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The dynamics of aqueous Zn^{2+} solutions: a study using incoherent quasi-elastic neutron scattering

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Abstract. The method of high-resolution incoherent quasi-elastic neutron scattering (IQENS) is used to study the proton diffusion and cation to water-proton binding time in 1.98 molal (mol kg^{-1}) and 2.58 molal aqueous $\text{Zn}(\text{ClO}_4)_2$ solutions and a 1.96 molal aqueous ZnCl_2 solution at room temperature. In the perchlorate solutions a lower limit of $\tau_1 > 10^{-10}$ s is found for the Zn^{2+} to water-proton binding time and an upper limit of $\tau_1 < 5 \times 10^{-9}$ s is estimated. The chloride solution cannot be described by a single proton population on the IQENS observation time scale. Furthermore, it cannot be described by a model which assumes that only those protons bound to free Zn^{2+} ions are in slow exchange, the fraction of these ions being taken from the published sets of stability constants used to describe the equilibria between the various zinc complexes present in solution.

1. Introduction

The rate of exchange of water with the Zn^{2+} ion is very fast compared with most other transition-metal cations and does not appear to have been measured by a direct method (Laurenczy *et al* 1989). For example, the exchange rate is too fast to render it accessible from isotopic dilution experiments and the diamagnetic nature of the nucleus, together with the fast water exchange rate, make NMR experiments unsuccessful.

The method of high-resolution incoherent quasi-elastic neutron scattering (IQENS) is, however, sensitive to fast exchange processes. If τ_1 ¶ is the magnitude of the cation to water-proton binding time, then water protons will be observed in fast exchange with the cation if $\tau_1 \leq 10^{-10}$ s, in intermediate exchange if 10^{-10} s $<$ $\tau_1 <$ 5×10^{-9} s and in slow exchange if $\tau_1 \geq 5 \times 10^{-9}$ s (Salmon 1987). Thus solutions which are in fast exchange on the NMR observation time scale may be observed in slow or intermediate exchange on the IQENS observation time scale. In aqueous neodymium solutions, for instance, τ_1 is too short for it to be measured using ^{17}O NMR, which gives an upper limit

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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 $n(t) = n(0) \exp(-t/\tau_1)$.

of $\tau_1 < 10^{-9}$ s (Cossy *et al* 1988), while IQENS experiments give a lower limit of $\tau_1 > 10^{-10}$ s (Salmon *et al* 1987). Furthermore, the Cr^{3+} to *second*-shell water-proton binding time in aqueous perchlorate solution has been measured as less than 5×10^{-9} s using the IQENS method (Salmon *et al* 1989).

In this paper the IQENS method is applied to 1.98 molal (mol kg^{-1}) and 2.58 molal aqueous $\text{Zn}(\text{ClO}_4)_2$ solutions and a 1.96 molal aqueous ZnCl_2 solution at room temperature. The perchlorate anion was chosen because it is not prone to inner-sphere complexing with cations (see, e.g., Berman and Stengle 1975, Agnew and Paterson 1978). The chloride anion, on the other hand, does form inner-sphere complexes with Zn^{2+} and a distribution of the species $\text{Zn}^{2+}(\text{aq})$ (i.e. completely dissociated Zn^{2+} ions), ZnCl^+ , ZnCl_2 , ZnCl_3^- and ZnCl_4^{2-} is expected (see, e.g., Powell *et al* 1988, Salmon 1989a). Indeed, as the concentration of a ZnCl_2 solution is increased from that of the present, the degree of complexing increases and it is possible to progress to a hydrated melt of formula $\text{ZnCl}_2 \cdot 1.8\text{H}_2\text{O}$ at 25 °C (Dreier and Rabe 1986, Yamaguchi *et al* 1989). The microscopic dynamics of concentrated ZnCl_2 solutions have been a subject studied using a variety of techniques, including quasi-elastic neutron scattering (Bellissent-Funel *et al* 1984, 1989), NMR (Nakamura *et al* 1982, van der Maarel 1989) and Raman and Rayleigh wing scattering (Maisano *et al* 1985). At the concentration of the present experiment, polymeric species involving Zn^{2+} and Cl^- are not thought to occur (Irish *et al* 1963).

The aim of the experiments is to establish firm limits on the Zn^{2+} to water-proton binding time in perchlorate solution and to gain information on the various water-proton environments that are present in chloride solution. Water protons coordinated to free ClO_4^- or Cl^- anions will be observed in fast exchange on the IQENS observation time scale (Salmon 1989b). The implications of this point will be explained more fully in section 2.

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.

