

A H, D, and ^{17}O Nuclear Magnetic Relaxation Study on the Structure and Dynamics of Water in Concentrated ZnCl_2

J. R. C. VAN DER MAAREL

*Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, Leiden University,
P.O. Box 9502, 2300 RA Leiden, The Netherlands*

Received February 4, 1988; revised April 18, 1988

The relaxation rates of D and ^{17}O and the rate of H due to dipolar coupling to ^{17}O were obtained in a series of 17.2 molal ZnCl_2 solutions. From these data conclusions are reached about the O-H bond distance, the D and ^{17}O quadrupole coupling constants, and the water reorientational dynamics. It is found that the O-H bond distance and quadrupole coupling constants are significantly changed with respect to the pure water values. Comparison of D and ^{17}O relaxation shows a reorientational anisotropy. Self-diffusion coefficients were determined by the NMR pulsed-field-gradient technique. The temperature dependences of the reorientational and translational motions are discussed. In the appendix the rotational contribution to the incoherent intermediate neutron scattering function is evaluated for anisotropic motion. © 1989 Academic Press, Inc.

In recent years the structure and dynamics in concentrated zinc halide solutions have attracted much attention. Many studies show inner shell Zn^{2+} -anion complexes in solution. In aqueous ZnCl_2 solutions ionic association is indicated by conductance, viscosity, tracer diffusion, and magnetic resonance experiments (1, 2). Unfortunately, a complete set of stability constants, which describes the behavior of all properties, could not be found. At saturation, the existence of zinc-anion extended polymeric structure is conjectured, due to the presence of tri- and tetrahedrally chloride-coordinated zinc (3). However, from a recent differential anomalous scattering (DAS) and extended X-ray absorption fine structure (EXAFS) study on ZnBr_2 solutions, the extent to which the ions form extended structures as compared to isolated complexes remains uncertain (4).

The water dynamics in concentrated ZnCl_2 solutions has been investigated by incoherent quasi-elastic neutron scattering (QENS) and nuclear magnetic resonance. The quasi-elastic spectrum consists of two components. The broad and narrow components can be associated with the reorientational and translational motion of the water molecule, respectively (5). Proton spin-lattice relaxation times and self-diffusion in concentrated ZnCl_2 have been investigated by Nakamura *et al.* (6). However, an unambiguous interpretation of the H relaxation is complicated because the contributions of the inter- and intramolecular dipolar interactions are estimated to be on the same order of magnitude and difficult to separate. Therefore, the value of the reorientational correlation time obtained by H relaxation is very sensitive to the correctness of the theoretically estimated intermolecular contribution.

In this study, the H- ^{17}O dipolar interaction contribution to the H relaxation in

^{17}O -enriched solutions is explored. This relaxation mechanism is nearly completely intramolecularly determined, due to the small O–H bond distance (7–9). Combination of this relaxation path with D and ^{17}O quadrupolar relaxation yields much more reliable values of the correlation times and interaction constants (i.e., the O–H bond distance and the field gradients at the D and ^{17}O nuclei). A possible motional anisotropy may be investigated due to the fact that the interaction tensors do not coincide (10). This method has been previously applied to investigate the hydration water properties in solutions of monovalent ions (11), Mg^{2+} (9, 12), and Al^{3+} (13).

THEORY

The nuclear relaxation rate can be expressed in terms of an interaction constant and a correlation time. Because the water reorientation occurs on the time scale of picoseconds, the extreme narrowing condition is fulfilled. The D and ^{17}O relaxation are determined intramolecularly by the quadrupolar interaction. The rates are

$$R_D = \frac{3}{8} (2\pi\chi_D)^2 (1 + \eta_D^2/3) \tau_D \quad [1]$$

for the D nucleus, and, for ^{17}O ,

$$R_O = \frac{3}{125} (2\pi\chi_O)^2 (1 + \eta_O^2/3) \tau_O \quad [2]$$

in which χ_D and χ_O denote the D and ^{17}O quadrupole coupling constants, respectively. The asymmetry parameters of the D and ^{17}O field gradient are η_D and η_O , respectively. The intramolecular part of the H– ^{17}O dipolar interaction contribution to the H relaxation rate is given by

$$R_{\text{OH}}^{\text{intra}} = \frac{35}{3} (\gamma_H^2 \gamma_{^{17}\text{O}}^2 \hbar^2) / r_{\text{OH}}^6 \tau_{\text{OH}} \quad [3]$$

in which r_{OH} is the O–H bond distance.

The correlation times τ_D , τ_O , and τ_{OH} are the time integrals of the correlation functions of the interaction tensors. Because the relaxation processes are intramolecularly determined, these correlation times refer to reorientational dynamics only. Because the principal directions of the interaction tensors of D and ^{17}O do not coincide, the symmetry of the motion may be investigated (10).

