118
	9	0.3569		1.01 (1)	0.70 (1)	161
	6	0.2380	0.14 (fixed)	0.80 (1)	0.65 (1)	81
			0.16 (fixed)	0.78 (1)	0.64 (1)	75
	5	0.1983	0.139 (15) (fitted)	0.74 (2)	0.62 (2)	69
	5.5	0.2181	0.154 (17) (fitted)	0.76 (2)	0.63 (2)	69
	6	0.2380	0.167 (16) (fitted)	0.77 (2)	0.63 (2)	68

---

(20) Berman, H. A.; Stengle, T. R. *J. Phys. Chem.* **1975**, *79*, 1001.

Table V. As Table II but for the $Fe(NO_3)_3$ Solution of Table I with D_0 = 1.98 (3) and with $\bar{D}_{tracer}$ = 0.52 (3)[a]

T, °C	n_h	c_1	D_1	D_2	$\bar{D}$	$\overline{\chi^2}$
19.0 (5)	0				0.48 (1)	255
	3	0.1143	0.12 (fixed)	0.56 (1)	0.51 (1)	198
	4	0.1524		0.59 (1)	0.52 (1)	186
	4.5	0.1714		0.60 (1)	0.52 (1)	182
	5	0.1904		0.62 (1)	0.53 (1)	180
	5.5	0.2095		0.64 (2)	0.53 (2)	180
	6	0.2285		0.66 (2)	0.54 (2)	182
	7	0.2666		0.71 (2)	0.55 (2)	195
	8	0.3047		0.75 (2)	0.56 (2)	220
	9	0.3428		0.81 (3)	0.65 (3)	262
	6	0.2285	0.11 (fixed)	0.67 (2)	0.54 (2)	186
			0.13 (fixed)	0.66 (2)	0.54 (2)	180
	5	0.1904	0.109 (11) (fitted)	0.62 (1)	0.52 (1)	176
	5.5	0.2095	0.125 (10) (fitted)	0.63 (2)	0.52 (2)	176
	6	0.2285	0.139 (10) (fitted)	0.64 (2)	0.53 (2)	175

[a] I.e., the value for a $Fe(ClO_4)_3$ aqueous solution (acidified with $HClO_4$) of the same ionic strength ($I^{1/2} = 3.444$ $M^{1/2}$ at 25 °C) and at the same temperature (19 °C).[14]

Table VI. As Table II but for the $Dy(ClO_4)_3$ Solutions of Table I

T, °C	n_h	c_1	D_1	D_2	$\bar{D}$	$\overline{\chi^2}$	D_0
26 (1)	0				0.98 (3)	167	2.36 (6)
	8	0.209	0.27 (fixed)	1.38 (3)	1.15 (3)	193	
			0.29 (fixed)	1.36 (3)	1.14 (3)	176	
			0.31 (fixed)	1.35 (3)	1.13 (3)	163	
			0.33 (fixed)	1.33 (3)	1.12 (3)	153	
			0.43 (2) (fitted)	1.25 (3)	1.08 (3)	133	
38 (1)	0				1.24 (5)	165	3.08 (6)
	8	0.209	0.35 (fixed)	1.79 (3)	1.49 (3)	151	
			0.38 (fixed)	1.77 (3)	1.48 (3)	137	
			0.40 (fixed)	1.75 (3)	1.47 (3)	131	
			0.42 (fixed)	1.73 (3)	1.46 (3)	127	
			0.48 (3) (fitted)	1.67 (4)	1.42 (4)	118	

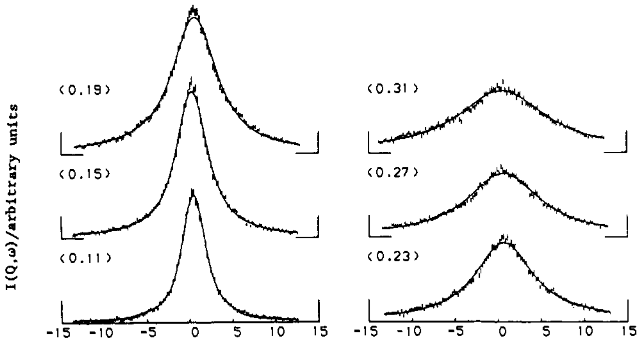

Figure 4. As Figure 2 but for a 1.45 molal $Dy(ClO_4)_3$ solution at 26 °C.

× 10^{-9} and (0.40 ± 0.02) × 10^{-9} m^2 s^{-1} for the solution at 38 °C.

3.2. Scheme for the Data Analysis. For each solution the measured spectra were first compared with the scattering law for fast exchange (eq 1). It was found that this model does not describe the proton dynamics in the Ga^{3+} (Figure 2), Al^{3+}, or Fe^{3+} (Figure 3) solutions, as attested to by large $\bar{\chi}^2$ values (Tables II–V) and by the poor fit in the region about $\Delta E = 0$, where the most significant differences between the fast- and slow-exchange scattering laws will occur (see, e.g., Figure 3 in ref 2). It follows that $\tau_1 > 10^{-10}$ s for each of these solutions. In the case of the Dy^{3+} solutions (Table VI) the results also indicate that the fast-exchange limit does not hold, i.e., $\tau_1 > 10^{-10}$ s. The discrepancy between the data and fitted curve (Figure 4) is not as marked as for the other solutions, which is believed to arise from the lower solution concentration that was chosen in view of the large absorption cross section of dysprosium (see section 2).

In the next stage of the analysis, the slow-exchange scattering law was used in which D_2 was fitted and c_1 was fixed at a value corresponding to a dynamic hydration number n_h of 6 (Ga^{3+}, Al^{3+}, and Fe^{3+}) or 8 (Dy^{3+}). The choice of these n_h values was influenced by the results obtained from other experimental methods, namely ^{17}O NMR[21-23] and proton NMR[23,24] in the case of Ga^{3+} solutions; ^{17}O NMR,[21,25,26] proton NMR,[24,27,28] ^{18}O isotopic dilution,[29] and X-ray diffraction[30] in the case of Al^{3+} solutions;