The general expression for the scattering law which describes a two-class model for the translational diffusive motion of water protons is given by

$$\begin{aligned} \tilde{S}(Q, \omega) = & (1/\pi\hbar) [A(Q)\mathcal{D}_1(Q)Q^2 / \{[\mathcal{D}_1(Q)Q^2]^2 + \omega^2\} \\ & + B(Q)\mathcal{D}_2(Q)Q^2 / \{[\mathcal{D}_2(Q)Q^2]^2 + \omega^2\}] \end{aligned} \quad (1)$$

with

$$\begin{aligned} A(Q) &= [c_1k_1 + c_2k_2 + \mathcal{D}_2(Q)Q^2] \{[\mathcal{D}_1(Q) - \mathcal{D}_2(Q)]Q^2\}^{-1} \\ B(Q) &= 1 - A(Q) \end{aligned}$$

and

$$\mathcal{D}_j(Q)Q^2 = \frac{1}{2}(k_1 + k_2 + k_3 + k_4) \pm \frac{1}{2}[(k_1 + k_3 - k_2 - k_4)^2 + 4k_3k_4]^{1/2}$$

where the label j is 1 if the summation is positive and 2 if the summation is negative. c_i

($i = 1, 2$) is the atomic fraction of protons in class i , k_i ($i = 1, 2$) = $D_i Q^2$, where D_i is the translational diffusion coefficient of protons in class i , and the k_i ($i = 3, 4$) = τ_i^{-1} are the reciprocal lifetimes of the protons in each of the classes. The relative values of the rate constants k_i determine the Q -dependence of the $\mathcal{D}_i(Q)$ functions and hence the shape of the scattering law. $\hbar Q$ and $\hbar\omega$ ($\equiv \Delta E$) are the momentum and energy transfers, respectively.

The interpretation of a measured spectrum using equation (1) is difficult owing to its complicated dependence on Q and the other parameters. There are, however, two important limiting cases.

When $k_3, k_4 \gg k_1, k_2$ (i.e. $\tau_1^{-1}, \tau_2^{-1} \gg D_1 Q^2, D_2 Q^2$) the protons undergo a rapid exchange between classes such that only a single-proton population is observed and equation (1) for this fast-exchange limit reduces to

$$\bar{S}(Q, \omega) = (1/\pi\hbar)\{\bar{D}Q^2/[(\bar{D}Q^2)^2 + \omega^2]\} \quad (2)$$

where \bar{D} is the average translational diffusion coefficient of the entire population. By contrast, when $k_3, k_4 \ll k_1, k_2$ (i.e. $\tau_1^{-1}, \tau_2^{-1} \ll D_1 Q^2, D_2 Q^2$) the exchange between classes is relatively slow and in this slow-exchange limit the general scattering law reduces to the sum of two weighted Lorentzians:

$$\bar{S}(Q, \omega) = (1/\pi\hbar)\{c_1 D_1 Q^2 / [(D_1 Q^2)^2 + \omega^2] + c_2 D_2 Q^2 / [(D_2 Q^2)^2 + \omega^2]\}. \quad (3)$$

The average diffusion coefficient of the protons in the system is then given by the expression

$$\bar{D} = c_1 D_1 + c_2 D_2 \quad (4)$$

where $c_1 + c_2 = 1$.

In most solutions, class 1 of the model is readily identified with those protons in the primary coordination sphere of the cation, since the ion-water interaction is usually much stronger for cations than for anions. τ_1 then represents the cation to water-proton binding time, as specified in section 1, and class 2 is identified with the remaining protons in solution. In the case of slow exchange the measured D_2 -value will then comprise a contribution from protons in the primary coordination shell of the anion but it is not possible to extract this contribution directly; models have to be used (see, e.g., Salmon *et al* 1987, Eastaie *et al* 1989). This follows since the protons in class 2 sample *all* of their accessible environments on the observation time scale of the IQENS measurement.

In systems such as $Zn(ClO_4)_2$ aqueous solutions, where the salt is completely dissociated and the anion coordinated protons are observed in fast exchange (see section 1), class 1 is readily identified with those protons bound to the $Zn^{2+}(aq)$ ion. In systems such as $ZnCl_2$ aqueous solutions, where a range of cationic (and anionic) species can occur, the identification of class 1 protons is, however, more difficult. This latter situation will be discussed in more detail in section 4.3.

For solutions that are in slow or intermediate exchange, water protons will be bound to the cation for times that are sufficiently long for them to acquire the translational self-diffusion coefficient D_{ion} of the cation (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 can be used to fix the value of c_1 . Hence the number of unknown parameters in the fast- and slow-exchange scattering laws is the *same*, provided that information is available on both n_h and D_{ion} . Tracer diffusion results for aqueous $Zn(ClO_4)_2$ (Price *et al* 1990) and $ZnCl_2$ (Weingärtner *et al* 1984) solutions are available.