To describe the water reorientational motion an internal diffusion model will be applied. The dynamics is represented by an element D_i for rotation about an internal diffusion axis, in combination with an isotropic overall diffusion process, D_{ov} . The internal rotation axis may be taken along the direction of the Zn^{2+} – OH_2 interaction. Under extreme narrowing conditions the correlation times are given by (14)

$$\tau_x = \frac{1}{2} \frac{\sum_k V_k^{(2)} V_l^{(2)*} \mathbf{D}_{km}^{(2)}(\Omega_x) \mathbf{D}_{lm}^{(2)*}(\Omega_x) \tau_m}{\sum_k |V_k^{(2)}|^2} \quad [4]$$

with

$$\tau_m = 6D_{\text{ov}} + m^2 D_i. \quad [5]$$

The Wigner matrix $\mathbf{D}^{(2)}$ describes the transformation of the principal-axis system of the interaction tensor to the axis system which is fixed to the internal rotation axis. The orientation of the internal diffusion axis is characterized by the angles α and β , as displayed in Fig. 1. The lattice part of the coupling Hamiltonian is given by the second-order spherical tensor elements $V_k^{(2)}$. In the principal-axis system of the dipolar interaction, one has $V_k^{(2)} = \delta_{0k}(2/3)^{1/2}r_{\text{OH}}^{-3}$. In the principal-axis system of the quadrupolar interaction these elements are defined as $V_0^{(2)} = (3/2)^{1/2}eq$, $V_{\pm 1}^{(2)} = 0$, and $V_{\pm 2}^{(2)} = -\eta/2eq$, with the asymmetry parameter η defined as $\eta = (V_{yy} - V_{xx})/V_{zz}$ (14).

However, to evaluate the dynamical properties, the coupling constants χ_{D} , χ_{O} , and r_{OH} should be known. This problem may be solved due to the fact that the correlation times for D quadrupolar and intramolecular H- ^{17}O dipolar relaxation are approximately equal, irrespective of the details of the motion. The basis of this reasoning is as follows. The principal axis of the H- ^{17}O dipolar interaction tensor coincides with the principal axis of the D quadrupolar interaction tensor. The D field gradient is nearly axially symmetric ($\eta_{\text{D}} = 0.135$, gas value). Hence, the $V_{\pm 2}^{(2)}$ D field gradient components are very small with respect to the main $V_0^{(2)}$ component. These two features combined lead to an approximate equality of the effective correlation times for these relaxation mechanisms. For isotropic reorientation this equality holds within 0.6%, as found in pure water (9). This equality is exact when the asymmetry parameter of the D field gradient is neglected. One must take into account a D solute isotope effect, which will be discussed below.

Ab initio calculations show the main factor determining the D field gradient to be the O-D bond length, while the dependence on bond angle is of minor importance (15). A semiempirical connection between χ_{D} and r_{OH} was proposed (9):

$$\chi_{\text{D}} = \frac{595 \pm 11}{r_{\text{OH}}^3} - (390 \pm 9)r_{\text{OH}}. \quad [6]$$

This relation reproduces experimental data and theoretical results well. A small difference in O-H and O-D bond length has been neglected. From the equality of τ_{D} and τ_{OH} and Eqs. [1], [3], and [6] one can obtain χ_{D} , r_{OH} , and $\tau_{\text{D}} (\simeq \tau_{\text{OH}})$.

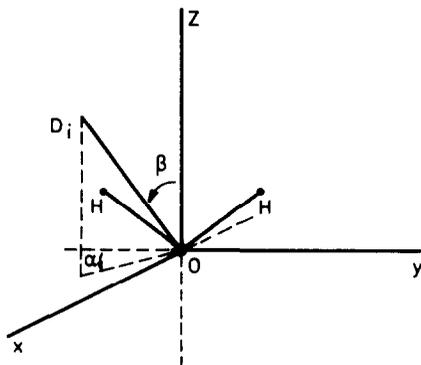


FIG. 1. Definition of the orientation of the internal diffusion axis with respect to the molecular frame, characterized by the angles α and β . The water molecule is positioned in the ZY plane.

For the ^{17}O quadrupole coupling constant a similar procedure is not possible. However, Poplett observed a correlation between χ_{O} and χ_{D} for crystal hydrates, different forms of ice, and water vapor from solid-state NQR (16)

$$\chi_{\text{O}} = (38.214 \pm 1.293)\chi_{\text{D}} - (1650 \pm 302) \text{ (kHz)}. \quad [7]$$

The ^{17}O quadrupole coupling constant will be obtained by inserting χ_{D} into this relation. The ^{17}O coupling constant of pure water, obtained by ^{17}O -enhanced H relaxation by applying this relation, compares favorably with a recent ab initio calculation by Cummins *et al.* (8, 9, 17).

EXPERIMENTAL

Water isotopically enriched in oxygen was obtained from Monsanto Research Corp., Miamisburg, containing 9.9% O-16, 51.1% O-17, and 39.0% O-18. D_2O was obtained from E. Merck, Darmstadt. Distilled water was deionized and filtered by a Milli-Q water purification system (Millipore Corp.). ZnCl_2 , gold label quality, originated from Aldrich.