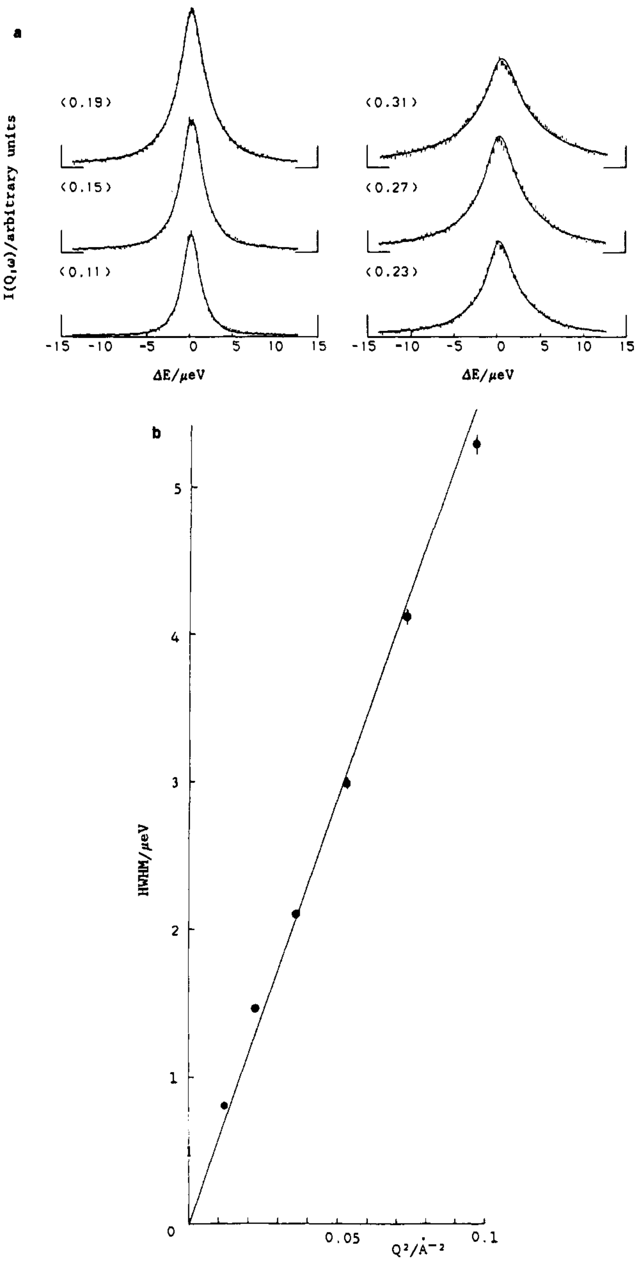

Figure 5. (a) IQENS data for the 2.357 molal $Ga(ClO_4)_3$ solution fitted by using the slow-exchange scattering law (eq 2) with D_1 fixed equal to D_{ion} (=0.163 × 10^{-9} m^2 s^{-1}) for the first Lorentzian and c_1 fixed at a value corresponding to $n_h = 6$. The vertical lines give the statistical error on $I(Q,\omega)$, and the full curve gives the fitted function. The Q values are given in parentheses (in $Å^{-1}$). (b) Fitted HWHM of the second Lorentzian in (a) plotted as a function of Q^2. The gradient gives D_2.

---

(21) Jackson, J. A.; Lemons, J. F.; Taube, H. *J. Chem. Phys.* **1960**, *32*, 553.

(22) Fiat, D.; Connick, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 4754.

(23) Swift, T. J.; Fritz, O. G., Jr.; Stephenson, T. A. *J. Chem. Phys.* **1967**, *46*, 406.

(24) Fratiello, A.; Lee, R. E.; Nishida, V. M.; Shuster, R. E. *J. Chem. Phys.* **1968**, *48*, 3705.

(25) Connick, R. E.; Fiat, D. N. *J. Chem. Phys.* **1963**, *39*, 1349.

(26) Alei, M., Jr.; Jackson, J. A. *J. Chem. Phys.* **1964**, *41*, 3402.

(27) Takahashi, A. *J. Phys. Soc. Jpn.* **1970**, *28*, 207.

(28) Miura, K.; Hashimoto, K.; Fukui, H.; Yamada, E.; Shimokawa, S. *J. Phys. Chem.* **1985**, *89*, 5098.

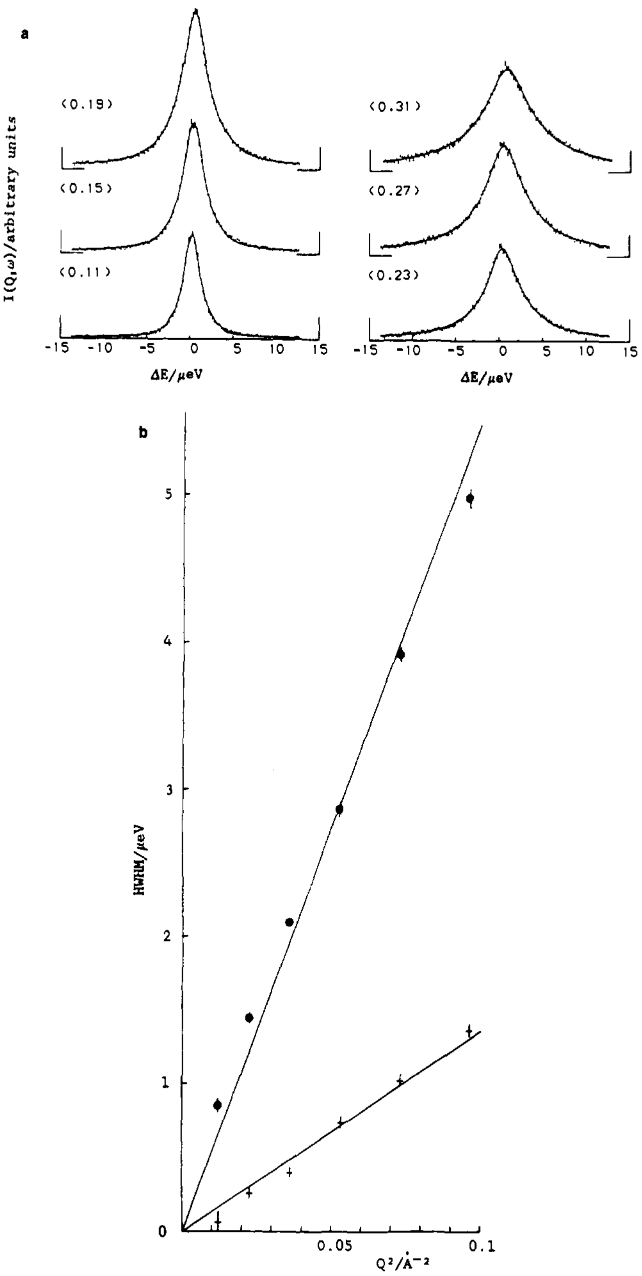

Figure 6. (a) IQENS spectra for the 2.357 molal $Ga(ClO_4)_3$ solution fitted by using the slow-exchange scattering law (eq 2) with both D_1 for the first Lorentzian and D_2 for the second Lorentzian allowed to be variable parameters. c_1 was fixed at a value corresponding to $n_h = 6$. The vertical lines give the statistical error on $I(Q,\omega)$, and the full curve gives the fitted function. The Q values are given in parentheses (in $Å^{-1}$). (b) Fitted HWHM of the first Lorentzian (+) and second Lorentzian (●) in (a) plotted as a function of Q^2. The gradients give D_1 and D_2, respectively.

