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P S Salmon†, G J Herdman‡§, J Lindgren||, M C Read¶ and M Sandström¶

† School of Physics, University of East Anglia, Norwich NR4 7TJ, UK
‡ H H Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
|| Institute of Chemistry, University of Uppsala, Box 531, S-75121 Uppsala, Sweden
¶ Department of Inorganic Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden

Abstract. The technique of high-resolution, incoherent quasi-elastic neutron scattering (IQENS) is applied to a 1.790 molal (mol kg^{-1}) solution of $Cr(ClO_4)_3$ at 26 ± 1 °C. The results are consistent with a dynamic hydration number of six water molecules, each having a Cr^{3+}–water-proton binding time described by the limit $\tau_1 \gtrsim 5 \times 10^{-9}$ s. The results do not show a second shell of water protons in slow exchange with the cation, which implies a Cr^{3+} to second-shell water-proton binding time that is $<5 \times 10^{-9}$ s. Values for the water-proton translational self-diffusion coefficients are presented.

1. Introduction

The lifetime of a water oxygen atom in the primary hydration shell of the Cr^{3+} ion is very long compared with most other aqua-ions (Hunt and Friedman 1983, Friedman 1985). This feature enabled Hunt and Plane (1954) to measure lifetimes of the order of 10^6 s using isotope ^{18}O dilution experiments. In view of these large lifetimes and the strongly polarising influence of the small Cr^{3+} ion there may also be a tendency for the hydrogen-bonded second-shell water molecules to have a relatively large binding time to the hydrated cation. There is, for example, some evidence for a well-defined second hydration shell from x-ray diffraction experiments (Caminiti *et al* 1976, 1977, 1978; Read and Sandström 1989). Furthermore, a preliminary investigation on the hydration of the Cr^{3+} ion in aqueous solution using the infra-red technique of Kristiansson *et al* (1988) indicates that the O–H vibrations in the second hydration shell are affected by the cation.

In this paper, results of high-resolution incoherent quasi-elastic neutron scattering (IQENS) experiments on a 1.790 molal (mol kg^{-1}) aqueous solution of $Cr(ClO_4)_3$ are presented. The IQENS method is sensitive to the magnitude of the cation water-proton

§ Present address: Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK.

binding time, τ_1†, such that water protons will be observed in fast exchange with the cation if $\tau_1 \lesssim 10^{-10}$ s, in intermediate exchange if 10^{-10} s $< \tau_1 < 5 \times 10^{-9}$ s and in slow exchange if $\tau_1 \gtrsim 5 \times 10^{-9}$. It follows that the second-shell water protons may be observed in slow exchange on the timescale of IQENS observations even though the cation–proton binding time for the second shell will be smaller than that for the first shell. This latter value has been given as $\simeq 5 \times 10^{-6}$ s from other techniques (see § 4).

The perchlorate anion was chosen because it is not prone to inner-sphere complexing with cations (Berman and Stengle 1975) and its coordinated water protons will be observed in fast exchange (Salmon *et al* 1987).

2. Theory

The IQENS method has been described in detail by Salmon (1987) and a summary of the main results will be presented here. Essentially, the choice of spectrometer parameters and the use of light water solutions ensure that the measured spectra are insensitive to the vibrational and rotational motions of water-protons but are dependent on the classical translational self-diffusive motion of the protons in addition to the magnitude of τ_1. The spatial and temporal scales covered in an experiment are sufficiently large to ensure that macroscopic translational proton diffusion coefficients are measured.

