

measured at ionic strengths ranging from 0 to 1.0 and plotted as shown in Figure 6. The theoretical curve calculated with eq 11 with $Z_A Z_B = 8$ and $a = 1.0$ is shown by the broken curve. The solid curve is obtained by the parameter fitting for k_p^0 and a . The value obtained for a is 2.9 which gives an r of 8.8 Å. This value of intermolecular distance seems reasonable according to the molecular size of ZnTMPyP⁴⁺ and viologen group.

Conclusion

The following features for photoinduced electron transfer from cationic zinc porphyrin to the polymer viologen were obtained.

- (1) Quantum yields Φ_i for the cation radical formation for polymer viologen are higher than that for MV²⁺.
- (2) Decreasing viologen-viologen distance in the polymer does not increase Φ_i .
- (3) Ionic pendant group decreases the reduction potential of viologen group, but does not increase Φ_i .
- (4) For the polymers used, Φ_i decreases monotonously with

increasing ionic strength, while that for MV²⁺ has a maximum value.

(5) The high rate of viologen radical formation for polymer viologen is due to the decrease of the reaction rate of back electron transfer.

(6) For the reaction between cationic zinc porphyrin and pendant viologen group in the polymer, the Debye-Hückel relationship is applicable.

Acknowledgment. We are grateful to Mr. K. Yamaguchi for his participation in the laser flash measurements. This study was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Science, Education and Culture.

Registry No. PV4(5), 100351-45-9; PV4(5+50), 100351-46-0; PV4-(5+), 100351-47-1; PV4(5-), 100351-48-2; AQN, 75855-87-7; AQN(+), 100367-06-4; MV²⁺, 4685-14-7; MV^{•+}, 25239-55-8; TEOA, 102-71-6; ZnTMPyP⁴⁺, 40603-58-5; ZnTMPyP^{•+}, 83294-32-0; ZnTPP, 14074-80-7; ZnTSP^{•+}, 80004-36-0.

Water Dynamics in Aqueous Electrolyte Solutions from Proton, Deuterium, and Oxygen-17 Nuclear Magnetic Relaxation

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The relaxation rates of ²H and ¹⁷O and the rate of ¹H due to ¹⁷O were obtained in a series of aqueous electrolyte solutions. From these data conclusions are reached about the influence of the ions on the dynamical behavior, the O-H bond distance, and the ²H coupling constant of neighboring water molecules. It is found that the changes in the O-H distance and the ²H coupling constant induced by most ions investigated are moderate. The dynamical behavior of the water molecules is changed significantly as shown by the correlation times and the emergence of moderate motional anisotropy. The concentration dependence of these effects will be discussed.

Introduction

In an attempt to isolate the influence of ions on the properties of neighboring water molecules from nuclear relaxation data on electrolyte solutions several problems have to be dealt with.

To begin with, a breakdown of the overall rates in terms of contributing "states" (i.e., environment) of the water molecules must be defined and the division of the electrolyte effect into contributions of the ionic species should be made in accordance with the results of other experimental techniques. Next, the influence of an ion on the molecular properties such as the intramolecular field gradients and the O-H bond distance have to be considered. Then a dynamical model for the water molecules in the hydration phase has to be introduced. In NMR such a model specifies the reorientation of the water molecules with respect to a laboratory fixed coordinate system, yielding, e.g., one or more components of a molecule fixed diffusion tensor. Therefore the last and probably most difficult question to resolve is the orientation of the diffusion tensor with respect to the neighboring ion.

In the work reported here some of these problems have been dealt with and for the last-mentioned question our data suggest a reasonable answer for at least the cations.

In this Introduction the problems just discussed are analyzed in a general manner leading to choices and solutions, which will be applied in the discussion of our results.

To describe the relaxation behavior of water nuclei in a salt solution a three-state model is introduced. Water molecules in the direct neighborhood of an ion are defined to be hydration water, thus forming the hydration shell. The remaining part is called bulk water. This concept only makes sense when the

residence times in the states are longer than the motional time scale within the states. With this model the motion within the hydration shell turns out to be in the picosecond range. The available residence times will be discussed below.¹

For ions with unpaired electrons it is possible to obtain the residence time of a water molecule in the hydration shell from the effect of these electrons on the H or ¹⁷O relaxation. This residence time appears to be in the range of microseconds. For diamagnetic ions this method cannot be applied. For these ions the residence time of a water molecule in the hydration shell will be shorter as a consequence of the lack of coordinating d-electron orbitals. Experimental evidence for these ions is scarce. The residence times of water molecules in the hydration shells of Mg²⁺ and Li⁺ have been determined by NMR methods. Neutron scattering experiments provide a means to determine the translational correlation time of pure water. These results will be briefly discussed and compared to some MD results.

The residence time of water molecules in the hydration shell of Mg²⁺ is 10⁻⁶ s (25 °C). This value was obtained by line-width measurements of oxygen-17 in a Mg(ClO₄)₂ solution, while the bulk water resonance was broadened by addition of paramagnetic Mn²⁺.² Fabricand and Goldberg examined the proton relaxation in a ⁷LiCl and a ⁶LiCl solution.³ The ⁷Li nucleus has a larger nuclear magnetic moment than ⁶Li, therefore by a careful comparison of proton relaxation rates in these two isotopic solutions it is possible to obtain information about the Li(H₂O)_n⁺ complex.

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TABLE I: Residence Time of Water Molecules in the Hydration Shell Obtained from MD Simulations and Some Experimental Results, as well as the Translational Correlation Time of Pure Water

ion	T, K	τ , ps	ion	T, K	τ , ps
Mg ²⁺	298	$\sim 10^6$ ^d	F ⁻	278	20.3 ^a
Li ⁺	278	33.3 ^a	Cl ⁻	287	4.5 ^a
	298	14 ^b	H ₂ O	286	4.5 ^a
Na ⁺	282	9.9 ^a	H ₂ O	298	1.7 ^c
K ⁺	274	4.8 ^a			

^aReference 6. ^bReference 1. ^cM.-C. Bellissent-Funel, R. Kahn, A. J. Dianoux, M. P. Fontana, G. Maisano, P. Migliardo, and F. Wandersingh, *Mol. Phys.*, **52**, 1479 (1984). ^dReference 2.