Solutions were prepared by weight in a cold room at 278 K to minimize exchange with atmospheric humidity. NMR tubes (Wilmad, 5 mm and homemade, quartz) were heated in a NaHCO_3 solution, heated in an EDTA solution, and then stored for at least 1 week with deionized and filtered water. Solutions were acidified with a drop of HCl to avoid hydrolysis. To remove gaseous oxygen, the solutions were shaken five times with argon. Zinc and chloride concentrations and isotopic compositions of the samples are collected in Table 1.

NMR experiments were performed on a homebuilt spectrometer equipped with a 2.1 T electromagnet (Bruker). The magnetic field was locked with an external probe, using the F resonance in trifluoroacetic acid doped with copper acetate. During field gradient pulses the lock was disabled. The temperature was maintained within ± 0.2 K by a fluid thermostat using Fluorinert FC-43 (3M Co.).

T_1 measurements were obtained, at least in duplicate, by the inversion-recovery method with an estimated reproducibility of 2%. FIDs were accumulated with a LSI-

TABLE 1
Concentrations and Isotopic Composition of ZnCl_2 Solutions^a

Sample	Molality		<i>n</i>	<i>p</i> 17	<i>p</i> 18
	Zn^{2+}	Cl^-			
a	17.2	35.3	0.0465	—	—
b	17.3	36.6	—	0.164	0.125
c	17.2	35.0	—	0.226	0.171
d	17.2	35.1	—	0.329	0.252
e	17.3	35.2	—	0.489	0.373

^a *n*, *p*17, and *p*18 denote the D, ^{17}O , and ^{18}O mol fraction, respectively. An isotope fraction denoted by (—) means natural abundance (i.e., $n_{\text{nat}} = 0.156 \times 10^{-3}$, $(p17)_{\text{nat}} = 0.37 \times 10^{-3}$, $(p18)_{\text{nat}} = 2.04 \times 10^{-3}$).

11 microcomputer, while the relative phase of the π and $\pi/2$ pulses was alternated (18). One hundred data points were collected and fitted to a single exponential. No field dependence of relaxation rates has been observed. Isotope effects on the relaxation rates were corrected as described before (11).

Water self-diffusion coefficients were determined by the NMR pulsed-field-gradient technique with a steady background gradient (19). Diffusion coefficients are based on a calibration using pure water as a reference with a value of $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K. The magnitude of the steady gradient was typically 0.8 G cm^{-1} , and the magnitude of the pulsed gradient was in the range $60\text{--}300 \text{ G cm}^{-1}$. The diffusion time between gradient pulses was 13 ms. Results are collected in Tables 2 and 3.

RESULTS AND DISCUSSION

Interaction constants. To discuss the correlation times, it is necessary to know the interaction constants. To this end, the contribution of the H- ^{17}O dipolar interaction to the H relaxation was determined experimentally and compared with the D relaxation rate. Proton relaxation rates in 17.2 molal ZnCl_2 solutions are displayed in Fig. 2 vs the oxygen-17 mole fraction. This concentration corresponds to 3.2 water molecules per cation. In view of the observed linearity, one has

$$R_{\text{H}} = R_{\text{HH}} + p^{17}R_{\text{OH}} \quad [8]$$

in which R_{HH} and R_{OH} denote, respectively, the H-H and H- ^{17}O dipolar interaction contribution to the H relaxation. Values of R_{HH} and R_{OH} , obtained from the fit of Eq. [8] to the data displayed in Fig. 2, are collected in Table 3. The D and ^{17}O relaxation rates, respectively R_{D} and R_{O} , are also shown in Table 3.

The intermolecular contribution to R_{OH} is unknown, but is taken to be 2% of the total H- ^{17}O dipolar interaction contribution, as it is in pure water (7). As discussed above, the correlation times for intramolecular H- ^{17}O dipolar and D quadrupolar relaxation, τ_{OH} and τ_{D} , respectively, must be nearly equal. However, the D solute isotope effect on the reorientational correlation time due to the molecular species involved must be taken into account. In concentrated ZnCl_2 this effect is unknown, but is taken to be the same as in pure water (7). One has

$$\tau_{\text{D}}(\text{HDO}) = (1.05 \pm 0.02)\tau_{\text{OH}}(\text{H}_2\text{O}), \quad [9]$$

TABLE 2
Proton Relaxation Rates Corrected for Oxygen Isotope Viscosity Effects

Sample	$R_{\text{H}}, \text{ s}^{-1}$				
	283 K	293 K	298 K	303 K	313 K
a	3.40	2.29	1.94	1.63	1.17
b	3.77	2.50	2.18	1.82	1.33
c	4.03	2.73	2.23	2.01	1.44
d	4.49	3.04	2.57	2.16	1.56
e	5.01	3.40	2.89	2.41	1.74

TABLE 3

Self-Diffusion Coefficients and Relaxation Rates in 17.2 Molal ZnCl₂ Corrected for Isotope Effects

T, K	R_D, s^{-1}	R_O, s^{-1}	R_{HH}, s^{-1}	R_{OH}, s^{-1}	$D_H, 10^{-9} m^2 s^{-1}$
283	16.9	1880	3.32	3.40	0.0742
293	11.3	1190	2.22	2.37	0.114
298	9.37	985	1.88	2.00	0.136
303	7.82	790	1.61	1.64	0.163
313	5.64	546	1.16	1.18	0.228

where the molecular species involved is given between parentheses. It was checked that small variations in the intermolecular H-¹⁷O interaction contribution and the D solute isotope effect do not significantly affect the results described below.