3. Experimental procedure

The IQENS experiments were 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 $0.11 \text{ \AA}^{-1} \leq Q \leq 0.31 \text{ \AA}^{-1}$ in an energy transfer window of about $\pm 15 \mu\text{eV}$ with an energy resolution function having a half-width at half-maximum (HWHM) of about $1 \mu\text{eV}$. The Q -resolution $\Delta Q = \pm 0.017 \text{ \AA}^{-1}$ at each Q -value was poor in order to maximise the detected flux.

The complete experiment required spectra to be taken of the solutions in their 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. The 1.98 molal $\text{Zn}(\text{ClO}_4)_2$ and 1.96 molal ZnCl_2 solutions were held in a planar container made from two tantalum windows of thickness 0.1 mm and spacing 1.6 mm. The 2.58 molal $\text{Zn}(\text{ClO}_4)_2$ solution was also held in a planar container but the window material was changed to sapphire of thickness 0.5 mm and the spacing reduced to 1.0 mm. This latter container gave some problems which resulted in some sample loss during the course of the experiment and hence an error in concentration of ± 0.08 molal. The sample details are summarised in table 1.

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 $\mathcal{F}(Q, \omega)$ at each Q -value were then compared with the scattering law corresponding to either fast exchange (equation (2)) or slow exchange (equation (3)) using the function

$$\bar{\mathcal{F}}(Q, \omega) = \alpha(Q) \int \frac{\hat{S}(Q, \omega') R(Q, \omega - \omega')}{R_1^*(Q, \omega)} d\omega'$$

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

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

where j labels the energy transfer channel, $N (= 122)$ is the total number of channels and σ_j is the statistical error on $\mathcal{F}(Q, \omega_j)$. 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 (1987).

4. Experimental results

4.1. The 1.98 molal $\text{Zn}(\text{ClO}_4)_2$ solution

The fast-exchange scattering law (equation (2)) was used to compare with the data in the first stage of the analysis. This model gave $\chi^2 = 149$ and did not describe the proton

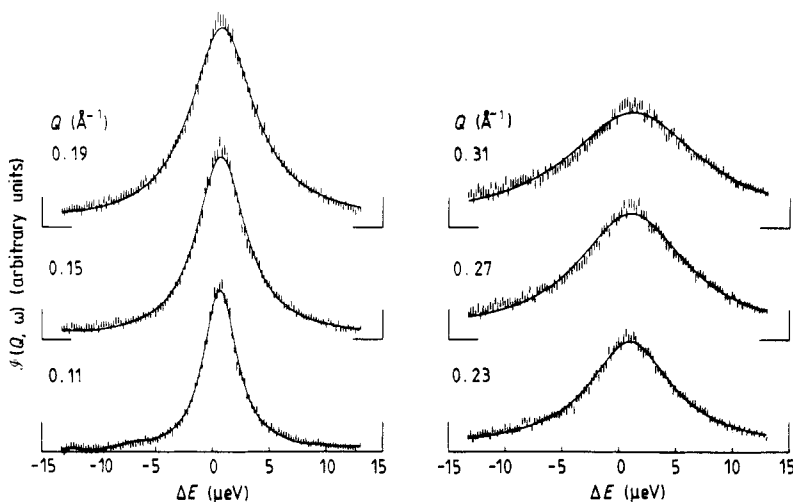


Figure 1. An attempt to fit the IQENS data for a 1.98 molal $\text{Zn}(\text{ClO}_4)_2$ solution using the single-Lorentzian scattering law for fast exchange (equation (2)): |||, statistical error on $I(Q, \omega)$; —, fitted function.

dynamics (figure 1); the fitted curves do not adequately fit the data in the region about $\Delta E = 0$ where the most significant differences between the fast- and intermediate- or slow-exchange scattering laws will occur (Salmon 1987). The Zn^{2+} -proton binding time is therefore described by the limit $\tau_1 > 10^{-10}$ s.

The slow-exchange scattering law (equation (3)) was used to compare with the data in the next stage of the analysis. D_2 was fitted and c_1 was fixed at a value of 0.2140, corresponding to $n_h = 6$. A hydration number of six water molecules for free Zn^{2+} ions, $\text{Zn}^{2+}(\text{aq})$, has been obtained from conventional x-ray diffraction experiments (Ohtaki *et al* 1976, Magini *et al* 1988), from anomalous x-ray scattering experiments (Matsubara and Waseda 1989), from Raman experiments (Kálmán *et al* 1983) and also from Monte Carlo simulations (Clementi *et al* 1980, Marchese and Beveridge 1986). Either D_1 was fixed at a value of $(0.47 \pm 0.02) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (figure 2) (which was estimated from the tracer diffusion measurements of Price *et al* (1990) for D_{Zn} in aqueous perchlorate solution at 25 °C and scaled to the temperature of the IQENS experiment by assuming an Arrhenius temperature dependence and an activation energy equal to that for pure water (Salmon *et al* 1987)), or it was fitted (figure 3).