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

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

where $\hbar Q$ and $\hbar\omega$ ($\equiv \Delta E$) are the momentum transfer and energy transfer respectively. If a solution is in slow exchange, however, two 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

$$\tilde{S}(Q, \omega) = \frac{1}{\pi\hbar} \left(c_1 \frac{D_1 Q^2}{(D_1 Q^2)^2 + \omega^2} + (1 - c_1) \frac{D_2 Q^2}{(D_2 Q^2)^2 + \omega^2} \right). \tag{2}$$

In equation (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

$$\bar{D} = c_1 D_1 + (1 - c_1) D_2. \tag{3}$$

For solutions that are in slow exchange, water protons will be bound to the cation for times that are sufficiently long for them to acquire the translational self-diffusion coefficient of the cation D_{ion} (see Salmon *et al* 1987). The average number of water molecules having protons for which $D_1 = D_{ion}$ will be termed the *dynamic hydration number*, n_h, and this is used to fix the value of c_1. D_{ion} values for $Cr(ClO_4)_3$ solutions are

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† τ_1 is defined such that the average number of protons that remain bound to a cation for a time t is given by $n(t) = n(0) \exp(-t/\tau_1)$.

available from the tracer diffusion measurements of Easteal *et al* (1988) and can therefore be used to fix D_1 during data analysis.

3. Experimental procedure

The IQENS experiment was performed using the back-scattering spectrometer IN10 at the Institut Laue–Langevin, Grenoble. Spectra were measured at six equally spaced Q-values in the range $0.11 \text{ Å}^{-1} \leq Q \leq 0.31 \text{ Å}^{-1}$ in an energy window of about $\pm 15 \mu\text{eV}$ with an energy resolution function having half-width at half-maximum (HWHM) $\simeq 1 \mu\text{eV}$. The Q-resolution, $\Delta Q = \pm 0.017 \text{ Å}^{-1}$ 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 analyser crystals shielded by cadmium) and, in order to give the energy resolution function, a vanadium disc of thickness 2 mm.

A freshly prepared solution of chromium(III) perchlorate hexahydrate, supplied by the G F Smith Chemical Company, was used for the measurements. The chromium content was found by standard methods (Vogel 1978) to be $1.516 \text{ mol dm}^{-3}$ at $25 \,^\circ\text{C}$, and an analysis of the total anion concentration by ion exchange showed no excess acidity. The density was measured by an Anton Paar precision densitometer and found to be 1.3779 g cm^{-3} at $25 \,^\circ\text{C}$. This gives a molality of $1.790 \text{ mol kg}^{-1}$ and a water-molecule number density of 0.0283 Å^{-3}.

The conditional equilibrium constants (after 1 year at $25 \,^\circ\text{C}$) given by Stünzi and Marty (1983) indicate that the amount of chromium in hydrolysis complexes should be low ($<1\%$) in a fresh 1.8 molal $Cr(ClO_4)_3$ solution. This observation was corroborated by a UV–visible spectrophotometric measurement which was made on the solution a few months after the IQENS experiment. The spectrophotometer data were analysed using the molar absorbance values given by Stünzi and Marty (1983) and it was found that no significant amount of hydrolysis products could be detected.

The $Cr(ClO_4)_3$ solution was held in a planar container made from two single-crystal sapphire windows each of thickness 0.5 mm. The spacing between the sapphires was defined by a PTFE O-ring of thickness $0.29 \pm 0.01 \text{ mm}$ which ensured a considerable reduction, compared to previous work, in the multiple scattering of neutrons by the sample (see Salmon 1987, appendix A). The solution was maintained at a temperature of $26 \pm 1 \,^\circ\text{C}$. The effective absorption and scattering cross sections per water molecule at $\lambda = 6.271 \text{ Å}$, the incident wavelength on IN10, are 14 b and 201 b respectively.