However, Fabricand and Goldberg were not able to explain their results by a rigid, long-lived Li(H₂O)_n⁺ complex. Hertz reinterpreted these results, taking into account an internal motion of a hydration molecule about the Li-O axis, but he also concluded that the hydration shell of Li⁺ is not rigid and not long lived.⁴ Finally, using the neutron diffraction results of Newsome et al.,⁵ Hunt and Friedman repeated the calculation of Hertz. They obtained a residence time of 14 ps, assuming a rotational correlation time of 30 ps for the whole Li(H₂O)₄⁺ complex.¹ Molecular dynamics simulations also provide information about these residence times. Impey et al., using an analytical potential energy function of Matsuoka, Clementi, and Yoshimine (MCY), obtained a value of the residence time of water molecules within the first hydration shell.⁶ During the MD run they noted the number $n_{\text{ion}}(t)$, i.e. the number of molecules which lie initially within the first hydration shell and are still there after a time t has elapsed. Except at short times, this number decays exponentially. These residence times together with the experimental residence times of water molecules in the hydration complexes of Li⁺ and Mg²⁺ as well as the translational correlation time of pure water are presented in Table I.

The translational correlation time of pure water and the lifetime of the hydration shell of Li⁺ as given by the MD results are a factor 2.5 longer than the corresponding NMR and neutron scattering values. The residence time of water molecules in the hydration shell of monovalent ions increases from about 2 ps (obtained by dividing the MD result by the factor 2.5) to about 14 ps in the case of Li⁺. From the work reported here reorientational correlation times within the hydration shell turn out to increase from 1 ps in case of I⁻ to about 5 ps when the solute is Li⁺. The residence times of water molecules in the hydration shells of Mg²⁺, Ca²⁺, Li⁺, Na⁺, and F⁻ are certainly longer than the motional time scale within the shell, but this condition is not with certainty met in the cases of K⁺, Cs⁺, Cl⁻, Br⁻, and I⁻.

The number of water molecules within a hydration shell n^{\pm} is also an unknown quantity. Neutron scattering experiments provide detailed information about the structure of electrolyte solutions. Hydration numbers obtained from the ion-water correlation functions are presented in Table II. An additional source of information consists of the results of MD simulations. The average number of hydration water molecules counted during the MD run is also presented in Table II.

To investigate the dynamics of a solution, different intramolecularly determined hydration water relaxation rates will be compared. These rates are calculated with equal hydration numbers for all ions. The conclusions appear not to be very sensitive to a particular choice of the hydration number within the range of the values presented in Table II. A value of six will be chosen for all ionic species. A homogeneous distribution of deuterium between hydration water and the bulk is assumed. This has been shown to be the case for Cl⁻, Br⁻, and I⁻.⁷

TABLE II: Hydration Numbers from Neutron Diffraction Experiments and MD Simulations

ion	solute	T, K	molality	n^{\pm}
Li ⁺	LiCl	278	3.57	5.5 ± 0.3 ^a
		278		5.3 ^b
Na ⁺	NaCl	293.5	1.0	8 ^c
		282		6.0 ^b
K ⁺		274		7.5 ^b
	KCl	293.5	1.0	8 ^c
Ni ²⁺	NiCl ₂		4.41	5.8 ± 0.2 ^a
			3.05	5.8 ± 0.2 ^a
			1.46	5.8 ± 0.2 ^a
			0.85	6.6 ± 0.5 ^a
			0.46	6.8 ± 0.8 ^a
			0.086	6.8 ± 0.8 ^a
Ca ²⁺	CaCl ₂	278	4.49	5.5 ± 0.2 ^a
F ⁻				5.8 ^b
Cl ⁻	LiCl	287	3.57	5.9 ± 0.2 ^a
				7.2 ^b

^aReference 26. ^bReference 6. ^cN. Ohtomo and K. Arakawa *Bull. Chem. Soc. Jpn.*, **53**, 1789 (1980).

According to the model used here each experimental relaxation rate is expressed as a weighted sum of relaxation rates in the three states. In eq 1 all relaxation rates are understood to be corrected

$$R_x^c = (1 - f^+ - f^-)R_x^0 + f^+R_x^+ + f^-R_x^- \quad (1)$$

for small solvent isotope effects. This is explicitly indicated by a superscript c for R_x^c only. In this equation f^{\pm} is the mole fraction of hydration water. The relaxation rate of bulk water is denoted by R_x^0 and the relaxation rate of cation or anion hydration water is represented by R_x^+ or R_x^- , respectively. The subscript x can be O, D, or OH when the relaxation path is respectively oxygen-17 quadrupolar, deuterium quadrupolar, or proton-oxygen-17 dipolar interaction. If we define a hydration number n^{\pm} , the mole fraction f^{\pm} may be expressed in terms of the molality m of the solution:

$$f^{\pm} = n^{\pm}m/55.5 \quad (2)$$

Equation 1 is valid when the residence time of water molecules in the defined states is shorter than the macroscopic relaxation times and longer than the motional time scale within the states. The former condition is easily satisfied, because the shortest relaxation time is about 5×10^{-3} s. The latter condition has just been discussed. The residence time of water molecules in the hydration shell of K⁺, Cs⁺, Cl⁻, Br⁻, and I⁻ approximates the motional time scale within the shell, but even in this case eq 1 is still a good approximation.⁸

As a consequence of the electric neutrality it is impossible to separate the cationic and anionic influence on the relaxation rates. Neutron scattering experiments on different chlorides show that Cl⁻ hydration is independent of type of cation and of ionic strength.^{9,10} These experiments show the hydration of K⁺ to be very weak.¹¹ Therefore it is possible to study the influence of cations by comparing different chlorides and for the anions potassium salts may be used. To calculate the hydration water relaxation rates R_x^+ or R_x^- the contribution of the Cl⁻ or K⁺ ion will be assumed zero, but for any small constant value the resulting trend will be the same. Under these conditions eq 1 reduces to

$$R_x^c = (1 - f^{\pm})R_x^0 + f^{\pm}R_x^{\pm} \quad (3)$$

The relaxation rates in the hydration spheres may now be calculated after evaluation of the relaxation rate R_x^0 in bulk water. Quasielastic neutron scattering experiments of Hewish et al.¹² show

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a small influence on water molecules beyond the first hydration shell of Ni^{2+} and Mg^{2+} . An influence on water molecules beyond the first hydration shell of Li^+ and Cs^+ , which both have a smaller electric field strength at the surface, could not be detected. Therefore the relaxation rate of bulk water will be assumed to be equal to the relaxation rate of pure water.