Values of the O-H bond distance and the D coupling constant, obtained by inserting the intramolecular H-¹⁷O and D relaxation rates into Eqs. [1] and [3], respectively, and applying Eqs. [6] and [9], are presented in Table 4. The ¹⁷O quadrupole coupling constant, obtained by inserting χ_D into Poplett's relation, Eq. [7], are also presented in Table 4. No temperature dependence between 283 and 313 K is observed. The average values are $\langle r_{OH} \rangle = 1.005 \pm 0.010 \text{ \AA}$, $\langle \chi_D \rangle = 194 \pm 6 \text{ kHz}$, and $\langle \chi_O \rangle = 5.8 \pm 0.4 \text{ MHz}$. In pure water, the corresponding values are $r_{OH} = 0.98 \text{ \AA}$, $\chi_D = 253 \text{ kHz}$, and $\chi_O = 8.0 \text{ MHz}$ (8, 9). These values are also independent of temperature (9). In concentrated ZnCl₂ solutions, the interaction constants are significantly changed with respect to the pure water values.

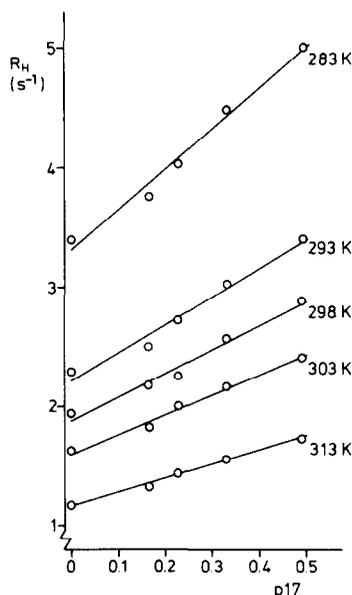


FIG. 2. Proton longitudinal relaxation rates, corrected for oxygen isotope viscosity effects (Ref. (11)), as a function of the ¹⁷O mol fraction in 17.2 molal ZnCl₂ solutions. The lines are drawn according to linear least-squares fits of Eq. [8].

In this evaluation no decomposition has been made with respect to possible additional classes of water in solution. If there exist several classes of water, the relaxation rates and derived properties should be interpreted as effective average quantities. This in contrast to the situation in more dilute electrolyte solutions, where the relaxation rates are usually decomposed into the contributions of hydration water and bulk water (11). However, it is interesting to compare the derived results with the hydration water properties of, e.g., Mg^{2+} . The crystal ionic radius of Zn^{2+} (0.74 Å) is comparable to the value of Mg^{2+} (0.66 Å).

The Mg^{2+} hydration water values are $r_{\text{OH}} = 1.005$ Å, $\chi_{\text{D}} = 193$ kHz, and $\chi_{\text{O}} = 5.7$ MHz, if the solute effect on reorientational motion beyond the hydration is assumed to be equal to the effect on self-diffusion (12). No temperature and concentration dependence of the interaction constants have been observed. The equality of the solute effect on the bulk water translational and reorientational motion was confirmed in aqueous AlCl_3 solutions (20). The values of the interaction constants in concentrated ZnCl_2 solutions are exactly the same as the values of Mg^{2+} hydration water, although the surface electric field intensity of Zn^{2+} is somewhat lower than the value of Mg^{2+} ($z/r_{\text{ion}}^2 = 3.65$ Å⁻² vs 4.59 Å⁻²). A correlation between the O-H bond distance and the surface electric field intensity was observed (13). Accordingly, the O-H bond distance of water coordinated to Zn^{2+} is expected to be somewhat shorter compared to the Mg^{2+} hydration water value. However, a possible explanation of the equality of the interaction constants may be simultaneous sharing of water molecules by Zn^{2+} and Cl^- .

Reorientational dynamics. Values of the reorientational correlation times, obtained by inserting the experimental D and ¹⁷O relaxation rates into Eqs. [1] and [2], respectively, and using the estimated quadrupole coupling constants, are presented in Table 4. As described in the theoretical section, the D field gradient is nearly axially symmetric. Accordingly, the corresponding asymmetry parameter, η_{D} , is negligible. For the evaluation of the ¹⁷O reorientational correlation time, the ice-phase value of the ¹⁷O asymmetry parameter has been used ($\eta_{\text{O}} = 0.93$). From the correlation times it is concluded that the water reorientation occurs on the picosecond time scale, in the temperature range studied.