The similarity between D_{ion} -values in $\text{Zn}(\text{ClO}_4)_2$, $\text{Ni}(\text{ClO}_4)_2$ and $\text{Cu}(\text{ClO}_4)_2$ solutions supports the interpretation of ClO_4^- as a non-inner-sphere complexing anion. At a concentration of 1.98 molal and 25 °C, $D_{\text{Zn}} = 0.436 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Price *et al* 1990), $D_{\text{Ni}} = 0.450 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{Cu}} = 0.441 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Salmon *et al* 1987).

The results are summarised in table 2. Both fits give improved χ^2 -values when compared with the single-Lorentzian fit given in figure 1. However, the \bar{D} -values are much less than the \bar{D} -value of $(1.52 \pm 0.04) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ which was obtained from the NMR spin-echo results of Price *et al* (1990) in aqueous $\text{Zn}(\text{ClO}_4)_2$ solution at 25 °C† by scaling for temperature in the same fashion as for D_{Zn} . This observation was not changed by fitting the IQENS data with n_h fixed at 6 and D_1 fixed either at a value of $0.9D_{\text{Zn}}$ or at

† The accuracy of these data is estimated at $\pm 2\%$ by comparison with tracer diffusion results.

Table 1. Experimental details of the solutions used for the IOENS experiments. The cross sections refer to the experimental wavelength of 6.271 Å.

Solute	Concentration (molal)	Temperature (°C)	Mass density (g cm ⁻³)	Water molecule number density (Å ⁻³)	Effective scattering cross section per water molecule (b)	Effective absorption cross section per water molecule (b)
Zn(ClO ₄) ₂	1.98(1)	28.0(5)	1.330	0.0292	200	11
	2.58(8)	26(2)	1.415	0.0281	201	13
ZnCl ₂	1.96(1)	28.6(6)	1.192	0.0314	199	11