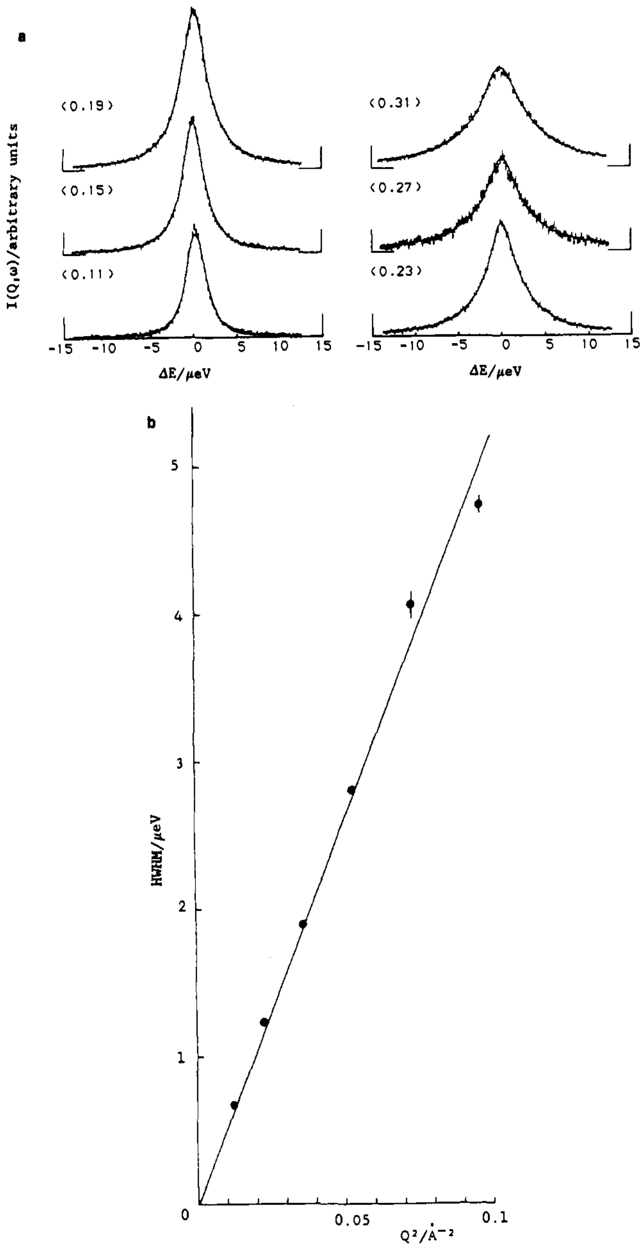

Figure 7. As Figure 5 but for a 2 molal acidified $Fe(ClO_4)_3$ solution with D_1 fixed equal to 0.15×10^{-9} m² s⁻¹.

neutron diffraction,[31] X-ray diffraction,[30] and optical spectroscopy[32] in the case of Fe^{3+} solutions in which hydrolysis is suppressed; and neutron diffraction[33] and X-ray diffraction[34] in the case of Dy^{3+} solutions. In these analyses the first attempt at fitting the spectra was made with D_1 fixed at the estimated values of D_{ion} given under section 3.1. This procedure was followed since it is important that the fast- and slow-exchange scattering laws be compared with the data when both expressions have the same number of fitted parameters.

The results obtained from these analyses for the Ga^{3+} (Figures 5 and 6, Table II), Al^{3+} (Table III), and Fe^{3+} (Figures 7 and 8, Tables IV and V) solutions reveal that the slow-exchange model, with D_1 treated either as a fixed or as a fitted parameter, provides a far better representation of the measured spectra than the fast-exchange model. In all cases the fits give improved $\bar{\chi}^2$ values. Furthermore, there is quantitative agreement between the $\bar{D}$ values obtained from eq 3 and those $\bar{D}$ values that are available in the literature for the Ga^{3+} and $Fe(ClO_4)_3$ solutions. For example, the $\bar{D}$ values for the Ga^{3+} solution are, within experimental error, in the range expected from tracer diffusion measurements which were made by using tritiated water (HTO).[13] For the purpose of this comparison the $\bar{D}$(HTO) data at 25 °C were converted to values for H_2O by using the mass extrapolation method of Mills[35] and scaled for temperature by assuming an Arrhenius dependence with an activation energy equal to that of pure water. The Ga^{3+} and Fe^{3+} perchlorate solution data are therefore con-

---

(29) Baldwin, H. W.; Taube, H. *J. Chem. Phys.* **1960**, *33*, 206.

(30) Magini, M.; Licheri, G.; Paschina, G.; Piccaluga, G.; Pinna, G. *X-ray diffraction of ions in aqueous solutions: Hydration and complex formation*; CRC Press: Boca Raton, FL, 1988.

(31) Herdman, G. J.; Neilson, G. W. Unpublished results.

(32) Hunt, J. P.; Friedman, H. L. *Prog. Inorg. Chem.* **1983**, *30*, 359.

(33) Cossy, C.; Barnes, A. C.; Enderby, J. E.; Merbach, A. E. *J. Chem. Phys.* **1989**, *90*, 3254.

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

(35) Mills, R. *J. Phys. Chem.* **1973**, *77*, 685.