Proton NMR experiments by Nakamura *et al.* show similar reorientational correlation times, although the intermolecular contribution to the H relaxation has been

TABLE 4

Interaction Constants and Reorientational Correlation Times for Water in 17.2 Molal ZnCl_2^a

T , K	r_{OH} , Å	χ_{D} , kHz	χ_{O} , MHz	$\tau_{\text{D}} = (1.05\tau_{\text{OH}})$, ps	τ_{O} , ps
283	1.003	199	5.9	28.7	43.6
293	1.006	193	5.7	20.4	29.8
298	1.006	191	5.7	17.3	25.2
303	1.005	193	5.7	14.1	19.7
313	1.005	194	5.8	10.1	13.5

^a The estimated errors in r_{OH} , χ_{D} , χ_{O} , τ_{D} , and τ_{O} are, respectively, 1, 3, 7, 6, and 14%. In pure water, one has $r_{\text{OH}} = 0.98$ Å, $\chi_{\text{D}} = 253$ kHz, and $\chi_{\text{O}} = 8.0$ MHz (8, 9).

estimated theoretically (6). The D and ^{17}O correlation times roughly agree with the reorientational correlation time extracted from the broad component of the incoherent QENS spectra ($\tau_{\text{QENS}} = 22$ ps (3)). The neutron scattering spectra are analyzed using an isotropic diffusion model. However, the differences between the D and the ^{17}O correlation times are significant and have equal signs, for all temperatures studied. This indicates anisotropic reorientation. In consequence, the NMR results are not simply comparable to the neutron scattering value. In the appendix the correlation function governing the rotational contribution to the incoherent intermediate scattering function is evaluated for anisotropic motion. It is shown that the H- ^{17}O intramolecular dipolar interaction correlation time is proportional to the $l = 2$ term in the expansion due to Sears (21). To interpret the correlation times, a dynamical model must be introduced at this stage of data analysis.

The reorientational dynamics will be described by an internal diffusion model, as detailed in the theoretical section. This model has the advantage of a limited number of parameters, the angles α and β which characterize the orientation of the internal diffusion axis with respect to the molecular frame (Fig. 1), and the two diffusion components D_{ov} and D_i . From the two correlation times τ_D and τ_O one can calculate the diffusion elements D_i and D_{ov} for a judiciously chosen orientation of the internal diffusion axis.

In simple electrolyte solutions the influence of Cl^- on the water dynamics is negligible and cannot account for the observed effect (11). In a $3\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ crystal two-thirds of the Zn^{2+} ions are tetrahedrally coordinated by four chloride ions. The remaining third are octahedrally coordinated by four water molecules and two chloride ions (22). In the 17.2 molal solution, the Zn^{2+} coordination may be similar. In this case, the ratio of octahedral to tetrahedral complexes is 0.8 to 0.2. Hence, the spatial orientation of all 3.2 water molecules with respect to Zn^{2+} is conjectured to be similar to the arrangement of water molecules in a cation-water complex. Theoretical considerations (23), MD results (24), and neutron scattering pair correlation functions (25) suggest that the interaction of water molecules and cations is symmetrical with respect to the plane perpendicular to the molecular plane and containing the bisectrix of the H_2O bond angle. For a coherent interpretation of the pair correlation functions and the NMR results it is assumed that the internal rotation axis is confined to this plane of the water molecule (i.e., $\alpha = 90^\circ$ in Fig. 1), leaving only the angle β an adjustable parameter.

The diffusion correlation times $\tau_{\text{ov}} (=1/6D_{\text{ov}})$ and $\tau_i (=1/6D_i)$, calculated from the experimental D and ^{17}O correlation times τ_D and τ_O , are displayed in Fig. 3 as a function of the angle β ($T = 298$ K). The values of τ_{ov} and τ_i depend strongly on the value of the angle β . At $T = 298$ K, the solutions are $4 \text{ ps} < \tau_i < 20 \text{ ps}$ and $270 \text{ ps} > \tau_{\text{ov}} > 25 \text{ ps}$, with the angle β in the range $30^\circ < \beta < 55^\circ$. From the symmetry of cation-water interaction, it is reasonable to choose the D_i orientation coincident with the electric field of the Zn^{2+} ion. Thus the angle β characterizes the orientation of the water molecule with respect to the cation. The hydration water molecule may form hydrogen bonds with surrounding water molecules, if the angle β increases to 55° . The correlation time τ_{ov} represents the overall motion of the $\text{Zn}^{2+}\text{-OH}_2$ axis. In the calculation, this correlation time diverges if β approaches the limiting value 30° . However, this orientation is inconsistent with the neutron scattering ion-water pair correlation functions. For Cu^{2+} and Ni^{2+} hydration water, neutron scattering pair correla-