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

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

where $\alpha(Q)$ is a normalisation factor, $R(Q, \omega)$ is the measured resolution function and $R_1^*(Q, \omega)$ is the correction for multiple scattering and attenuation of the neutron beam
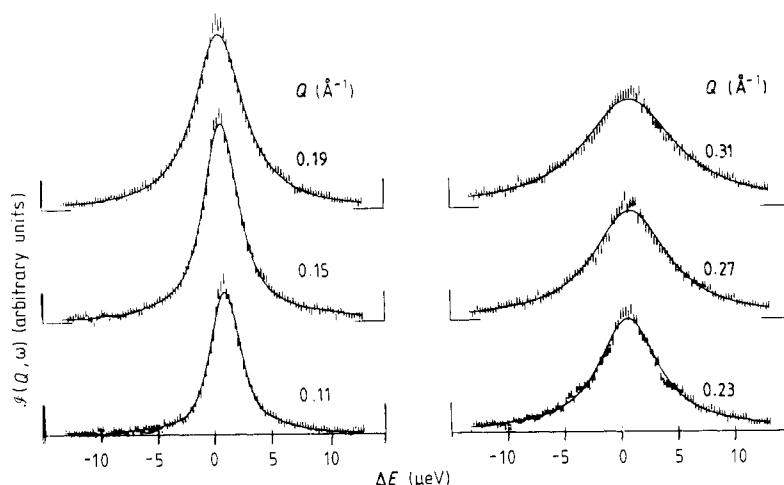
Figure 1. An attempt to fit the IQENS spectra for a 1.790 mol kg^{-1} Cr(ClO$_4$)$_3$ solution using the single Lorentzian scattering law for fast exchange (equation (1)). The vertical lines give the statistical error on $J(Q, \omega)$ and the full curve gives the fitted curve. The Q-values are given above each curve.

in the sample. The minimised quantity at each Q-value in the fitting procedure was χ^2, given by

$$\chi^2 = \sum_{j=1}^{N} \frac{[\bar{\mathscr{F}}(Q, \omega_j) - \mathscr{F}(Q, \omega_j)]^2}{\sigma_j^2} \tag{5}$$

where j labels the energy transfer channel, $N(=114)$ is the total number of channels and σ_j is the statistical error on $\mathscr{F}(Q, \omega_j)$. A measure of the overall goodness-of-fit is given by the average $\overline{\chi^2}$, of the χ^2 over all measured Q-values. Further details of the correction procedure have been reported by Salmon (1987).

4. Experimental results

In the first stage of data analysis, the measured spectra were fitted using the fast exchange scattering law. This model gave $\overline{\chi^2} = 129$ and did not describe the proton dynamics (see figure 1): the fitted curves do not adequately fit the data in the region about $\Delta E = 0$ where the most significant difference between the fast- and slow-exchange scattering laws will occur (see e.g. figure 3 of Salmon 1987).