Under extreme narrowing conditions the hydration water relaxation rate R_x^\pm is the product of an interaction constant C_x^\pm and a dynamical effective correlation time τ_x^\pm :

$$R_x^\pm = C_x^\pm \tau_x^\pm \quad (4)$$

The interaction constant of the $\text{H}-^{17}\text{O}$ dipolar interaction is given by

$$C_{\text{OH}}^\pm = \frac{35}{3} \frac{\gamma_{\text{H}}^2 \gamma_{^{17}\text{O}}^2 \hbar^2}{r_{\text{OH}}^6} \quad (5a)$$

Here r_{OH}^\pm denotes the O-H bond length of a hydration water molecule. The interaction constants of the quadrupolar interaction are

$$C_{\text{D}}^\pm = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar} \right)_D^{\pm 2} (1 + \eta_D^2/3) \quad (5b)$$

when the relaxing nucleus is D and

$$C_{\text{O}}^\pm = \frac{3}{125} \left(\frac{e^2 q Q}{\hbar} \right)_O^{\pm 2} (1 + \eta_O^2/3) \quad (5c)$$

when it is ^{17}O . To enable a discussion of the dynamical features of hydration water the coupling constants C_x^\pm should be known, thus allowing the calculation of the effective correlation times from the experimental values of R_x^\pm . Although the coupling constants are known reasonably well in bulk water, their values for water molecules in close proximity to an ion is unknown. This problem may be solved in a manner similar to the determination of the coupling constants in pure water.¹³ This possibility arises due to the fact that some of the effective correlation times are in fact equal.

The effective correlation times τ_x^\pm characterize the orientational correlation loss of a particular interaction tensor for each nucleus studied. This can be caused by reorientational motion of water molecules within the first hydration shell or by an overall reorientational diffusion process of the whole ion-hydration water complex. The correlation time of the latter process will be approximately 30 ps, while the experimental correlation times turn out to be a few picoseconds. Because the time scale of this overall diffusion process is much longer than the experimental correlation times this process will be neglected.

The lattice part of the coupling Hamiltonian, i.e. the interaction tensor, will be described by the irreducible elements $V_k^{(2)}$. In the principal axis system of the dipolar interaction tensor, one has $V_k^{(2)} = \delta_{0k}(2/3)^{1/2} r_{\text{OH}}^{-3}$. In the principal axis system of the quadrupolar interaction, one has $V_0^{(2)} = eq(3/2)^{1/2}$, $V_{\pm 2}^{(2)} = -\eta/2eq$, with the asymmetry parameter η being defined as $\eta = (V_{yy} - V_{xx})/V_{zz}$.¹⁴

The orientation of the principal axis system of the $\text{H}-^{17}\text{O}$ dipolar interaction tensor coincides with the orientation of the principal axis system of the D quadrupolar interaction tensor. The asymmetry parameter of the D field gradient is very small ($\eta_D = 0.135$, gas value). As a consequence the $V_{\pm 2}^{(2)}$ field gradient component is small with respect to the dominant $V_0^{(2)}$ component. A combination of these two features results in an equality of the experimental correlation times τ_D^\pm and τ_{OH}^\pm within experimental accuracy and this equality is independent of the symmetry of the

diffusion tensor (one has to take a small isotope effect into account; this will be discussed later). Therefore if the correlation times τ_D^\pm and τ_{OH}^\pm as determined from the relaxation rates and the application of eq 5 with the use of molecular properties of bulk water molecules are not equal, this would indicate that C_D^\pm and C_{OH}^\pm change when the water molecule becomes a member of the hydration shell.

Rephrased in concrete experimental terms this means that a change in the ratio $R_D^\pm/R_{\text{OH}}^\pm$ with respect to its pure water value is a direct indication of a change in the values of r_{OH}^\pm and C_D^\pm upon transfer of a water molecule from the bulk to a hydration shell. As quantum chemical and empirical relations connecting C_D^\pm and r_{OH}^\pm are known it is possible to calculate these quantities from the observed values of R_D^\pm and R_{OH}^\pm as will be shown in the next section. For most ions considered here the effects are small and the dynamical behavior of hydration water will be discussed by using effective correlation times as calculated from the relaxation rates assuming bulk water coupling constants.

The motion within the hydration shell will be represented by a rotational diffusion process having axial symmetry. The reader is referred to ref 15. For a study of the intramolecularly determined relaxation paths and the relative relaxation behavior as a function of the diffusion tensor properties, ref 16 may be consulted. The diffusion tensor is characterized by two components D_{\parallel} and D_{\perp} and by the orientation of the principal axis system of this tensor with respect to the principal axis system of the interaction tensor. Under extreme narrowing conditions the effective correlation time will be given by

$$\tau_x^\pm = \frac{1}{\sum_{k=2}^{\infty} |V_k^{(2)}|^2} \sum_{k=2}^{\infty} \sum_{l,m} V_k^{(2)} V_l^{(2)*} D_{km}^{(2)}(\Omega_x) D_{lm}^{(2)*}(\Omega_x) \tau_{|m|} \quad (6)$$

with

$$\tau_m^{-1} = 6D_{\perp} + m^2(D_{\parallel} - D_{\perp}) \quad (7)$$

The Wigner matrix elements $D_{lm}^{(2)}$ describe the transformation of the principal axis system of the interaction tensor to the principal axis system of the diffusion tensor, characterized by the orientation Ω_x .

Experimental Section

Chemicals and Solutions. Oxygen isotopically enriched water 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.).

MgCl_2 , analytical reagent, was obtained from Baker; the remaining salts are Suprapur quality from Merck. The solutions were prepared by weight in a cold room at 5 °C to minimize exchange with atmospheric humidity. The solutions prepared for proton measurements were shaken five times with argon to remove gaseous oxygen and relaxation rates were measured within 2 h.

NMR tubes (Wilmad 10 mm) were heated in a NaHCO_3 solution, heated in an EDTA solution, and then stored for at least 1 week filled with deionized and filtered water. Before drying the conductance of the contents was checked; it never exceeded $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. For proton measurements of KF solutions, quartz sample tubes were used.