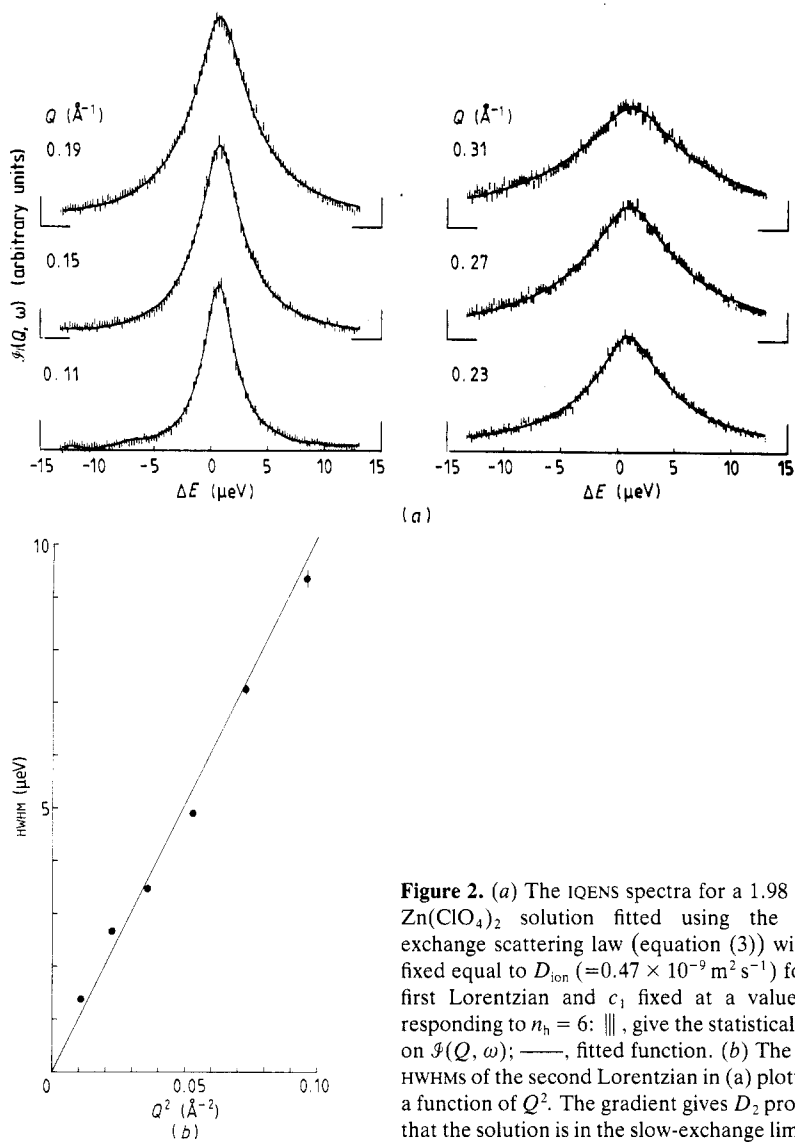


Figure 2. (a) The IQENS spectra for a 1.98 molal $Zn(ClO_4)_2$ solution fitted using the slow-exchange scattering law (equation (3)) with D_1 fixed equal to D_{ion} ($=0.47 \times 10^{-9} m^2 s^{-1}$) for the first Lorentzian and c_1 fixed at a value corresponding to $n_h = 6$; $\| \| \|$, give the statistical error on $\mathcal{I}(Q, \omega)$; —, fitted function. (b) The fitted HWHMs of the second Lorentzian in (a) plotted as a function of Q^2 . The gradient gives D_2 provided that the solution is in the slow-exchange limit.

1.1 D_{Zn} (table 2). A similar discrepancy between the \bar{D} -values also arises from fitting the data with $D_1 = D_{Zn}$ and c_1 fixed at a value corresponding to n_h in the range from 4 to 8 (table 2).

4.2. The 2.58 molal $Zn(ClO_4)_2$ solution

An initial comparison of the data with the fast-exchange scattering law gave $\bar{\chi}^2 = 203$ and showed that this model does not describe the proton dynamics (figure 4). Further comparisons were made using the slow-exchange scattering law with D_1 either set at a value of $0.37 \times 10^{-9} m^2 s^{-1}$ (estimated from the tracer diffusion results of Price *et al* (1990) for D_{Zn} as in section 4.1) or allowed to be fitted and with n_h fixed at values of 4,

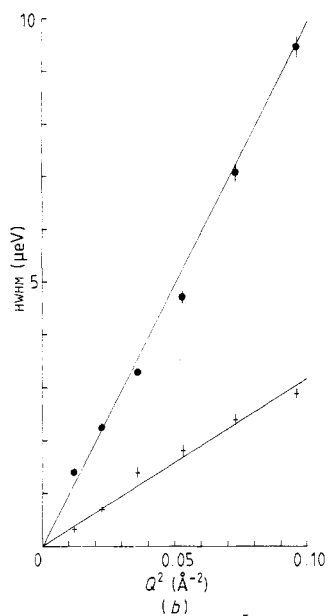
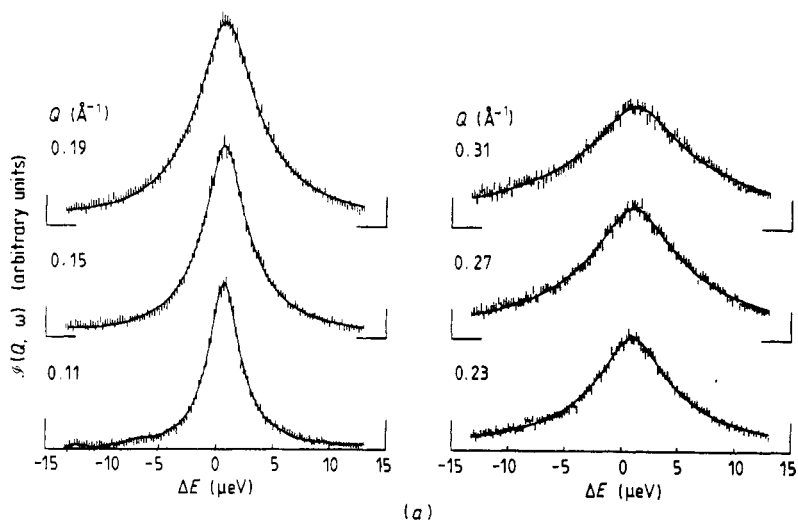


Figure 3. (a) The IQENS spectra for a 1.98 molal $\text{Zn}(\text{ClO}_4)_2$ solution fitted using the slow-exchange scattering law (equation (3)) with both D_1 for the first Lorentzian and D_2 for the second Lorentzian allowed to be variable parameters and where c_1 was fixed at a value corresponding to $n_h = 6$; $\|$, statistical error on $\mathcal{F}(Q, \omega)$; —, fitted function. (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 provided that the solution is in the slow-exchange limit.

6 or 8 (table 2). As for the less concentrated perchlorate solution the analyses gave \bar{D} -values that are significantly less than the average diffusion coefficient obtained from the NMR spin-echo results of Price *et al* (1990).