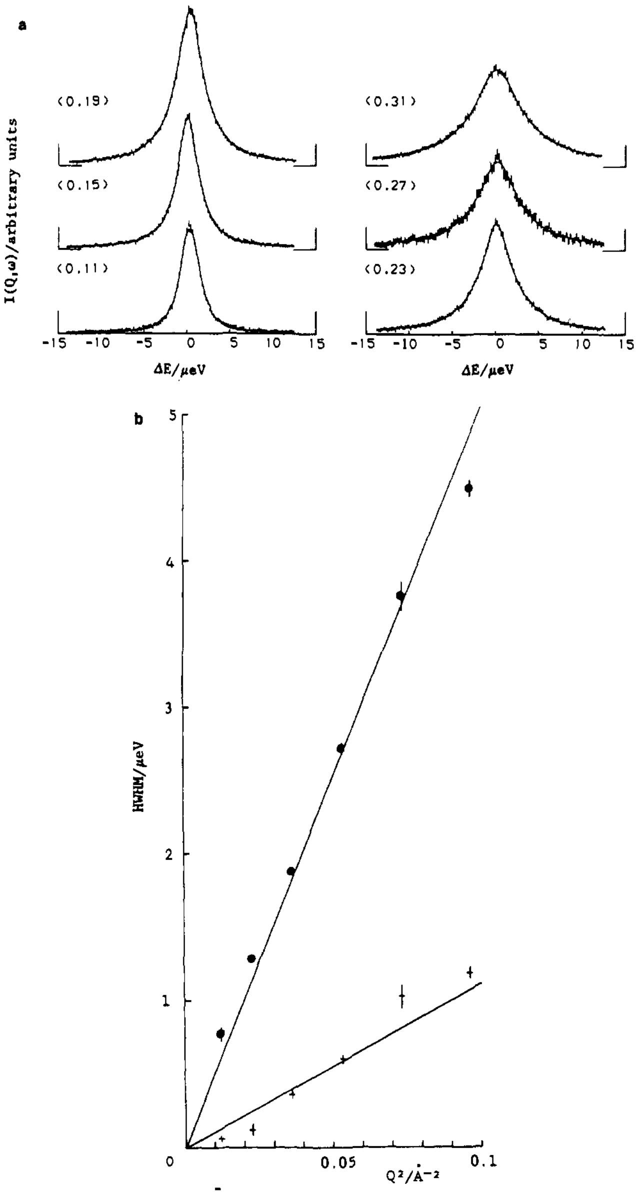

Figure 8. As Figure 6 but for a 2 molal acidified $Fe(ClO_4)_3$ solution.

sistent with these solutions being in the slow-exchange limit with a dynamic hydration number $n_h = 6$.

At the present stage of the analysis it is more difficult to be certain that this latter statement holds true for the Al^{3+} and $Fe(NO_3)_3$ solutions since $\bar{D}$ values are not available from other experimental methods. However, it is noteworthy that in the case of the Al^{3+} solution the measured $\bar{D}$ values are greater than that for an aqueous $AlCl_3$ solution of the same concentration and temperature,[18] which suggests that $\bar{D}$ is counterion dependent (Table III). Also, the measured $\bar{D}$ values for the $Fe(NO_3)_3$ solution (Table V) are, within experimental error, in agreement with the value estimated for a $Fe(ClO_4)_3$ solution of the same ionic strength;[14] i.e., in this case no significant counterion effect on the proton diffusion is observed.

For the Dy^{3+} solutions the slow-exchange model with $n_h = 8$ and D_1 fitted gives a better representation of the data than the model for fast exchange (Figure 9 and Table VI). This is perhaps unsurprising in view of the additional variable in the slow-exchange scattering law that occurs when both D_1 and D_2 are treated as fitted parameters. The fitted D_1 values are, however, significantly larger than the estimates of D_{Dy} obtained from both the lower and upper branches of Figure 1 (section 3.1). Indeed, the fits obtained for the solution at 26 °C with D_1 fixed at D_{Dy} values taken from the lower branch are worse than those obtained when a single Lorentzian is used.

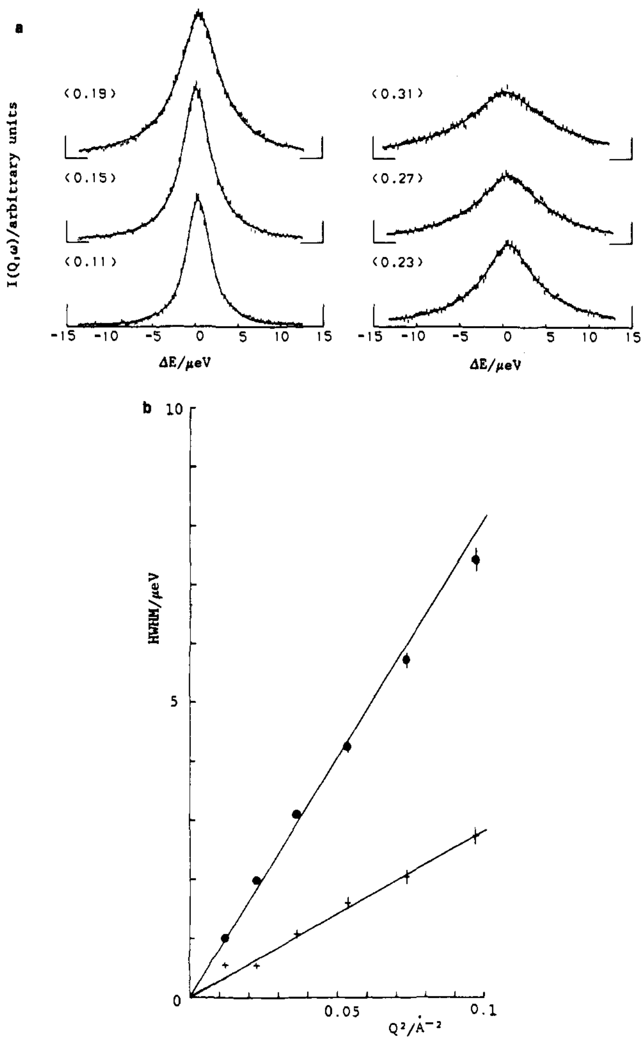

Figure 9. As Figure 6 but for a 1.45 molal $Dy(ClO_4)_3$ solution at 26 °C with $n_h = 8$.

As a final step in the main analysis the sensitivity of the slow-exchange scattering law fits to n_h was investigated with D_1 fixed equal to D_{ion} for the Ga^{3+}, Al^{3+}, and Fe^{3+} solutions. The object was first to test for any hydrolysis effects and second to test for any second-shell water protons in slow exchange with the cation. The solution compositions can be written as $Ga(ClO_4)_3{\cdot}23.6H_2O$, $Al(ClO_4)_3{\cdot}27.8H_2O$, $Fe(ClO_4)_3{\cdot}0.5HClO_4{\cdot}25H_2O$, and $Fe(NO_3)_3{\cdot}0.5HNO_3{\cdot}26H_2O$, and each anion is typically coordinated to ≈4.5 water molecules.[36] Hence, for a cation primary hydration number of 6, the maximum number of unshared water molecules in the cation second shell is, respectively, 4, 6, ≈3, and ≈3. These values determine the maximum values of n_h used in the data analyses, the results of which are presented in Tables II–V. The χ^2 values are illustrated in Figure 10.

For the Ga^{3+} solution the best fit occurs for $n_h \approx 4.5$, but the minimum in $\chi^2(n_h)$ is not a strong function of n_h. Indeed, in the absence of systematic errors, representative data sets fitted with the correct model will yield average chi-squared values equal to the number of degrees of freedom ν (≈120) with a standard deviation of $(2\nu)^{1/2}$ (≈±15).[37] The observed small changes in $\chi^2(n_h)$ about its minimum are not therefore statistically significant,

---

(36) Neilson, G. W.; Enderby, J. E. *J. Phys. C: Solid State Phys.* **1982**, *15*, 2347. Neilson, G. W.; Schiöberg, D.; Luck, W. A. P. *Chem. Phys. Lett.* **1985**, *122*, 475.