Determination of Relaxation Rates. Solutions of CsCl , KCl , KI , and KBr were measured on a home-modified Bruker SXP spectrometer equipped with a 6.3-T superconducting magnet (Oxford Instruments). The temperature was maintained at $298 \pm 0.5 \text{ K}$ with a variable-temperature unit (Bruker B-VT 1000). Solutions of MgCl_2 , CaCl_2 , LiCl , and NaCl were measured on a home-built spectrometer equipped with a 2.1-T electromagnet (Bruker). The temperature was maintained at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ by

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TABLE III: Isotope Effect Corrected Relaxation Rates and Isotopic Composition of the Samples^a

TABLE III. Isotope Effect Corrected Relaxation Rates and Isotopic Composition of the Samples																
solute	molality, mol/kg of L ₂ O	<i>n</i>	p17	p18	<i>R</i> _H ^c , s ⁻¹	<i>R</i> _D ^c , s ⁻¹	<i>R</i> _O ^c , s ⁻¹	solute	molality, mol/kg of L ₂ O	<i>n</i>	p17	p18	<i>R</i> _H ^c , s ⁻¹	<i>R</i> _D ^c , s ⁻¹	<i>R</i> _O ^c , s ⁻¹	
MgCl ₂	4.74	0.110	0.024	0.070	—	7.54	512	KCl	3.89	0.023	0.0057	0.0042	—	1.86	—	
	3.47	0.042	0.010	0.028	—	5.60	367		3.96	—	—	—	0.254	—	—	
	1.86	0.052	0.012	0.034	—	3.61	241		3.89	—	0.110	0.085	0.281	—	—	
	1.84	0.097	0.021	0.062	—	3.63	240		4.00	—	0.235	0.180	0.314	—	—	
	1.09	0.045	0.010	0.030	—	2.87	197		4.10	—	0.338	0.258	0.348	—	—	
CaCl ₂									4.00	—	0.511	0.390	0.382	—	—	
	5.36	0.115	0.026	0.073	—	4.87	366	3.67	0.019	0.005	0.003	—	1.86	143		
	3.63	0.051	0.012	0.033	—	3.58	254	2.94	0.021	0.005	0.004	—	1.86	141		
	2.05	0.016	0.0039	0.0029	—	2.72	192	1.94	0.017	0.004	0.003	—	1.88	139		
	1.18	0.014	0.0034	0.0024	—	2.43	165	1.56	0.015	0.004	0.003	—	1.88	140		
	1.20	0.024	0.0059	0.0043	—	2.39	165	0.93	0.022	0.005	0.004	—	1.90	140		
	0.78	0.015	0.0036	0.0026	—	2.26	153	0.58	0.017	0.004	0.003	—	1.93	140		
	0.46	0.016	0.0039	0.0029	—	2.13	150									
LiCl	5.17	0.042	0.010	0.028	—	3.17	235	KF	5.73	0.091	0.020	0.058	—	3.32	270	
	4.00	0.048	0.011	0.032	—	2.88	210		4.35	0.038	0.009	0.025	—	2.78	229	
	3.91	—	—	—	0.410	—	—		3.90	0.067	0.017	0.014	—	2.73	212	
	4.04	—	0.094	0.073	0.450	—	—		3.99	—	—	—	0.436	—	—	
	3.88	—	0.176	0.135	0.498	—	—		3.99	—	0.197	0.152	0.517	—	—	
	3.92	—	0.271	0.208	0.522	—	—		4.07	—	0.312	0.239	0.576	—	—	
	3.98	—	0.374	0.286	0.570	—	—		3.89	—	0.374	0.286	0.591	—	—	
	4.01	—	0.472	0.360	0.621	—	—		4.06	—	0.511	0.390	0.662	—	—	
	2.32	0.020	0.0049	0.0036	—	2.43	173		2.34	0.099	0.022	0.063	—	2.41	181	
	1.79	0.013	0.0031	0.0023	—	2.32	164		1.03	0.044	0.010	0.029	—	2.18	156	
	1.84	—	—	—	0.350	—	—	CsCl	4.95	0.0045	0.0011	0.0008	—	1.78	140	
	1.86	—	0.111	0.086	0.395	—	—		4.00	0.0038	0.0009	0.0007	—	1.78	137	
	1.82	—	0.229	0.176	0.422	—	—		2.60	0.0046	0.0011	0.0008	—	1.80	137	
	1.82	—	0.390	0.298	0.485	—	—		1.95	0.0039	0.0010	0.0007	—	1.82	135	
	1.83	—	0.494	0.377	0.509	—	—		1.09	0.0075	0.0018	0.0013	—	1.86	137	
	NaCl	1.28	0.020	0.0050	0.0036	—	2.18	154	KBr	4.88	0.0130	0.0032	0.0023	—	1.72	136
		0.91	0.013	0.0032	0.0024	—	2.08	151		3.87	0.0099	0.0024	0.0018	—	1.72	132
		3.97	0.030	0.128	0.099	—	2.43	192		2.60	0.0048	0.0012	0.0009	—	1.76	132
		4.07	—	—	—	0.353	—	—		1.92	0.0093	0.0023	0.0017	—	1.77	132
		4.05	—	0.130	0.100	0.400	—	—		0.90	0.0074	0.0018	0.0013	—	1.84	135
		3.90	—	0.237	0.182	0.431	—	—	KI	4.98	0.0078	0.0019	0.0014	—	1.61	132
		3.95	—	0.354	0.271	0.485	—	—		3.83	0.0095	0.0023	0.0017	—	1.61	124
		4.00	—	0.511	0.390	0.539	—	—		2.84	0.0064	0.0016	0.0011	—	1.66	125
		3.71	0.058	0.0141	0.010	—	2.39	188		1.91	0.0096	0.0023	0.0017	—	1.70	127
		2.47	0.016	0.0038	0.0028	—	2.19	162		0.69	0.0100	0.0024	0.0018	—	1.83	132
	1.88	0.014	0.0034	0.0025	—	2.18	157									
	1.32	0.020	0.0050	0.0036	—	2.06	149									
	0.99	0.049	0.011	0.032	—	2.03	147									
	0.89	0.017	0.0040	0.0029	—	2.01	146									

^a An isotope fraction denoted by (—) means abundance (i.e., $n_{\text{nat}} = 0.156 \times 10^{-3}$, $(p17)_{\text{nat}} = 0.37 \times 10^{-3}$, $(p18)_{\text{nat}} = 2.04 \times 10^{-3}$).

fluid thermostat using Fluorinert grade FC-43 (3M Co.). The magnetic field was locked with an external lock probe, using the F resonance in trifluoroacetic acid doped with copper acetate.

T_1 measurements were obtained in duplicate at least, by the inversion recovery method with an estimated accuracy of 1%. FID were accumulated with a LSI-11 microcomputer, while the relative phase of π and the $\pi/2$ pulses was alternated.¹⁷ One hundred data points were collected and fitted to a single exponential by a nonlinear least-squares procedure. The results are presented in Table III.