4.3. The ZnCl_2 solution

The data were first compared with the fast-exchange scattering law and a value of $\bar{D} = (1.39 \pm 0.05) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was obtained with $\bar{\chi}^2 = 161$ (figure 5). The measured diffusion coefficient compares with a value of $\bar{D} = (1.73 \pm 0.03) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ estimated

Table 2. The results obtained from fitting the IQENS data for $Zn(ClO_4)_2$ and $ZnCl_2$ aqueous solutions. In the analyses, c_1 was fixed and D_1 was treated as either a fixed or a fitted parameter. \bar{D} is the average diffusion coefficient of all water protons in solution and is obtained from the fitted spectra using equation (4). \bar{D}_{NMR} is the same quantity but is obtained from NMR measurements as described in section 4.

Solution	Concentration (molal)	T ($^{\circ}C$)	n_h	c_1	D_1	D_2	\bar{D}	$\bar{\chi}^2$	\bar{D}_{NMR}
$Zn(ClO_4)_2$	1.98	28.0(5)	4	0.1427	0.47 (fixed)	1.37(5)	1.24(5)	113	1.52(4)
			6	0.2140		1.54(6)	1.31(5)	111	
			8	0.2854		1.76(8)	1.26(6)	135	
			6	0.2140	0.49(2) (fitted)	1.52(7)	1.30(6)	108	
					0.42 (fixed)	1.59(7)	1.34(5)	118	
					0.52 (fixed)	1.50(6)	1.29(5)	110	
	2.58	26(2)	4	0.1859	0.37 (fixed)	1.05(1)	0.93(1)	167	1.24(8)
			6	0.2789		1.20(2)	0.96(1)	183	
			8	0.3718		1.37(2)	0.99(2)	259	
			6	0.2789	0.44(2) (fitted)	1.12(1)	0.93(1)	160	
$ZnCl_2$	1.96	28.6(6)	6	0.051	0.51 (fixed)	1.49(6)	1.44(5)	151	1.73(3)
			6	0.051	0.47 (fixed)	1.50(6)	1.44(6)	150	
			6	0.051	0.56 (fixed)	1.48(6)	1.43(6)	152	
			6	0.071	0.51 (fixed)	1.53(6)	1.46(6)	148	
			6	0.031	0.51 (fixed)	1.45(6)	1.42(6)	154	

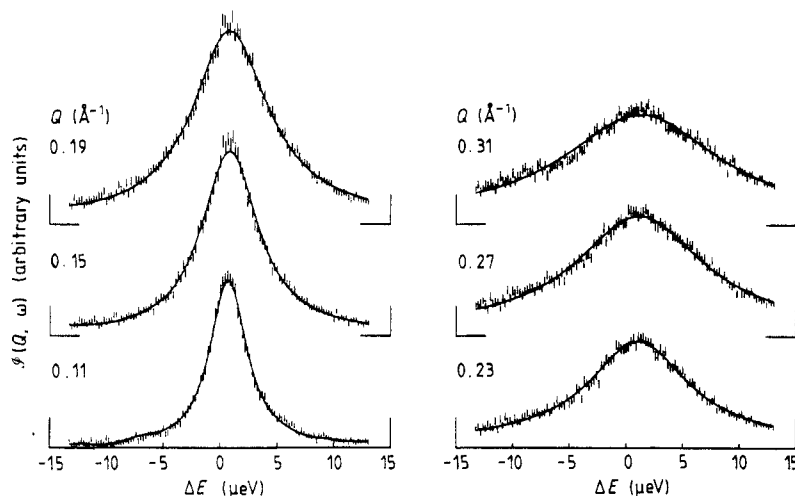


Figure 4. As for figure 1 but for a 2.58 molal $Zn(ClO_4)_2$ solution.

for the present solution from the NMR spin-echo values of Weingärtner *et al* (1984)[†] measured for $ZnCl_2$ aqueous solutions at 25 $^{\circ}C$ and scaled to the temperature of the IQENS experiment in the manner described in section 4.1. A single-proton population does not appear to describe the proton dynamics (also see section 5.1).

[†] The data of McCall and Douglas (1965) and Yagodarov and Khramov (1976) for \bar{D} were not used in this comparison because the data of Weingärtner *et al* (1984) is regarded as the more accurate at about $\pm 2\%$ (Mills and Lobo 1989).