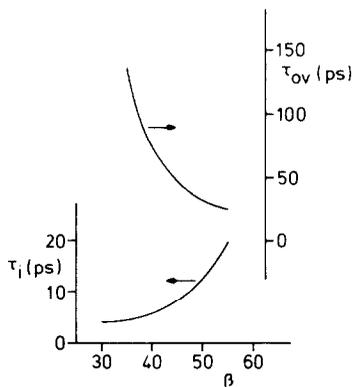


FIG. 3. Water reorientation correlation times as a function of the angle β , $\alpha = 90^\circ$. Upper curve, τ_{ov} ($=1/6D_{ov}$); lower curve, τ_i ($=1/6D_i$). $T = 298$ K.

tion functions show the tilting angle between the cation–oxygen axis and the axis bisecting the water plane to be on the order of 40° (25). For $\beta = 40^\circ$, one has $\tau_i = 5.5$ ps and $\tau_{ov} = 75$ ps. The relatively low value of the overall reorientational correlation time does not support the existence of polymeric structures in solution.

Figure 4 shows the temperature dependence of τ_i and τ_{ov} for $\alpha = 90^\circ$ and $\beta = 40^\circ$. Arrhenius behavior is observed. The activation energy of the overall diffusion process equals 36 ± 2 kJ/mol and does not depend on the value of the angle β . The activation energy of the internal diffusion process ranges from 10 to 25 kJ/mol for β in the range $30^\circ < \beta < 55^\circ$ (20 kJ/mol for $\beta = 40^\circ$). The activation energy of the overall reorientational motion is comparable to the activation energy of the macroscopic viscosity (35 kJ/mol (6)). This may indicate a concurrent structural rearrangement of the surrounding medium for the latter type of motion. For the internal reorientational motion this effect is probably less important, as judged from the relatively lower value of the corresponding activation energy.

As mentioned earlier, the experimental rates may include an average over more fast exchanging dynamical classes of water, e.g., regions near cations and water not

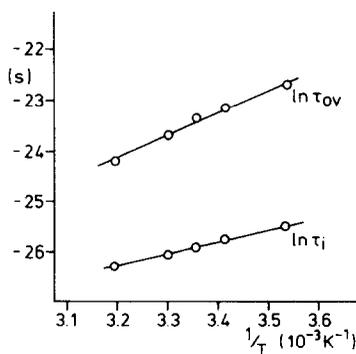


FIG. 4. Plots of $\ln \tau_{ov}$ and $\ln \tau_i$ vs $1/T$ for water in 17.2 molal ZnCl_2 . The orientation of the internal diffusion axis is characterized by $\alpha = 90^\circ$, $\beta = 40^\circ$. The lines are drawn according to linear least-squares fits.

directly coordinated to Zn^{2+} . In this case the observed anisotropy is not characteristic for Zn^{2+} hydration water.

Translational dynamics. Water self-diffusion coefficients D_{H} are presented in Table 3. In 17.2 molal ZnCl_2 at 298 K, the self-diffusion is a factor 17 smaller compared to the pure water value ($D_{\text{H}} = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). There is agreement with the results obtained by Nakamura *et al.* (6). However, at 298 K the self-diffusion coefficient is lower compared to the QENS result ($D_{\text{H}} = 0.41 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) (3). The water self-diffusion coefficient, as well as the overall reorientational correlation time, are not proportional to the macroscopic viscosity of the solution ($\eta = 41 \text{ cP}$ (6)). This has also been observed in other electrolyte solutions such as AlCl_3 (20).

Figure 5 shows the temperature dependence of the self-diffusion coefficient. Arrhenius behavior is observed. The self-diffusion activation energy equals 27 kJ/mol. Nakamura *et al.* reported an activation energy of 31 kJ/mol (6), in reasonable agreement with the former value. The activation energy of the translational motion is somewhat lower than the activation energy of the overall reorientational motion. However, one must consider the difference in time scales involved. The overall reorientational diffusion correlation times refer to the picosecond time scale, while the self-diffusion constants describe the translational motion on the millisecond time scale.

CONCLUSIONS

Comparison of the H relaxation due to dipolar coupling to ^{17}O and D relaxation shows an increase of the O–H bond length of water in concentrated ZnCl_2 . D and ^{17}O relaxation show anisotropic reorientational motion, which was interpreted by an axially symmetric diffusion model. The internal diffusion axis may consistently be taken to lie in the bisectric plane of the water molecule, in accordance with the spatial orientation of water molecules near cations as shown by neutron scattering pair correlation functions. The correlation times show a fast reorientation of the water molecule about the cation–water axis. The overall correlation time of this axis is on the order of 75 ps. Therefore, the conjecture of extended structures could not be confirmed. A comparison of the activation energies for the different motional processes shows the energy for the overall reorientational motion to be higher than the energy for translational motion. The activation energy of the internal diffusion process has the smallest values, but depends on the actual choice of the angle β .