In the next stage, the slow-exchange scattering law was used, in which D_2 was fitted and c_1 was fixed at a value of 0.1940, corresponding to a dynamic hydration number n_h of 6. This value of n_h is expected from a wide variety of techniques including isotopic dilution (Hunt and Taube 1950, 1951), ^{17}O NMR (Alei 1964, Alei and Jackson 1964) and x-ray diffraction (Caminiti *et al* 1976, 1977, 1978). In view of the uncertainty in the actual temperature of the solution, fits were made with D_1 fixed at two different values. Firstly, D_1 was held at 0.174×10^{-9} m^2 s^{-1} (see figure 2), corresponding to D_{ion} for Cr^{3+} in a 1.7946 mol kg^{-1} Cr(ClO$_4$)$_3$ solution at 25 °C (Easteal *et al* 1988). Secondly, D_1 was held at 0.183×10^{-9} m^2 s^{-1}, which is an estimate of D_{ion} for the solution at 27 °C. This latter value was obtained from the D_{ion} value at 25 °C by assuming an Arrhenius temperature
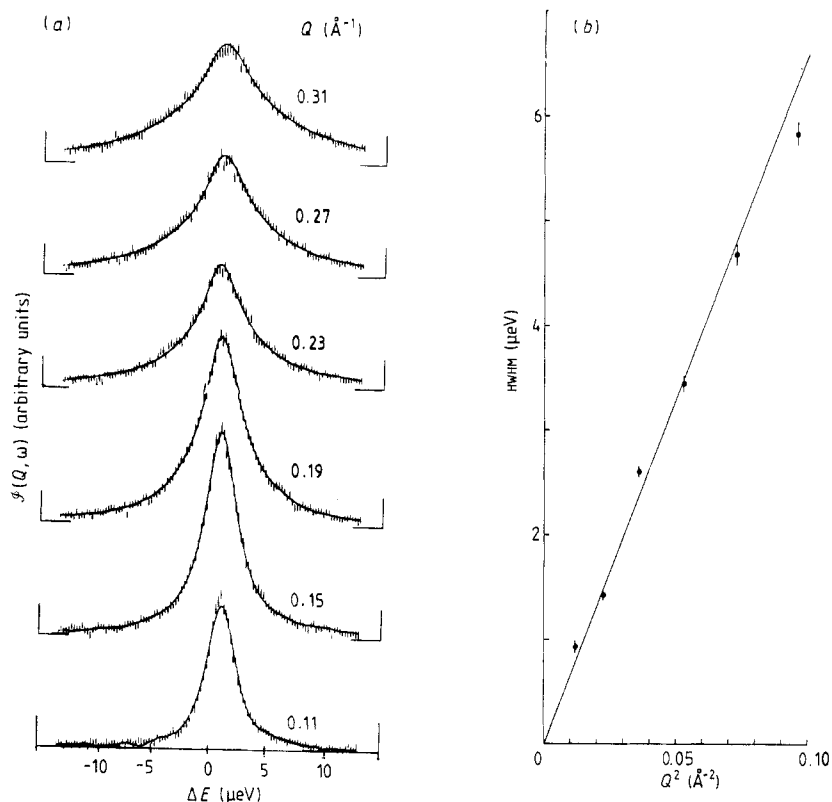
Figure 2. (*a*) The IQENS spectra for a 1.790 mol kg⁻¹ Cr(ClO₄)₃ solution, fitted using the slow-exchange scattering law (equation (2)) with D_1 fixed equal to D_{ion} ($= 0.174 \times 10^{-9}$ m² s⁻¹) for the first Lorentzian and c_i fixed at a value corresponding to $n_h = 6$. The vertical lines give the statistical error on $\mathcal{S}(Q, \omega)$ and the full curve gives the fitted curve. The Q-values are given above each curve. (*b*) The fitted half-width at half-maximum (HWHM) of the second Lorentzian in (*a*) plotted as a function of Q^2. The gradient gives D_2.

dependence and an activation energy equal to that for pure water (see Salmon *et al* 1987).

The results are summarised in table 1. Both fits gave improved $\overline{\chi^2}$ values when compared with the single Lorentzian fit given in figure 1. Furthermore, the $\bar{D}$ values obtained are, within experimental error, in the range expected from the tracer diffusion measurements of Easteal *et al* (1988), namely 0.830×10^{-9} m² s⁻¹ $\leqslant \bar{D} \leqslant 0.870 \times 10^{-9}$ m² s⁻¹. The first limit is the tracer diffusion result obtained for water in a 1.7946 mol kg⁻¹ Cr(ClO₄)₃ solution at 25 °C using tritiated water (HTO) as a tracer. The second limit was obtained from the first limit by scaling to a temperature of 27 °C as described above for D_{ion}. These limits will be increased by ≃2.8% if the mass extrapolation procedure of Mills (1973) is used to correct the tracer results for isotope effects.

The slow-exchange scattering law was also used to analyse the data with both D_1 and D_2 treated as fitted parameters and c_1 fixed at a value corresponding to $n_h = 6$. This fit (see figure 3) was also better than that obtained assuming fast exchange. The fitted diffusion coefficients are given in table 1.

Table 1. The results obtained from fitting the IQENS data for a 1.790 mol kg^{-1} Cr(ClO$_4$)$_3$ solution at (26 ± 1) °C. In the analyses, c_1 was fixed at a value of 0.1940 corresponding to a dynamic hydration number, n_h, of 6 and D_1 was treated as being either a fixed or a fitted parameter. $\bar{D}$ is the average diffusion coefficient of all water protons in a solution and is obtained from the fitted spectra using equation (3). The overall goodness-of-fit for a particular model is indicated by the value of $\overline{\chi^2}$.