Results and Discussion

Corrections for Isotope Effects on the Relaxation Rates. Oxygen isotope effects on the reorientational motion of the solvent are expected to be proportional to the small effects on the viscosity of the solvent. The linear correction (10) in ref 13 will be applied. Relaxation rates corrected for this effect will be denoted by R_{x}^{c} . Samples prepared for proton measurements were not enriched with deuterium; therefore the oxygen isotope correction is sufficient:

$$R_{\text{H}}^{\text{c}} = R_{\text{H}}^{\text{oc}} \quad (8)$$

Deuterium isotope effects on the reorientational motion of the solvent are assumed to be the same as in H₂O/D₂O mixtures. The

observed D relaxation rate $R_{\text{D}}^{\text{bsd}}$ and the ¹⁷O relaxation rate R_{O}^{c} (corrected for oxygen isotope effects) as a function of the deuterium mole fraction in these mixtures are given by¹³

$$R_{\text{D}}^{\text{bsd}}(n) = (1.944 \pm 0.004) + (0.423 \pm 0.004)n \quad (9a)$$

$$R_{\text{O}}^{\text{c}}(n) = (141.6 \pm 0.5) + (39.6 \pm 1.1)n \quad (9b)$$

The intercept of eq 9a and 9b is just R_{D}^0 and R_{O}^0 , respectively, in eq 3, i.e. the corrected values of pure water. Correction for D isotope effects was performed after correcting for oxygen isotope effects:

$$R_{\text{D}}^0 = \frac{1.944}{1.944 + (0.423n)} R_{\text{D}}^{\text{c}} \quad (10a)$$

$$R_{\text{O}}^0 = \frac{141.6}{141.6 + (39.6n)} R_{\text{O}}^{\text{c}} \quad (10b)$$

Samples were enriched as little as possible, leading to small corrections on the order of 0.6%.

Correlation times $\tau_{\text{D}}^{\text{c}}$ determined by the D relaxation rates R_{D}^{c} refer to HDO molecules. The transformation to correlation times for H₂O molecules is¹³

$$\tau(\text{HDO})_{\text{H}_2\text{O}} = (1.05 \pm 0.02)\tau(\text{H}_2\text{O})_{\text{H}_2\text{O}} \quad (11)$$

where the molecular species involved is given within parentheses and the surrounding medium is denoted outside the parentheses.

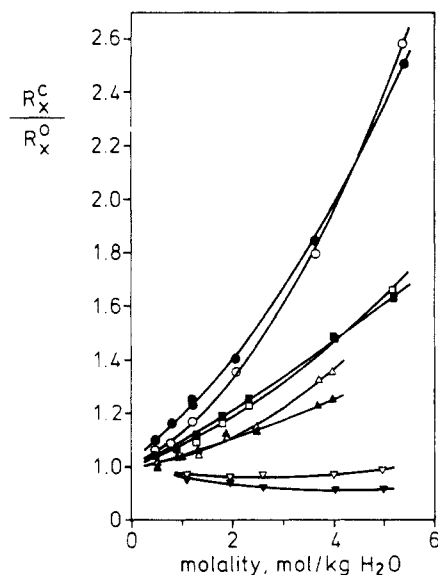


Figure 1. Isotope effect corrected relaxation rates divided by the pure water values vs. the molality. For the different nuclei the following notations are used: D, filled symbols; ^{17}O , open symbols. The symbols employed for the various salts are the following: CaCl_2 , \circ ; LiCl , \square ; NaCl , Δ ; and CsCl , ∇ . Curves are drawn according to a quadratic polynomial fit.

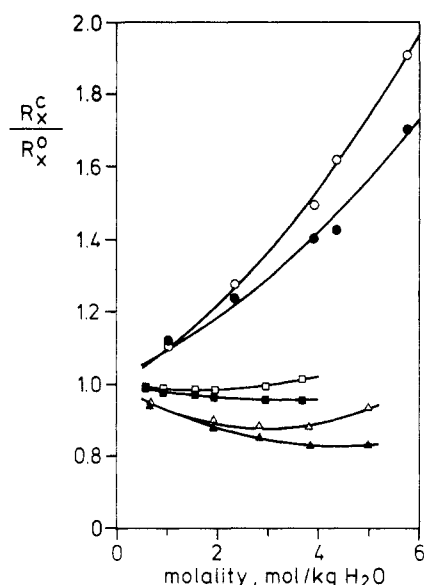


Figure 2. As in Figure 1. The symbols employed for the various salts are the following: KF , \circ ; KCl , \square ; and KI , Δ .

As a first approximation this solute isotope effect on hydration water is expected to be the same as on pure water. For ^{17}O the analogous effect will be neglected. Deuterium correlation times corrected for this effect will be denoted by $\tau_D^{\pm}(\text{H}_2\text{O})$. Corrected relaxation rates are presented in Table III. Deuterium and oxygen-17 relaxation rates R_D^{\pm} and R_O^{\pm} , respectively, divided by the values of pure water R_D^{\pm} and R_O^{\pm} , respectively, are displayed in Figures 1 and 2 as a function of the molality. Large effects are observed when small and/or highly charged ions are in solution.

Determination of the Coupling Constants. To obtain the effective correlation times it is necessary to know the interaction constants. With the intramolecular dipolar $\text{H}-^{17}\text{O}$ interaction contribution to the H relaxation rate of pure water it is possible to obtain the reorientational correlation time τ^0 . A value of 1.71 ps was reported earlier, but the O-H distance was assumed to be 0.958 Å, i.e. the gas value. Also with this correlation time and the quadrupole relaxation rates of pure water, values of quadrupole coupling constants have been obtained.¹³ Because recent neutron diffraction experiments show a somewhat larger O-H bond

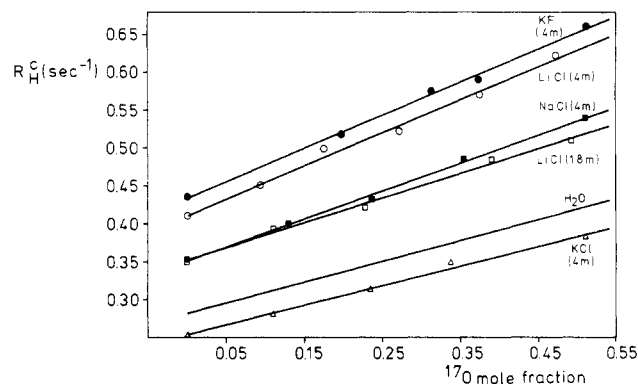


Figure 3. Oxygen isotope effect corrected proton relaxation rates vs. the ^{17}O mole fraction. Lines are drawn according to a linear least-squares fit. The line displayed for pure water is reported in ref 13.