APPENDIX

Rotational Incoherent Neutron Scattering Function for Anisotropic Motion

The relevant correlation function governing the rotational contribution to the incoherent intermediate scattering function is given by (21)

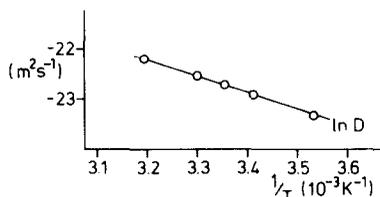


FIG. 5. As in Fig. 4, but for $\ln D_{\text{H}}$.

$$\chi(\bar{\kappa}, t) = \frac{1}{2} \sum_{\nu=1}^2 \langle e^{-i\bar{\kappa} \cdot \bar{r}_{\nu}(0)} e^{i\bar{\kappa} \cdot \bar{r}_{\nu}(t)} \rangle \quad [\text{A1}]$$

in which \bar{r}_{ν} denotes the H position relative to the center of mass of the water molecule. The momentum transfer is denoted by $\bar{\kappa}$. Applying the Rayleigh expansion and transforming to the principal-axis system of \bar{r}_{ν} , one obtains (26)

$$\chi(\bar{\kappa}, t) = \underbrace{\sum_{l=0}^{\infty} (2l+1)^2 j_l^2(\kappa r)}_{\text{A}} \times \underbrace{\sum_{m', m=-l}^l \frac{1}{2} (\mathbf{D}_{0m}^{(l)}(\Omega_{\text{H}}) \mathbf{D}_{0m'}^{(l)*}(\Omega_{\text{H}}) + \mathbf{D}_{0m}^{(l)}(\Omega_{\text{H}'}) \mathbf{D}_{0m'}^{(l)*}(\Omega_{\text{H}'})) \langle \mathbf{D}_{m0}^{(l)}(\Omega(0)) \mathbf{D}_{m'0}^{(l)*}(\Omega(t)) \rangle}_{\text{B}}. \quad [\text{A2}]$$

The transformation of the principal-axis system of \bar{r}_{ν} to the molecule-fixed principal-axis system of the diffusion tensor is characterized by the Euler angles Ω_{H} and $\Omega_{\text{H}'}$, for the two proton positions. The Euler angle $\Omega(t)$ characterizes the time-dependent transformation of the principal-axis system of the diffusion tensor to the laboratory system.

The center of mass nearly coincides with the position of the oxygen nucleus. Therefore, the principal axis of the H-¹⁷O intramolecular dipolar interaction tensor nearly coincides with the \bar{r}_{ν} vector. Accordingly, the time integral of the $l = 2$ term of the B component in expansion [A2] nearly equals the intramolecular H-¹⁷O dipolar interaction correlation time. This equality holds irrespective of the details of the motion.

The correlation function $\langle \mathbf{D}_{m0}^{(l)}(\Omega(0)) \mathbf{D}_{m'0}^{(l)*}(\Omega(t)) \rangle$ may be evaluated for different types of motion (14). For isotropic diffusion, one obtains

$$\langle \mathbf{D}_{m0}^{(l)}(\Omega(0)) \mathbf{D}_{m'0}^{(l)*}(\Omega(t)) \rangle = \frac{\delta_{mm'}}{2l+1} e^{-l(l+1)Dt} \quad [\text{A3}]$$

in which D denotes the reorientational diffusion constant. The correlation function is independent of m . For axially symmetric anisotropic diffusion, one has

$$\langle \mathbf{D}_{m0}^{(l)}(\Omega(0)) \mathbf{D}_{m'0}^{(l)*}(\Omega(t)) \rangle = \frac{\delta_{mm'}}{2l+1} e^{-(\mathbf{D}_{\perp}(l(l+1)+m^2(\mathbf{D}_{\parallel}-\mathbf{D}_{\perp}))t)}. \quad [\text{A4}]$$

The internal diffusion model is mathematically equivalent to the axially symmetric anisotropic diffusion model, but with $\mathbf{D}_{\text{ov}} = \mathbf{D}_{\perp}$ and $\mathbf{D}_{\text{i}} = \mathbf{D}_{\parallel} - \mathbf{D}_{\perp}$ (27). For the general anisotropic diffusion model the correlation function is discussed in Ref. (14) (for $l = 1, 2$).

In the experimental analysis of QENS spectra, one usually assumes a decoupling of translational and rotational motion. Terms of order $l > 2$ are also neglected. Additionally, for anisotropic motion, each l term in expansion [A2] is multiexponential. This renders it difficult to detect anisotropy by the QENS method. However, using NMR data to evaluate QENS spectra may be helpful to establish the former assumptions.

ACKNOWLEDGMENTS

Dr. M. C. Bellissent-Funel is thanked for initiating discussions during my stay at C.E.N. de Saclay. I thank Professor Dr. J. C. Leyte for many stimulating discussions during the course of this work.

Note added in proof. Recently, more extended QENS results were analysed using an uniaxial diffusion model. The slow overall correlation time has not been detected due to the limited resolution of the spectrometer. The correlation time representing the internal motion is of the order 1 ps and, hence, is smaller than the NMR value. (M.-C. Bellissent-Funel, A. J. Dianoux, M. P. Fontana, G. Maisano, and P. Migliardo, *Physica B*, in press.