D_1 $(10^{-9}\,\text{m}^2\,\text{s}^{-1})$		D_2 $(10^{-9}\,\text{m}^2\,\text{s}^{-1})$	$\bar{D}$ $(10^{-9}\,\text{m}^2\,\text{s}^{-1})$	$\overline{\chi^2}$
0.174	(fixed)	1.00 ± 0.03	0.84 ± 0.03	95
0.183	(fixed)	0.99 ± 0.03	0.84 ± 0.03	93
0.22 ± 0.01	(fitted)	0.97 ± 0.04	0.82 ± 0.03	87

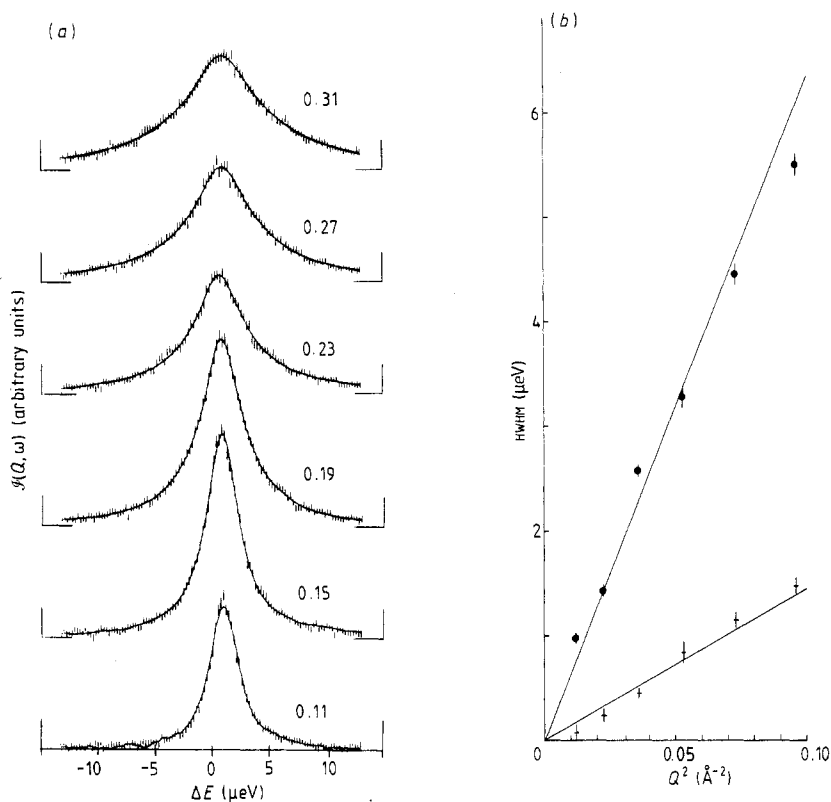**Figure 3.** (*a*) The IQENS spectra for a 1.790 mol kg^{-1} Cr(ClO$_4$)$_3$ solution fitted using the slow-exchange scattering law (equation (2)) with both D_1 for the first Lorentzian and D_2 for the second Lorentzian allowed to be variable parameters. c_1 was fixed at a value corresponding to $n_h = 6$. The vertical lines give the statistical error on $\mathcal{S}(Q, \omega)$ and the full curve gives the fitted curve. The Q-values are given above each curve. (*b*) The 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.

In the last stage of the analysis, an attempt was made at extracting n_h from the measured IQENS spectra by comparing them with the slow-exchange scattering law with n_h fixed at various values chosen in the range from 3.5 to 12. For each n_h value, D_1 was

fixed either at $0.174 \times 10^{-9} \, \text{m}^2 \, \text{s}^{-1}$ or at $0.183 \times 10^{-9} \, \text{m}^2 \, \text{s}^{-1}$ and D_2 was fitted. The individual χ^2 values, in addition to $\overline{\chi^2}$ (see Salmon 1989), were then plotted as a function of n_h in order to determine the minima in $\chi^2(n_h)$ and $\overline{\chi^2}(n_h)$. It was found that the minima in $\chi^2(n_h)$ were consistent with a dynamic hydration number in the range $4 \leqslant n_h \leqslant 6$, whilst the minima in $\overline{\chi^2}(n_h)$ occurred at $n_h \approx 5$. The range of n_h values is considered to reflect uncertainties in the present technique arising, for example, from the limited energy transfer window of IN10 rather than the presence of substantial amounts of hydrolysis products as emphasised in § 3. Notwithstanding, there is no evidence from the present analysis in support of a n_h value greater than 6.