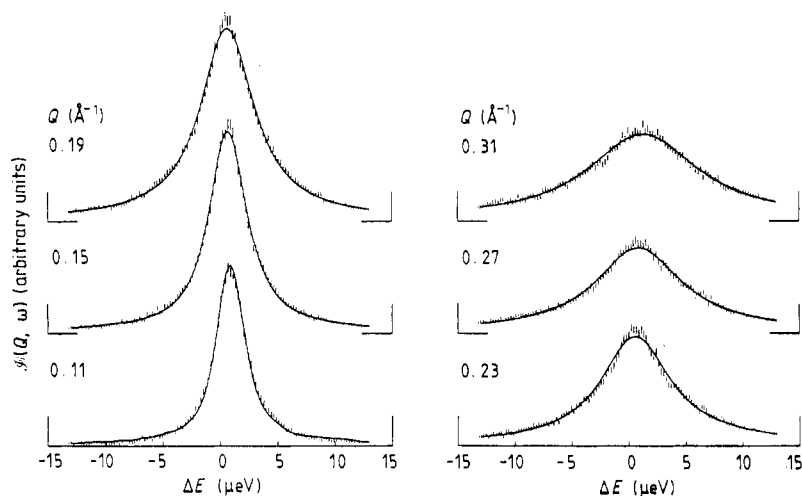
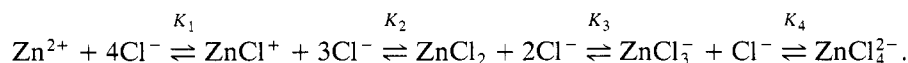


Figure 5. As for figure 1 but for a 1.96 molal ZnCl_2 solution.

An analysis using the slow-exchange scattering law with D_1 fixed at the value of $D_{\text{Zn}} = (0.66 \pm 0.02) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, obtained from the tracer diffusion results of Weingärtner *et al* (1984) for aqueous ZnCl_2 solutions, is not appropriate owing to the range of complex species present in the solution. D_{Zn} represents an *average* taken over all of the zinc species present whereas the observation of water protons in slow exchange will depend on the type of complex species to which the protons are bound.

In order to progress we recognise that, of the solutions so far studied using the IQENS technique, only those involving divalent or trivalent cations have been observed in intermediate or slow exchange (Salmon 1989b). It is therefore likely that those protons bound to the ZnCl^+ , ZnCl_2 and ZnCl_3^- species in the ZnCl_2 solution are in fast exchange on the IQENS observation time scale. Protons bound to ZnCl_4^{2-} species are also likely to be in fast exchange owing to the large size of the anion. Hence only that component of the proton population which is bound in the primary hydration sphere of free Zn^{2+} ions, $\text{Zn}^{2+}(\text{aq})$, will be taken to be in the slow-exchange limit on the IQENS observation time scale (i.e. only these protons will be identified with class 1 in the two-class model in section 2).

The concentration $[\text{Zn}^{2+}(\text{aq})]$ of $\text{Zn}^{2+}(\text{aq})$ is estimated from the stability constants K_i ($i = 1, 2, 3, 4$) that describe the reaction scheme



Owing to the lack of self-consistency between the published sets of K_i and the high ionic strength of the solution studied $[\text{Zn}^{2+}(\text{aq})]$ was evaluated for each available set of four K_i (Salmon 1989a) and a value of 0.45 ± 0.17 molar obtained. If a hexa-aquo complex for $\text{Zn}^{2+}(\text{aq})$ is assumed, then this $[\text{Zn}^{2+}(\text{aq})]$ gives $c_1 = 0.051 \pm 0.020$. A coordination number of six water molecules is found for free Zn^{2+} ions in solutions containing non-complexing anions (section 4.1) and a similar coordination number for $\text{Zn}^{2+}(\text{aq})$ is reported in solutions containing complexing (e.g. Cl^- , Br^-) anions (see, e.g., Irish *et al* 1963, Kálmán *et al* 1983, Goggin *et al* 1984).

D_{ion} for $Zn^{2+}(aq)$ in the $ZnCl_2$ solution is likely to be greater than D_{Zn} in a $Zn(ClO_4)_2$ solution of the same concentration and temperature since the solution viscosities are different. For instance, at 1.96 molal and 25 °C the shear viscosity of a $ZnCl_2$ solution (equal to 1.62 Pa s) is about 12% less than the shear viscosity of a $Zn(ClO_4)_2$ solution (equal to 1.84 Pa s) (Weingärtner *et al* 1984, Price *et al* 1990). D_{ion} for $Zn^{2+}(aq)$ in $ZnCl_2$ was therefore estimated by finding D_{Zn} in a $Zn(ClO_4)_2$ solution of viscosity 1.62 Pa s at 25 °C and the result was then scaled to the temperature of the IQENS experiment, in the way previously described, to give $D_{ion}(Zn^{2+}(aq) \text{ in } ZnCl_2) = 0.51 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This compares with a value of $D_{Zn}(1.96 \text{ molal } Zn(ClO_4)_2 \text{ at } 28.6 \text{ °C}) = 0.47 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ which was also used for analysis.

The results obtained using the above model for slow exchange with c_1 and D_1 fixed at various combinations are shown in table 2. The model gives a small improvement in $\bar{\chi}^2$ compared with the single-Lorentzian fit (figure 5) but the measured \bar{D} -values remain significantly (about 17%) less than the \bar{D} -value obtained from the Weingärtner *et al* (1984) measurements.