(37) For large ν the chi-squared distribution is approximately Gaussian with a mean ν and standard deviation of $(2\nu)^{1/2}$. There is consequently a 68% probability that chi-squared values will lie between the limits $\nu \pm (2\nu)^{1/2}$. (Mulvey, J. H. *High energy and nuclear physics data handbook*, 2nd ed.; Galbraith, W., Williams, W. S. C., Eds.; National Institute for Research in Nuclear Science: Harwell, England, 1964; p XIV-i).

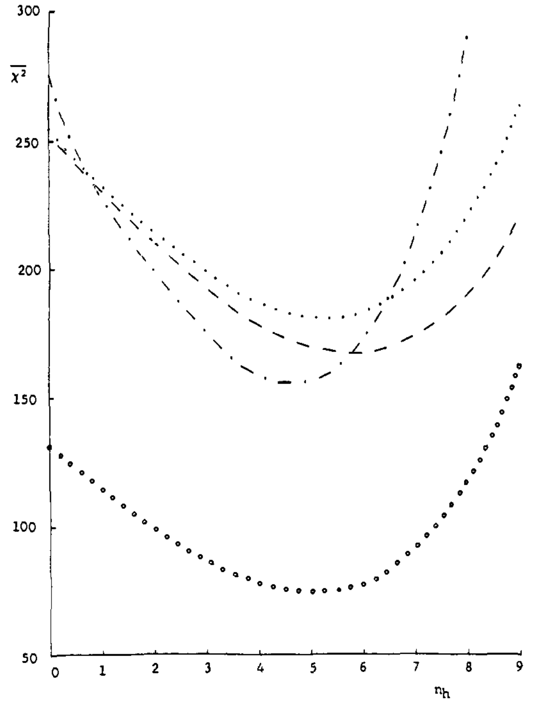

Figure 10. The $\bar{\chi}^2$ obtained from fitting IQENS solution data with the slow-exchange scattering law (eq 2) with D_l fixed equal to D_{ion} and n_h (and hence c_l) fixed at various values. The $\bar{\chi}^2$ values corresponding to n_h = 0 are those obtained by using the fast-exchange scattering law of eq 1. (–•–) $Ga(ClO_4)_3$; (---) $Al(ClO_4)_3$; (∘∘∘) $Fe(ClO_4)_3$; (•••) $Fe(NO_3)_3$.

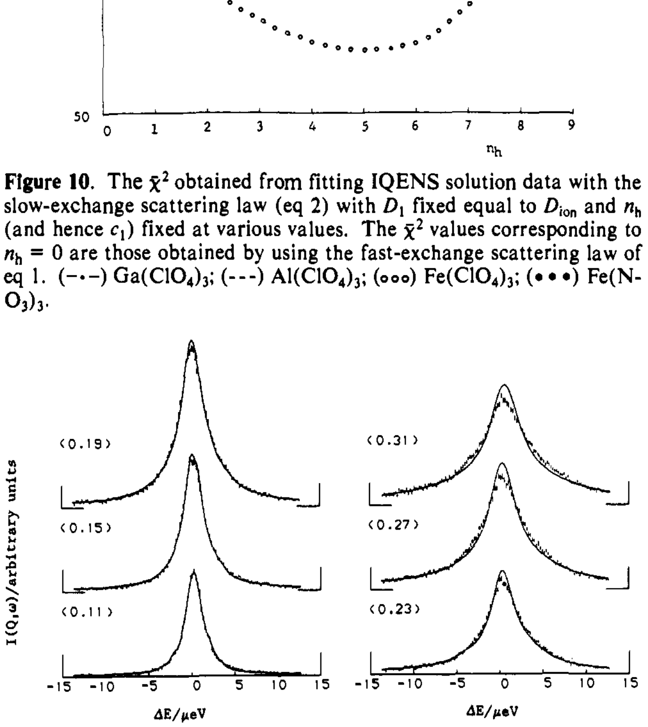

Figure 11. As Figure 5a for the $Ga(ClO_4)_3$ solution but with n_h = 9.

and the data are consistent with a range of values about $n_h \approx 4.5$. A measure of $4 \lesssim n_h \lesssim 6$ is given for this range from consideration of the minima in the individual $\chi^2(n_h)$. For this range the measured $\bar{D}$ are, within experimental error, in agreement with the tracer diffusion $\bar{D}$ value. The IQENS data are therefore consistent with $4 \lesssim n_h \lesssim 6$, and the possibility of hydrolysis cannot be ruled out on the basis of the IQENS data alone. However, the data are not consistent with $n_h \gg 6$: the second-shell water protons are not observed to be in slow exchange with the cation as is emphasized in Figure 11.

Similar results are found for the other solutions. In the case of the Al^{3+} solution the minimum in $\bar{\chi}^2(n_h)$ occurs at $n_h \approx 6$, and the minima in the individual $\chi^2(n_h)$ occur for $5 \lesssim n_h \lesssim 7$. The IQENS data are therefore consistent with a small range of n_h values about 6 but are not consistent with there being a significant number of second-shell water protons in slow exchange with the cation. The Fe^{3+} perchlorate solution gives a minimum in $\bar{\chi}^2(n_h)$ at $n_h \approx 5.5$ and minima in the individual $\chi^2(n_h)$ at $4.5 \lesssim n_h \lesssim 6.5$. The measured $\bar{D}$ values are also in agreement, within experimental error, with the tracer diffusion $\bar{D}$ for several of these n_h values ($n_h \geq 5.5$). Comparable results are obtained for the Fe^{3+} nitrate solution from consideration of $\bar{\chi}^2(n_h)$ and the individual $\chi^2(n_h)$.

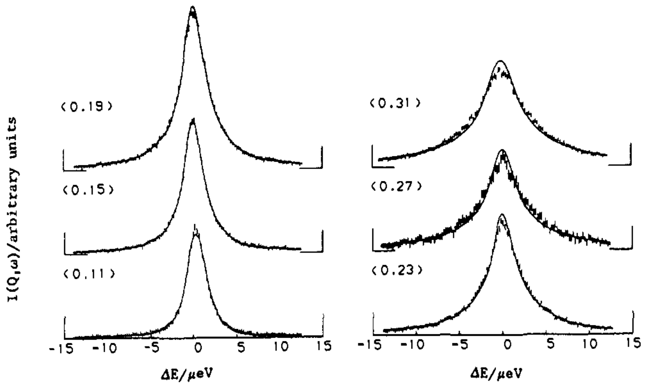

Figure 12. As Figure 5a but for a 2 molal acidified $Fe(ClO_4)_3$ solution with D_l fixed equal to 0.15×10^{-9} m^2 s^{-1} and n_h = 9.