5. Discussion

The IQENS results show that the solution is in slow exchange and are consistent with a dynamic hydration number n_h of 6. The fits obtained when keeping D_1 and n_h ($=6$) fixed gave a mean $\bar{D}$ value that is within the bounds expected from the tracer diffusion measurements, and the fits aimed at showing the sensitivity of the IQENS spectra to the dynamic hydration number gave results that are consistent with n_h in the range $4 \leqslant n_h \leqslant 6$. The Cr^{3+} to primary-shell water-proton binding time is therefore $\geqslant 5 \times 10^{-9}$ s, a value which is entirely consistent with the Cr^{3+}-oxygen lifetime of 8.5×10^5 s at 25 °C and 1.516 mol dm^{-3} obtained from isotopic dilution experiments using water enriched in ^{18}O (see table 2 of Easteal *et al* 1988)†, and the Cr^{3+}-proton binding time of between 10^{-5} s and 10^{-6} s at 25 °C obtained from proton magnetic resonance (Swift and Stephenson 1966, Hertz 1973) and electric field relaxation time (Rich *et al* 1969) experiments. The second-shell water protons are not in slow exchange on the IQENS timescale and the Cr^{3+} to second-shell water-proton binding time is therefore $<5 \times 10^{-9}$ s.

In order to emphasise the latter point, we consider the case when $n_h = 12$, i.e. when 6 second-shell water molecules are in slow exchange with the Cr^{3+} ion in addition to the 6 water molecules in the primary hydration shell. In the present work the solution composition can be written as $Cr(ClO_4)_3 \cdot 30.9H_2O$ and the perchlorate anion is typically coordinated to 4.5 water molecules (Neilson *et al* 1985). A second-shell hydration number of six does not, therefore, necessitate the sharing of water molecules and compares with a second-shell coordination number of (15 ± 2) water molecules in the case of dilute $NiCl_2$ solutions (e.g. Hewish *et al* 1983). The fit assuming slow exchange with $D_1 = 0.174 \times 10^{-9} \, \text{m}^2 \text{s}^{-1}$ and $n_h = 12$ yields $\overline{\chi^2} = 352$ and clearly does *not* represent the proton dynamics (see figure 4).

The fitted D_1 obtained from the IQENS spectra with $n_h = 6$ (see table 1) is 23% greater than D_{ion} obtained from tracer diffusion measurements. This discrepancy is much larger than that expected on the basis of other IQENS studies on Ni^{2+} solutions where D_1 was obtained with an estimated accuracy of 10% (Salmon *et al* 1987). A possible explanation lies in the small cation diffusion coefficient in the present study. This leads to a problem in clearly resolving the first Lorentzian in the slow-exchange scattering law (equation 2), as its width is comparable with that of the resolution function at all Q-values (see Appendix).

† Easteal *et al* (1988) find that a lifetime for oxygen in this solution of 1.25×10^6 s is more consistent with their tracer diffusion results. This value does not affect the conclusions drawn from our results.
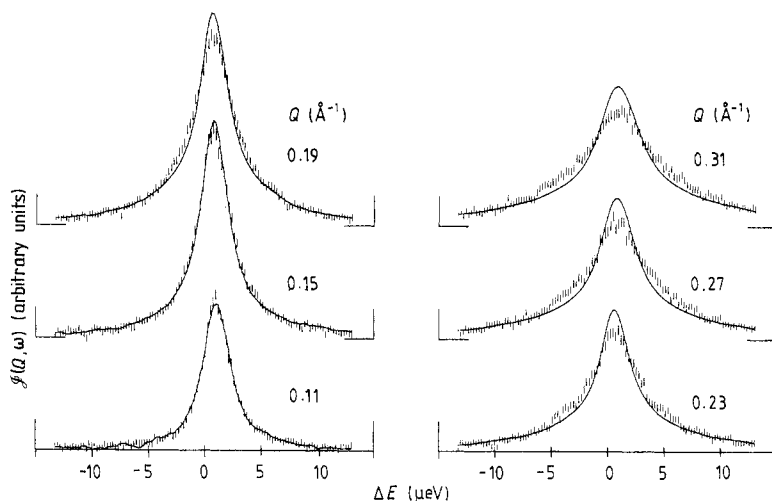
Figure 4. As for figure 2(*a*) but with $n_h = 12$.