5. Discussion

5.1. The $Zn(ClO_4)_2$ solutions

The discrepancy between the IQENS and NMR \bar{D} -values given in table 2 is large and there is no agreement between the values even allowing for their combined estimated errors. This observation does *not* result from a neglect of anion effects since the anion species is common to the solutions used in both experiments. The discrepancy may result from an inaccurate multiple-scattering correction. However, a comparison of the \bar{D} -values obtained by Hewish *et al* (1983), who applied the IQENS method to a variety of solutions of *comparable thickness* to the 1.98 molal solution and who used the same basic analysis procedure, with the \bar{D} -values obtained from tracer diffusion and/or NMR spin-echo techniques shows that the present discrepancy is larger than previously obtained (see table 1 of Hewish *et al* (1983)). Furthermore, a large discrepancy is also observed for the 2.58 molal solution experiment wherein multiple-scattering effects are reduced. The $Zn(ClO_4)_2$ solutions may therefore be in intermediate exchange, i.e. $10^{-10} \text{ s} < \tau_1 < 5 \times 10^{-9} \text{ s}$. A direct comparison of the data with the general scattering law given by equation (1) is not, however, feasible owing to the complications given in section 2.

The lower-limit assignment of $\tau_1 > 10^{-10} \text{ s}$ is not effected by the sample multiple scattering (Salmon 1987). Our estimate of an upper limit of $\tau_1 < 5 \times 10^{-9} \text{ s}$ is not, however, in agreement with a previous value for the Zn^{2+} -water binding time of $\tau_w \approx 3 \times 10^{-8} \text{ s}$ at 25 °C obtained from sound absorption experiments (Hewkin and Prince 1970). Notwithstanding, Laurenczy *et al* (1989) have recently estimated limits of $1.7 \times 10^{-9} \text{ s} < \tau_w < 3.3 \times 10^{-8} \text{ s}$ at 25 °C, albeit through another indirect method involving a spectrophotometric study of the complex formation of 2-chloro-1,10-phenanthroline with Zn^{2+} in aqueous solution. This result is consistent with our estimation of the upper limit for τ_1 in aqueous $Zn(ClO_4)_2$ solution and the combined results give $1.7 \times 10^{-9} \text{ s} < \tau_w < 5 \times 10^{-9} \text{ s}$.

5.2. The $ZnCl_2$ solution

The data are consistent neither with a single-proton population nor with the two-state model of section 4.3 wherein protons bound to free $Zn^{2+}(aq)$ ions are assumed to be in

slow exchange on the IQENS observation time scale and the concentration of this species is taken from the sets of stability constants in the literature. A comparison of the χ^2 -values obtained from the models does, however, indicate that there is a component of the proton population in slow or intermediate exchange.

The existence of several types of zinc complex within the ZnCl_2 solution implies a range of dynamic environments for the water protons. The results for the $\text{Zn}(\text{ClO}_4)_2$ solutions also suggest that the binding time of water protons to $\text{Zn}^{2+}(\text{aq})$ has an intermediate character. It is therefore open to speculation, on the basis of the present data, as to whether the discrepancy between the IQENS and NMR spin-echo \bar{D} -values results from an intermediate character for water exchange at $\text{Zn}^{2+}(\text{aq})$ or from a range of dynamic environments for water protons on the IN10 observation time scale which renders the two-state description of the IQENS spectra (section 2) invalid. Further experiments are required to resolve this point, especially at lower concentrations than present where the fractional content of the $\text{Zn}^{2+}(\text{aq})$ species will be higher.

6. Conclusions

A lower limit of $\tau_1 > 10^{-10}$ s is established for the Zn^{2+} to water-proton binding time in aqueous $\text{Zn}(\text{ClO}_4)_2$ solution and an upper limit of $\tau_1 < 5 \times 10^{-9}$ s is estimated from a comparison of the IQENS spectra with various models describing slow exchange. The experiments demonstrate the power of the IQENS technique when applied to solutions where the ion to water-proton binding time is too fast to make it measurable by more traditional methods (see section 1). Information of this nature is important when trying to elucidate reaction mechanisms. For example, the formation of complexes by divalent metal ions is believed to take place according to the Eigen–Wilkins mechanism, wherein the rate-limiting step depends on the rate of water liberation from the metal ion (see, e.g., Laurency *et al* 1989, Tamura 1989).

The ZnCl_2 solution IQENS spectra are consistent with the presence of protons in slow or intermediate exchange but the dynamical model cannot be unambiguously identified. This reflects the complexity of water molecule environments when there is inner-sphere complexing in ionic solutions.

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