TABLE IV: Fitted Parameters of the Lines Displayed in Figure 3, along with the Values for Pure Water

solute	molality	R_{HH}^{\pm} , s^{-1}	R_{OH}^{\pm} , s^{-1}
LiCl	3.96 ± 0.06	0.411 ± 0.005	0.44 ± 0.02
	1.83 ± 0.02	0.353 ± 0.005	0.32 ± 0.02
NaCl	4.00 ± 0.07	0.351 ± 0.004	0.37 ± 0.01
KCl	3.99 ± 0.07	0.254 ± 0.004	0.26 ± 0.01
KF	4.00 ± 0.06	0.434 ± 0.005	0.44 ± 0.02
H_2O^a		0.282 ± 0.003	0.275 ± 0.009

^aReference 13.

TABLE V: Hydration Water Relaxation Rates and Correlation Times, Calculated with the Pure Water Values of the O-H Bond Length and Deuterium Quadrupole Coupling Constant

ion	m	R_D^{\pm} , s^{-1}	R_{OH}^{\pm} , s^{-1}	τ_D^{\pm} , (H_2O) , ps	τ_{OH}^{\pm} , ps
Li^+	4	4.11 ± 0.07	0.64 ± 0.04	4.1 ± 0.2	4.6 ± 0.3
	1.8	3.9 ± 0.1	0.51 ± 0.09	3.9 ± 0.2	3.7 ± 0.7
Na^+	4	3.10 ± 0.06	0.48 ± 0.03	3.1 ± 0.2	3.5 ± 0.2
K^+	4	1.74 ± 0.05	0.23 ± 0.03	1.8 ± 0.1	1.7 ± 0.2
F^-	4	3.81 ± 0.07	0.64 ± 0.02	3.9 ± 0.2	4.7 ± 0.3

length,¹⁸⁻²⁰ a value of 0.98 Å seems preferable. Using this value in the calculations in ref 13 one obtains

$$\tau^0 = 1.95 \pm 0.08 \text{ ps} \quad (12)$$

$$\left(\frac{e^2 q Q}{h} \right)_D^0 = 252 \pm 6 \text{ kHz} \quad (13a)$$

$$\left(\frac{e^2 q Q}{h} \right)_O^0 = 8.0 \pm 0.2 \text{ MHz} \quad (13b)$$

with $\eta_D = 0.135$ and $\eta_O = 0.75$ (gas values).

The coupling constants of the water molecules in the hydration shell may be discussed now. To this end the contribution of ^{17}O to the proton relaxation was determined experimentally to allow a comparison with the deuterium relaxation rate.

Proton relaxation rates R_H^{\pm} are displayed in Figure 3 as a function of the oxygen-17 mole fraction. In view of the observed linearity one has

$$R_H^{\pm} = R_{\text{HH}}^{\pm} + (p^{17})R_{\text{OH}}^{\pm} \quad (14)$$

in which R_{HH}^{\pm} and R_{OH}^{\pm} denote the H-H and H- ^{17}O , respectively, dipolar interaction contribution to the H relaxation rate. The

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(19) J. G. Powles, *Mol. Phys.*, **42**, 757 (1981).

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

TABLE VI: Some Calculated Quantities of Hydration Water

ion	<i>m</i>	τ_{OH}^{\ddagger} , ps	r_{OH}^{\ddagger} , Å	$(e^2qQ/h)_D^{\ddagger}/$ $(e^2qQ/h)_D^0$	$(e^2qQ/h)_O^{\ddagger}/$ $(e^2qQ/h)_O^0$
Li ⁺	4	5.0 ± 0.8	0.993 ± 0.009	0.91 ± 0.07	0.89 ± 0.08
	1.8	3 ± 1	0.97 ± 0.03		
Na ⁺	4	3.7 ± 0.6	0.992 ± 0.009	0.92 ± 0.07	0.90 ± 0.08
	4	1.6 ± 0.4	0.97 ± 0.02		
K ⁺	4	5.3 ± 0.6	1.001 ± 0.006	0.85 ± 0.05	0.82 ± 0.06

intermolecular contribution to R_{OH}^0 in pure water, obtained with a formula derived by Hubbard accounting for translational diffusion,²¹ appears to be 0.0054 s⁻¹.¹³ In salt solutions this intermolecular contribution is unknown but will be taken to be 2% of the total H-¹⁷O dipolar interaction contribution, as it is in pure water. Relaxation rates R_{HH}^0 and R_{OH}^0 resulting from the fit of eq 14 to the data of Figure 3 are presented in Table IV.

Hydration water relaxation rates R_D^{\ddagger} and R_{OH}^{\ddagger} calculated according to eq 3 with R_D^0 and the intramolecular part of R_{OH}^0 are presented in Table V. Hydration water effective correlation times obtained with the pure water values of the O-H bond length and the D quadrupole coupling constant are also presented in Table V. These correlation times, $\tau_D^{\ddagger}(H_2O)$ and τ_{OH}^{\ddagger} , of 4 *m* LiCl, NaCl, and KF solutions differ just outside experimental error. This is not the case when the solute is 4 *m* KCl. In case of a 1.8 *m* LiCl solution the experimental accuracy is not good enough to justify a discrimination. Another choice of hydration number or a small influence of the counterion (Cl⁻) cannot abolish these effects. Because the principal directions of the interaction tensors coincide and the value of the D asymmetry parameter is small, these correlation times are expected to be equal within experimental error as was discussed in the Introduction. The difference between the effective correlation times $\tau_D^{\ddagger}(H_2O)$ and τ_{OH}^{\ddagger} of water molecules within the hydration shell of 4 *m* Li⁺, Na⁺, and F⁻ indicate that the O-H distance and/or the D quadrupole coupling constant have changed with respect to pure water.

A change of the quadrupole coupling constant from pure water to hydration water can be caused by a polarization of the water molecule by the ionic charge which also induces a change in geometry of the molecule. Ab initio quantum chemical calculations show the main factor determining the D quadrupole coupling constant to be the O-D bond length. An increase in bond angle was found to produce only a small reduction, while the dependence on bond length is nearly linear and independent of whether the molecule is isolated or incorporated in dimer or ice.^{22,23} For a small change of O-H distance this dependence is approximately linear:

$$\left(\frac{e^2qQ}{h}\right)_D^{\ddagger} = \left(\frac{e^2qQ}{h}\right)_D^0 - a(r_{OH}^{\ddagger} - r_{OH}^0) \quad (15)$$

in which r_{OH}^0 denotes the pure water O-H bond length. The constant *a* is obtained by interpolating the gas and ice value of the coupling constant. A value of 1805.8 kHz/Å will be used. With eq 4, 5, and 15, the hydration water relaxation rates R_D^{\ddagger} and R_{OH}^{\ddagger} and the condition, $\tau_D^{\ddagger}(H_2O) = \tau_{OH}^{\ddagger}$, together with the pure water values of the D quadrupole coupling constant and O-H distance it is possible to derive the hydration water values of the O-H distance, the D quadrupole coupling constant, and the effective hydration water correlation time. These values are presented in Table VI. A deuterium isotope effect on the O-H bond length has been neglected.