The presence of hydrolysis in the Fe^{3+} solutions cannot therefore be ruled out on the basis of the IQENS data alone. However, the Fe^{3+} data are *not* consistent with there being a significant number of second-shell water protons in slow exchange with the cation as demonstrated in Figure 12.

4. Discussion

A direct comparison of the binding times and n_h values obtained from the present experiments with those in the literature is hampered on several accounts. First, experiments are rarely made on solutions in which the salt concentration, ionic strength, and pH are the same. These parameters will affect binding times and can therefore affect the observed dynamic hydration number in a given experiment. For example, stability constants describing hydrolysis are usually measured for solutions in which the concentration of the metal ion species of interest is low and in which the ionic strength is maintained at some large value by means of a high concentration of supporting electrolyte such as $NaClO_4$.[38] The literature stability constant values cannot therefore be readily used to estimate the degree of hydrolysis in solutions where the metal ion of interest is present in high concentrations. Second, the species that is probed in ^{17}O NMR and isotopic dilution experiments is oxygen and not hydrogen. In the present context, the results from these and the IQENS experiments can only be taken as equivalent provided the lifetime of a proton within a water molecule is $\gg 5 \times 10^{-9}$ s, i.e., such that there is negligible probability of water molecules dissociating on the observation time scale of the IQENS method. When hydrolysis occurs, this condition may not necessarily hold.

In view of the lack of suitable literature information on hydrolysis effects in the present solutions and the *proton* sensitivity of the IQENS method, a full discussion of hydrolysis effects is required. In interpreting the present IQENS data the results from the other experimental techniques provide a useful guide.

4.1. The Ga^{3+} Solution. Hydrolysis has an important effect on water exchange with the metal ion in aqueous gallium solutions. Indeed, the water binding time at 25 °C for the $Ga(OH_2)_5OH^{2+}$ complex (5×10^{-6} to 1.7×10^{-5} s) is estimated, from ^{17}O NMR experiments,[39] to be between a factor of 150 and 500 smaller than the water binding time for the $Ga(OH_2)_6{}^{3+}$ complex (2.5×10^{-3} s). However, the binding time of the water molecules in either of these complexes is too long to account for exchange of whole (i.e., undissociated) water molecules giving rise to a dynamic hydration number <6, at least for the acidified perchlorate solutions studied by Hugi-Cleary et al.[39] Hemmes et al.,[40] from electric field jump relaxation experiments on dilute acidified perchlorate solutions ($I \lesssim 10^{-3}$ molar), found a proton binding time of $\tau_1 \approx 5 \times 10^{-6}$ s. However, this value was later revised

---

(38) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cation*; Wiley: New York, 1976.

(39) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 4444.

(40) Hemmes, P.; Rich, L. D.; Cole, D. L.; Eyring, E. M. *J. Phys. Chem.* **1970**, *74*, 2859.

to a much shorter value of ca. 10^{-8} s.[41] Hydrolysis may therefore account for a dynamic hydration number <6 as indicated under section 3.2, especially as the present IQENS solution was not acidified. The discrepancy between the D_1 value measured by the IQENS method for $n_h = 6$ and D_{Ga} (Table II) may not therefore result entirely from a problem in accurately fitting the IQENS data when the width of the resolution function is comparable with the width of the narrow first Lorentzian in eq 2 (see the Appendix in ref 6).

An attempt was consequently made to further fit the data by using the slow-exchange scattering law with n_h fixed at values <6 and with D_1 and D_2 allowed to be fitted parameters (Table II). These fits were indistinguishable, on the basis of $\bar{\chi}^2$ values, from those obtained by using $n_h = 6$. However, the fitted D_1 values are in better agreement with the measured D_{Ga} and the fitted $\bar{D}$ are in better agreement with the tracer diffusion $\bar{D}$. The data are therefore consistent with the model for slow exchange wherein there is a degree of hydrolysis. However, the extent of hydrolysis cannot be unambiguously identified in view of the broad minimum in $\bar{\chi}^2(n_h)$ (Figure 10), the similar widths of the resolution function and first Lorentzian in eq 2, and uncertainties in the multiple scattering correction for the large thickness of the present solution.[2] Notwithstanding the results give a cation to water proton binding time of $\tau_1 \gtrsim 5 \times 10^{-9}$ s for protons in the hexa-aquo gallium [$Ga(OH_2)_6^{3+}$] complex. This limit also holds for protons in any gallium hydrolysis products [e.g., $Ga(OH_2)_5OH^{2+}$] while an upper bound of $\tau_1 < 5 \times 10^{-9}$ s is provided for any dissociated protons.[42] It is interesting to note that mononuclear hydrolysis species containing up to four hydroxyl groups, i.e., as high as $Ga(OH)_4^-$(aq), can occur as stable complexes in aqueous solution.[38]

The second-shell water protons are not observed to be in slow exchange, which gives a cation to second-shell water proton binding time of $\tau_1^{(2)} < 5 \times 10^{-9}$ s. Indeed, the proton dynamics is well represented by the slow-exchange scattering law which implies that these protons are in fast exchange, i.e., $\tau_1^{(2)} \lesssim 10^{-10}$ s.

4.2. The Al^{3+} Solution. The binding time of oxygen in the primary hydration shell of aluminum in aqueous solution is much longer than that for water protons.[43-46] The most recent ^{17}O NMR experiments on a dilute (0.5 molal) acidified $Al(ClO_4)_3$ solution give a binding time of ≈0.78 s for oxygen in the hexa-aquo species at 25 °C, while a shorter binding time of 0.06 s is reported in solutions where hydrolysis species are expected.[47] Both of these values are very much longer than the IQENS observation time scale, and exchange of whole (i.e., undissociated) water molecules is not expected to give an observed dynamic hydration number <6.

The binding time of a proton in the primary hydration shell of hexa-aquo aluminum species has been given as 9.2×10^{-6} s at 25 °C in dilute acidified aqueous solutions of $AlCl_3$ by the dissociation field effect relaxation method[48] and as $\approx 10^{-5}$ s at 25 °C in dilute acidified chloride solutions by proton NMR.[44,49] The lifetime of protons in dimeric and higher polymeric species is also relatively short[45] at ca. 10^{-7} s. These values for the proton lifetime are, however, longer than the IQENS observation time scale and are consistent with the observed minimum in $\bar{\chi}^2(n_h)$ at $n_h \approx 6$. Baes and Mesmer[38] also report an absence of hydrolysis products in Al^{3+} solutions at pH below 3 (see Table I).