The values of D_2 given in table 1 are substantially less than the diffusion coefficient for pure water of $D_0 = 2.35 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ at 26 °C (Mills 1973). The two-state model of bound and free water cannot, therefore, be used to provide a realistic picture of the translational proton self-diffusion in the solution investigated here. This conclusion is consistent with that obtained from the previous IQENS study on solutions of another trivalent cation, Nd^{3+} (Salmon *et al* 1987). Moreover, if we neglect the effect of the anions on proton diffusion and interpret the measured D_2 in terms of a second shell of water associated with the cation and free water (Hewish *et al* 1983) then

$$D_{\mathrm{sec}} = D_0 + (c_2/c_{\mathrm{sec}})(D_2 - D_0) \tag{6}$$

where D_{sec} and c_{sec} are the diffusion coefficient and atomic fraction of protons in the second shell, D_0 and c_0 are the corresponding quantities for protons in bulk water and $c_2 = c_{\mathrm{sec}} + c_0$. It is found that the self-diffusion coefficient results for the present solution do not support a zonal model of the Frank–Wen (Frank and Wen 1957) type, in which $D_{\mathrm{sec}} > D_0$, since $D_2 \ll D_0$ (table 1).

6. Conclusions

The IQENS results show that the water protons in the primary hydration sphere of the Cr^{3+} ion are in slow exchange and are consistent with a hydration number $n_h = 6$. The second-shell water protons are not in slow exchange with the Cr^{3+} ion on the timescale of IQENS observations: the binding time of these protons to the Cr^{3+} ion is therefore $<5 \times 10^{-9}\,\mathrm{s}$.

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Appendix

The resolution function will have its largest affect on the first Lorentzian term of equation (2), since $D_1 \ll D_2$. This can be shown by approximating the measured resolution function at each Q-value by the expression (Birr *et al* 1971, Heidemann *et al* 1980, Howells 1981)

$$R(Q, \omega) = a(Q) \frac{\Delta R(Q)}{\Delta R(Q)^2 + \omega^2} + b(Q) \tag{A1}$$

where $\Delta R(Q)$ is a half-width at half-maximum and $a(Q)$ and $b(Q)$ are independent of ω. The convolution with respect to energy transfer of the scattering law given by equation (2) with $R(Q, \omega)$ (cf. equation (4)) is then given by

$$\frac{a(Q)}{\pi \hbar} \left[c_1 \frac{D_1 Q^2 + \Delta R(Q)}{(D_1 Q^2 + \Delta R(Q))^2 + \omega^2} + (1 - c_1) \frac{D_2 Q^2 + \Delta R(Q)}{(D_2 Q^2 + \Delta R(Q))^2 + \omega^2} \right] + \frac{b(Q)}{\hbar}. \tag{A2}$$

In the event that $\Delta R(Q) \simeq D_1 Q^2$, as in the case of the present $Cr(ClO_4)_3$ solution, the fractional broadening of the first narrow Lorentzian in equation (2) is much larger ($\simeq 100\%$) than that of the second Lorentzian ($\simeq 18\%$, using the values of D_1 and D_2 in table 1). It is therefore feasible that the fitting procedure wherein both D_1 and D_2 are allowed to vary will lead to an apparent D_1 that is larger than D_{ion}.

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