The O-H distance in pure water is assumed to be 0.98 Å. In this first experimental NMR determination of the influence of ions on the bond length of water in the hydration shell the results are marginally outside the estimated error margin. The O-H bond of hydration water molecules of 4 *m* Li⁺, Na⁺, and F⁻ is lengthened due to the polarization by the ionic charge. This effect is most

TABLE VII: Linear Coefficients, B_x , of the Polynomial Expansion of R_x^{\ddagger}/R_x^0 in the Molality, *m*

solute	B_D	B_O
MgCl ₂	0.372 ± 0.009	0.23 ± 0.04
CaCl ₂	0.14 ± 0.02	0.08 ± 0.01
LiCl	0.102 ± 0.008	0.072 ± 0.009
NaCl	0.05 ± 0.01	0.022 ± 0.008
KCl	-0.027 ± 0.003	-0.021 ± 0.001
CsCl	-0.041 ± 0.003	-0.030 ± 0.005
KBr	-0.056 ± 0.005	-0.051 ± 0.005
KI	-0.077 ± 0.005	-0.080 ± 0.007
KF	0.06 ± 0.02	0.08 ± 0.01

pronounced in the hydration shell of F⁻. Neutron scattering experiments have not detected such a change of the O-H bond length.¹⁸ A recent MD study of the structure of the Li⁺ hydration shell shows a similar increase of the O-H bond length, using the central force potential.²⁴ The O-H distance does not change significantly in the hydration shell of 4 *m* K⁺. It is not possible to study a wide range of concentrations, because the experimental error increases at lower concentrations.

The effect on the D quadrupole coupling constant is somewhat more pronounced but so is the estimated error. The D coupling constant in the hydration shell of 4 *m* Li⁺, Na⁺, or F⁻ is somewhat smaller than the pure water value. In the hydration shell of K⁺ the coupling constant does not change significantly. The ¹⁷O coupling constant will also be affected by the ionic charge, but in the liquid state, under extreme narrowing conditions, there appears to be no experimental procedure to obtain the effective ¹⁷O correlation time separately. Solid-state NQR provides a method to determine the quadrupole coupling constants in crystal hydrates and different forms of ice. Poplett observed a correlation between the ¹⁷O and D coupling constants for crystal hydrates, ice, and water vapor:²⁵

$$\left(\frac{e^2qQ}{h}\right)_O = (38.214 \pm 1.293) \left(\frac{e^2qQ}{h}\right)_D - (1650 \pm 302) \text{ kHz} \quad (16)$$

The pure water values, eq 13a and 13b, also satisfy this relation. As the coupling constants were calculated by assuming isotropy, this confirms the isotropy in pure water. Relation 16 will be used to determine the hydration water ¹⁷O coupling constant. The hydration water ¹⁷O quadrupole coupling constant divided by the value of pure water, obtained according to this procedure for 4 *m* salt solutions, is also presented in Table VI.

A study of water dynamics by interpreting the ratio of the ¹⁷O and D relaxation rates is not sensitive to a particular choice of the coupling constants, because as a consequence of relation 16 the ¹⁷O coupling constant is nearly proportional to the D coupling constant, as was indicated in the case of 4 *m* Li⁺, Na⁺, and F⁻. Therefore the pure water values of the coupling constants will be used.

Relaxation Rates of Hydration Water at Infinite Dilution. The relaxation rates in the limit of infinite dilution are now estimated to obtain the relaxation behavior of an isolated hydration complex. The procedure proposed by Hertz⁹ will be used. Hertz proposed a polynomial expansion of the relaxation rates in the molality of the solution. Fitted quadratic polynomials are displayed in Figures 1 and 2; they describe the relaxation behavior well. Under the assumptions discussed in the Introduction the hydration water relaxation rates of the complex at infinite dilution are related to the linear coefficients B_x of the polynomial expansion according to

$$R_x^{\ddagger}(m \rightarrow 0)/R_x^0 = \frac{55.5}{n^{\ddagger}} B_x + 1 \quad (17)$$

(21) P. S. Hubbard, *Phys. Rev.*, **131**, 275 (1963).

(22) E. R. Davidson and K. Morokuma, *Chem. Phys. Lett.*, **111**, 7 (1984).

(23) P. L. Cummins, G. B. Bacskey, N. S. Hush, B. Halle, and S. Engstrom, *J. Chem. Phys.*, **82**, 2002 (1985).

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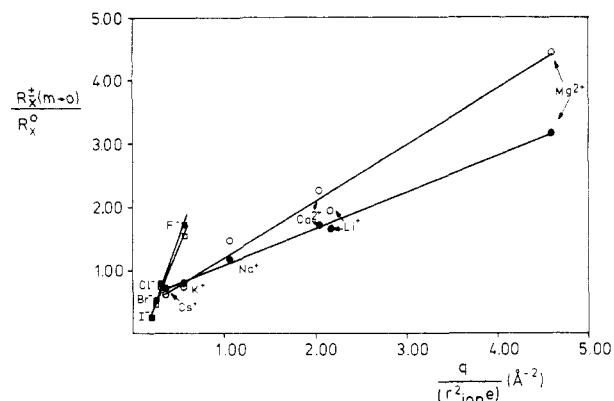


Figure 4. Hydration water relaxation rates of an infinitely diluted complex divided by the pure water values as a function of the electric field intensity on the surface of the ion. For the different nuclei the following notations are used: ^{17}O , filled symbols; D, open symbols. Squares denote the anions, while for cations circles are used.