REFERENCES

1. H. WEINGÄRTNER, K. J. MÜLLER, H. G. HERTZ, A. V. J. EDGE, AND R. MILLS, *J. Phys. Chem.* **88**, 2173 (1984).
2. H. G. HERTZ, "The Chemical Physics of Solvation" (Dogonadze, Kálmán, Kornyshev, and Ulstrup, Eds.), Part B, p. 311, Elsevier, Amsterdam, 1986.
3. M.-C. BELLISSENT-FUNEL, A. J. DIANOUX, M. P. FONTANA, G. MAISONA, AND P. MIGLIARDO, "Water and Aqueous Solutions" (G. W. Neilson and J. E. Enderby, Eds.), p. 199, Adam Hilger, Bristol, 1986.
4. K. F. LUDWIG, JR., W. K. WARBURTON, AND A. FONTAINE, *J. Chem. Phys.* **87**, 620 (1987).
5. J. TEIXEIRA, M.-C. BELLISSENT-FUNEL, S. H. CHEN, AND A. J. DIANOUX, *Phys. Rev. A* **31**, 1913 (1985).
6. Y. NAKAMURA, S. SHIMOKAWA, K. FUTAMATA, AND M. SHIMOJI, *J. Chem. Phys.* **77**, 3258 (1982).
7. D. LANKHORST, J. SCHRIEVER, AND J. C. LEYTE, *Ber. Bunsenges. Phys. Chem.* **86**, 215 (1982).
8. J. R. C. VAN DER MAAREL, D. LANKHORST, J. DE BLEUSER, AND J. C. LEYTE, *Chem. Phys. Lett.* **122**, 541 (1985).
9. R. P. W. J. STRUIS, J. DE BLEUSER, AND J. C. LEYTE, *J. Phys. Chem.* **91**, 1639 (1987).
10. C. W. R. MULDER, J. SCHRIEVER, AND J. C. LEYTE, *J. Phys. Chem.* **87**, 2336 (1983).
11. J. R. C. VAN DER MAAREL, D. LANKHORST, J. DE BLEUSER, AND J. C. LEYTE, *J. Phys. Chem.* **90**, 1470 (1986).
12. R. P. W. J. STRUIS, J. DE BLEUSER, AND J. C. LEYTE, *J. Phys. Chem.* **91**, 6309 (1987).
13. J. R. C. VAN DER MAAREL, H. R. W. M. DE BOER, J. DE BLEUSER, D. BEDEAUX, AND J. C. LEYTE, *J. Chem. Phys.* **86**, 3373 (1987).
14. H. W. SPIESS, "NMR, Basic Principles and Progress" (Diehl, Ed.), Vol. 15, Springer, Berlin, 1978.
15. E. R. DAVIDSON AND K. MOROKUMA, *Chem. Phys. Lett.* **111**, 7 (1984); P. L. CUMMINS, G. B. BACSKAY, N. S. HUSH, B. HALLE, AND S. ENGSTRÖM, *J. Chem. Phys.* **82**, 2002 (1985); H. HUBER, *J. Chem. Phys.* **83**, 4591 (1985).
16. I. J. F. POPLETT, *J. Magn. Reson.* **50**, 397 (1982).
17. P. L. CUMMINS, G. B. BACSKAY, AND N. S. HUSH, *Mol. Phys.* **61**, 795 (1987).
18. D. E. DEMCO, P. VAN HECKE, AND J. S. WAUGH, *J. Magn. Reson.* **16**, 467 (1974).
19. M. I. HROVAT AND C. G. WADE, *J. Magn. Reson.* **44**, 62 (1981); *J. Magn. Reson.* **45**, 67 (1981).
20. J. R. C. VAN DER MAAREL AND J. DE BLEUSER, *Chem. Phys. Lett.* **141**, 251 (1987).
21. V. F. SEARS, *Can. J. Phys.* **44**, 1299 (1966); *Can. J. Phys.* **45**, 237 (1966).
22. V. H. FOLLNER AND B. BREHLER, *Acta Crystallogr. B* **26**, 1679 (1970).
23. E. J. W. VERWEY, *Recl. Trav. Chim. Pays-Bas* **61**, 127 (1942).
24. P. BOPP, "The Physics and Chemistry of Aqueous Ionic Solutions" (M.-C. Bellissent-Funel and G. W. Neilson, Eds.), p. 217, Reidel, Dordrecht, 1987.
25. J. E. ENDERBY, S. CUMMINGS, G. J. HERDMAN, G. W. NEILSON, P. S. SALMON, AND N. SKIPPER, *J. Phys. Chem.* **91**, 5851 (1987).
26. M. E. ROSE, "Elementary Theory of Angular Momentum," Wiley, New York, 1957.
27. H. VERSMOLD, *Z. Naturforsch. A* **25**, 367 (1970).