In view of the broad minimum in $\bar{\chi}^2(n_h)$ and the high solution concentration used in the IQENS experiment, it was felt advisable to examine the sensitivity of the slow-exchange scattering law to n_h (<6) with both D_1 and D_2 treated as fitted parameters. The results (Table III) show no change in the overall $\bar{\chi}^2$ values but do reveal a decrease in the fitted D_1 value relative to the case when $n_h = 6$. The $\bar{D}$ values, do, however, remain larger than $\bar{D}$ for an $AlCl_3$ solution of the same concentration and temperature, which suggests a relative structure-breaking role for the ClO_4^- counterion. Similar behavior was observed in aqueous $NiCl_2$ and $Ni(ClO_4)_2$ solutions by the IQENS method.[3]

The results are not consistent with a significant number of second-shell water protons being in slow exchange with the cation which places a firm limit on the binding time for these protons of $\tau_1^{(2)} < 5 \times 10^{-9}$ s. Indeed, the slow-exchange model seems to represent the dynamics well, although it is not possible to compare the fitted $\bar{D}$ with a literature value. The second-shell water protons are therefore likely to be in fast exchange, i.e., $\tau_1^{(2)} \lesssim 10^{-10}$ s. These limits compare with an estimate of $\tau_1^{(2)} \gtrsim 10^{-10}$ s at 25 °C obtained from proton NMR experiments on dilute acidified solutions and compare with a value of 2.5×10^{-8} s at 30 °C for water protons bound to the hydrolytic species $Al(OH_2)_5OH^{2+}$.[44]

4.3. The Fe^{3+} Solutions. Hydrolysis provides an important kinetic pathway for water exchange in aqueous Fe^{3+} solutions.[50-52] Indeed, the rate of water exchange from $Fe(OH_2)_6^{3+}$ is several orders of magnitude smaller than the rate of water exchange from $Fe(OH_2)_5(OH)^{2+}$. ^{17}O NMR experiments have given for the total rate of water exchange at 25 °C in acidified solution the expression

$$k = k_1 + k_2[H^+]^{-1}$$

where $[H^+]$ is the hydrogen ion concentration in molal, $k_1 = 1.6 \times 10^2$ s^{-1}, and $k_2 = 1.5 \times 10^2$ mol kg^{-1} s^{-1}.[39] k_1 is the rate coefficient for exchange of an aqua ligand on $Fe(OH_2)_6^{3+}$ with bulk solvent, and $k_2 = k_{OH}K_a$ in which K_a is the equilibrium quotient for the hydrolysis reaction

$$Fe(OH_2)_6^{3+} \rightleftharpoons Fe(OH_2)_5OH^{2+} + H^+ \qquad (6)$$

k_{OH} ($= 1.2 \times 10^5$ s^{-1}) is the rate coefficient for aqua exchange on $Fe(OH_2)_5OH^{2+}$. On the basis of these values and the $[H^+]$ estimated from the concentration of added acid (Table I), exchange of entire water molecules will not account for a dynamic hydration number of <6 in either of the solutions used for the IQENS experiments.

The lifetime of protons in the primary hydration sphere of Fe^{3+} is, however, much shorter than oxygen. Electric field jump relaxation experiments on dilute $Fe(ClO_4)_3$ solutions show that the rate of proton exchange for the reaction given by eq 6 is too fast to be measured by using this technique, although a proton lifetime of $\approx 3 \times 10^{-8}$ s at 25 °C is estimated.[41] This value compares with 3.6×10^{-7} s at 25 °C obtained in dilute acidified $Fe(NO_3)_3$ solutions by proton NMR.[53] Both of these binding times are, however, consistent with a dynamic hydration number of 6 for the Fe^{3+} solutions.

The minimum in $\bar{\chi}^2(n_h)$ does, however, occur at $n_h < 6$, and the concentrations of the present solutions are high. A further analysis of the IQENS data was therefore made by using the slow-exchange scattering law with D_1 and D_2 fitted and n_h fixed at values <6. The results (Tables IV and V) do not show any significant change in the $\bar{\chi}^2$ values but do reveal a reduction in the magnitude of the fitted D_1. The best agreement with the tracer diffusion D_{ion} and $\bar{D}$ values is obtained when $n_h \approx 5.5$. The data are therefore consistent with the model for slow exchange wherein there is a degree of hydrolysis.[54] As in the case of the Ga^{3+} solution (section 4.1) the water proton binding time for protons in the hexa-aquo ferric [$Fe(OH_6)_6^{3+}$] complex is $\tau_1 \gtrsim 5 \times 10^{-9}$

---

(41) Hemmes, P.; Rich, L. D.; Cole, D. L.; Eyring, E. M. *J. Phys. Chem.* **1971**, *75*, 1971.

(42) It is assumed that all dissociated protons exchange rapidly on the IQENS observation time scale. If there are, however, several different hydrolysis species, then it is possible that $\tau_1 > 5 \times 10^{-9}$ s for protons which dissociate from some of the species.

(43) Fiat, D.; Connick, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 608.

(44) Fong, D.-W.; Grunwald, E. *J. Am. Chem. Soc.* **1969**, *91*, 2413.

(45) Akitt, J. W.; Greenwood, N. N.; Khandelwal, B. L.; Lester, G. D. *J. Chem. Soc., Dalton Trans.* **1972**, 604.

(46) Hertz, H. G. *Water: A Comprehensive Treatise*; 1973; Franks, F., Ed.; Plenum: New York, Vol. 3, p 301.

(47) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545.

(48) Holmes, L. P.; Cole, D. L.; Eyring, E. M. *J. Phys. Chem.* **1968**, *72*, 301.

(49) Thomas, S.; Reynolds, W. L. *Inorg. Chem.* **1970**, *9*, 78.

(50) Dodgen, H. W.; Liu, G.; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 1002.

(51) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.

(52) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.

(53) Luz, Z.; Shulman, R. G. *J. Chem. Phys.* **1965**, *43*, 3750.

(54) It should be noted that some inner sphere complexing of Fe^{3+} by NO_3^- may occur in the nitrate solution (Sharma, S. K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3831). A reduction in n_h from the value of six may therefore result, in part, from this effect.

Table VII. Ion to Water-Proton Binding Times, τ_1, Obtained from 1QENS Experiments on Concentrated Aqueous Ionic Solutions at Room Temperature (≈25 °C) (Present Work and Refs 3, 5, 6)[a]

$\tau_1 \lesssim 10^{-10}$ s	$\tau_1 > 10^{-10}$ s	$\tau_1 \gtrsim 5 \times 10^{-9}$ s
Li^+	Zn^{2+}[b]	Mg^{2+}
Cs^+	Nd^{3+}	Ni^{2+}
Ca^{2+}	Dy^{3+}	Al^{3+}
Cu^{2+}		Cr^{3+}
F^-		Fe^{3+}
Cl^-		Ga^{3+}
I^-		
ClO_4^-		

[a] In this table the notation τ_1 is used to refer to both cations and anions. In some of the trivalent metal ion solutions (Ga^{3+}, Fe^{3+}) there is evidence for hydrolysis which gives a binding time $<5 \times 10^{-9}$ s for dissociated protons. [b] An upper limit of $\tau_1 < 5 \times 10^{-9}$ s has been estimated.[5]

s. This limit also holds for protons in ferric ion hydrolysis products [e.g., $Fe(OH_2)_5OH^{2+}$], while an upper bound of $\tau_1 < 5 \times 10^{-9}$ s is provided for dissociated protons.

Second-shell water protons are not observed to be in slow exchange, which implies that $\tau_1^{(2)} < 5 \times 10^{-9}$ s. Since the proton dynamics in the $Fe(ClO_4)_3$ solution is fully described by the slow-exchange model, the second-shell protons are most likely to be in the fast-exchange limit, i.e., $\tau_1^{(2)} \lesssim 10^{-10}$ s. This binding time compares with an estimate of $\tau_1^{(2)} > 10^{-10}$ s obtained for dilute acidified ferric ion solutions by ^{17}O NMR.[51]

4.4. The Dy^{3+} Solutions. The fast-exchange scattering law does not appear to be consistent with the data which implies a cation–proton binding time $\tau_1 > 10^{-10}$ s. The slow-exchange scattering law model, with D_1 fixed equal to estimates of D_{Dy}, gives a better representation of the data but, for the low-temperature solution, only when D_{Dy} is taken from the upper branch of Figure 1. The slow-exchange scattering law model with D_1 and D_2 fitted also yields D_1 values that are much larger than those obtained from the lower branch of Figure 1. It is therefore tempting to suggest that the data for $LaCl_3$ lie on the upper branch of Figure 1 by virtue of an enhancement of D_{ion} in aqueous solution for the lanthanide elements as a whole rather than by a result of inner-sphere complexing effects alone (see section 3.1). The slow-exchange model is consistent with an early ^{17}O NMR experiment that gave an upper limit on the water molecule binding time of $<5 \times 10^{-8}$ s in concentrated perchlorate solutions.[55]

However, an absolute value of 2.3×10^{-9} s at 25 °C has recently been measured for the water molecule binding time in dilute acidified $Dy(ClO_4)_3$ solutions by ^{17}O NMR using high magnetic field spectrometers.[4,56] This value, if appropriate for high concentrations, places the IQENS solution in the intermediate-exchange regime. The lower limit of $\tau_1 > 10^{-10}$ s obtained from the IQENS experiment is consistent with this value. The slow-exchange model cannot be tested rigorously owing to an absence of independent values for D_{ion} and $\bar{D}$ from other techniques.[12] The IQENS method cannot therefore presently be used to estimate an upper limit on τ_1.[5]

A water proton binding time for Dy^{3+} that is significantly less than that for Ga^{3+}, Al^{3+}, and Fe^{3+} is not unreasonable given the relatively large ionic radius of the Dy^{3+} ion (0.908 Å compared with 0.62, 0.51, and 0.64 Å, respectively). Hydrolysis is not thought to have an appreciable effect in the present Dy^{3+} solution.[38]

5. Conclusions

The Ga^{3+}, Al^{3+}, and Fe^{3+} solution data are consistent with the slow-exchange model wherein $n_h = 6$. The proton dynamics in the Ga^{3+} and Fe^{3+} solutions is, however, better represented if hydrolysis is assumed. The degree of hydrolysis cannot, on the basis of the present data, be quantified, particularly in view of the broad minimum in $\bar{\chi}^2(n_h)$. However, limits can be placed on the cation to water proton binding time: $\tau_1 \gtrsim 5 \times 10^{-9}$ s for protons in the hexa-aquo species $M(OH_2)_6{}^{3+}$ or in any hydrolysis product species such as $M(OH)_5OH^{2+}$ and $\tau_1 < 5 \times 10^{-9}$ s for any dissociated protons. The former limit is in agreement with previous ^{17}O NMR results. The latter limit is shorter than the value estimated in previous proton NMR and electric field relaxation experiments made on dilute acidified solutions (see sections 4.1–4.3). A summary of the ion to primary solvation shell water proton binding times in aqueous solution, as determined by IQENS experiments, is presented in Table VII.

The question of the accuracy of the D_1 value measured by using the IQENS method depends on the accuracy to which n_h is known. In the absence of hydrolysis $n_h = 6$ and the fitted D_1 for the Ga^{3+} and the Fe^{3+} solutions are up to 30% larger than the tracer diffusion D_{ion}. Better agreement is, however, obtained for $n_h < 6$. In the case of a 1.8 molal $Cr(ClO_4)_3$ solution,[6] in which significant hydrolysis products were not detected, it was argued that the same discrepancy between the fitted D_1 and the measured D_{ion} resulted from the comparability in widths of the resolution function and first Lorentzian in eq 2, leading to a significant resolution broadening of this first Lorentzian. This factor cannot be neglected for the present solutions, since the existence of hydrolysis products was not tested by using another experimental method such as spectrophotometry. The type and concentration of hydrolysis products cannot be readily calculated for the present IQENS solutions by using stability constant data owing to the problems noted under section 4.

The second-shell water protons are not observed to be in slow exchange with the cation which gives $\tau_1^{(2)} < 5 \times 10^{-9}$ s. For the Ga^{3+} and $Fe(ClO_4)_3$ solutions it is argued that the second-shell water protons are in fast exchange, i.e., $\tau_1^{(2)} \lesssim 10^{-10}$ s, else there would not be the quantitative agreement between the $\bar{D}$ obtained from the slow-exchange scattering law and the tracer diffusion $\bar{D}$.[5] $\tau_1^{(2)}$ is not readily available from other techniques, but its value is of importance since the formation of outer-sphere complexes often precedes exchange of primary shell solvent ligands.[57,58]

Acknowledgment. G.J.H. thanks the U.K. SERC for a studentship during the course of which this work was carried out. We thank also Laurie Woolf for his help with the ion diffusion work, Phil Gullidge for his help with sample preparation, and George Neilson and Spencer Howells for helpful conversations. We gratefully acknowledge the support of the ILL staff, particularly Andreas Magerl, Sabina Mahling, and Henri Godfrin, and the support of the U.K. SERC (Grant GR/D 76455 to P.S.S.).

Supplementary Material Available: Figures A1–A10 of IQENS spectra and the fitted HWHM of the first and second Lorentzian plotted as a function of Q^2 (18 pages). Ordering information is given on any current masthead page.

---

(55) Reuben, J.; Fiat, D. *J. Chem. Phys.* **1969**, *51*, 4918.

(56) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1989**, *28*, 2699.

(57) Wilkins, R. G. *The study of kinetics and mechanism of reactions of transition metal complexes*; Allyn and Bacon: Boston, 1974.

(58) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.