Linear coefficients B_x are presented in Table VII, relative hydration water relaxation rates $R_x^+(m \rightarrow \text{O})/R_x^0$ are displayed in Figure 4 as a function of the relative electric field strength $q/(r^2e)$ on the surface of the isolated ion. A linear correlation is found between $R_x^+(m \rightarrow \text{O})/R_x^0$ and the electric field strength according to

$$R_D^+/R_D^0 = (0.32 \pm 0.13) + (0.89 \pm 0.06)q/(r^2e) \quad (18a)$$

$$R_O^+/R_O^0 = (0.52 \pm 0.04) + (0.57 \pm 0.02)q/(r^2e) \quad (18b)$$

$$R_D^-/R_D^0 = (-0.42 \pm 0.08) + (3.5 \pm 0.2)q/(r^2e) \quad (18c)$$

$$R_O^-/R_O^0 = (-0.51 \pm 0.11) + (4.0 \pm 0.3)q/(r^2e) \quad (18d)$$

The relative trend will be equal if one chooses another value of n^\pm in eq 17 or a certain influence of the counterion. The importance of the polarity of the ionic field (i.e., the cationic and anionic lines in Figure 4 do not coincide) shows that the interaction of a water molecule with its surrounding medium is not only the ion point charge-dipole interaction.

The quantity $R_x^+(m \rightarrow \text{O})/R_x^0$ reflects the relative change of the quadrupole coupling constant and the correlation time of infinitely diluted hydration water with respect to pure water according to

$$\frac{R_x^+(m \rightarrow \text{O})}{R_x^0} = \frac{\tau_x^\pm}{\tau^0} \left\{ \left(\frac{e^2 q Q}{h} \right)_x^\pm / \left(\frac{e^2 q Q}{h} \right)_x^0 \right\}^2 \quad (19)$$

As the relative effect of ionic field strength on the D and ^{17}O coupling constants is nearly equal, the different behavior of the D and ^{17}O relaxation rates cannot be explained by a change of the coupling constants. Therefore the data displayed in Figure 4 directly indicate the effectiveness of the relaxation mechanisms, i.e. the effective correlation times.

As depicted in Figure 4 the anionic ^{17}O and D hydration water effective correlation times coincide within experimental accuracy. The motion within the hydration shell is not expected to be isotropic, because (especially in case of F^-) several experimental methods indicate a significant anion-water interaction. Neutron scattering pair correlation functions indicate that the anion-water axis coincides with the O-H axis.²⁶ Recent NMR experiments suggest a symmetric orientation.²⁷ The orientation as given by MD simulations depends strongly on the interaction functions.^{6,28} However, from these results, the anion and hydration water molecule are expected to be coplanar as indicated in Figure 5. Now, if the $D_{||}$ axis of the diffusion tensor is positioned in the molecular plane of the water molecule, i.e. $\beta = 0$ in Figure 7, the

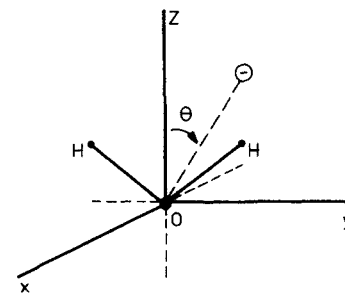


Figure 5. Theoretically expected orientation of the anion-oxygen axis. Polar coordinates: $\phi = 90^\circ$, θ .

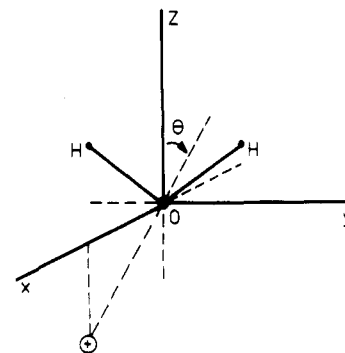


Figure 6. Theoretically expected orientation of the cation-oxygen axis. Polar coordinates: $\phi = 0^\circ$, θ .

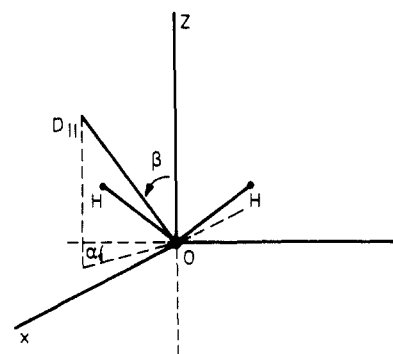


Figure 7. Definition of the orientation of the $D_{||}$ axis of the diffusion tensor with respect to the molecular frame, characterized by the angles α and β .

effective correlation time for D relaxation should be longer than the ^{17}O correlation time. This conflicts with the observed equality of the correlation times. If we assume anisotropic axially symmetric diffusion for the hydrated water molecules it turns out that equal correlation times for D and ^{17}O are obtained within experimental accuracy for a set of values for α and β depending on the ratio $D_{||}/D_{\perp}$. No solution is obtained, however, for $\beta \leq 45^\circ$. Therefore, the $D_{||}$ axis does not lie within the molecular plane.

In case of cation hydration water the D and ^{17}O effective correlation times differ outside experimental error. The difference in the effect of the cationic field intensity on the relaxation rates of D and ^{17}O directly confirms the anisotropy of the environment of the water molecules in the hydration shell of the cations. The experimental cationic effective hydration water correlation times will now be discussed in terms of the orientation of the diffusion tensor and the amount of anisotropy.

The orientation of the principal axis system of the diffusion tensor with respect to the molecular frame is characterized by the angles α and β defined in Figure 7. Theoretical considerations,²⁹ MD results,⁶ and the neutron scattering ion-water pair correlation functions²⁶ strongly suggest that the interaction of water molecules and cations is symmetrical with respect to the plane containing the bisectrix of the H_2O bond angle and the cation.

(26) J. E. Enderby and G. W. Neilson, *Rep. Prog. Phys.*, **44**, 38 (1981).

(27) K. J. Müller and H. G. Hertz, *Z. Phys. Chem. (Frankfurt am Main)*, **140**, 31 (1984).

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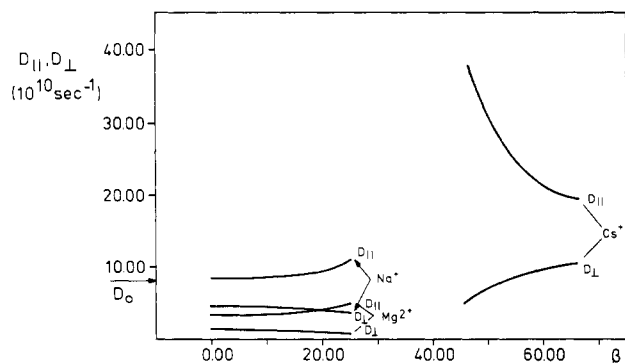


Figure 8. Reorientational diffusion constants, D_{\parallel} and D_{\perp} , of cationic hydration water of an infinitely diluted complex as a function of the angle β , $\alpha = 90^\circ$. The pure water constant is denoted by D_0 .

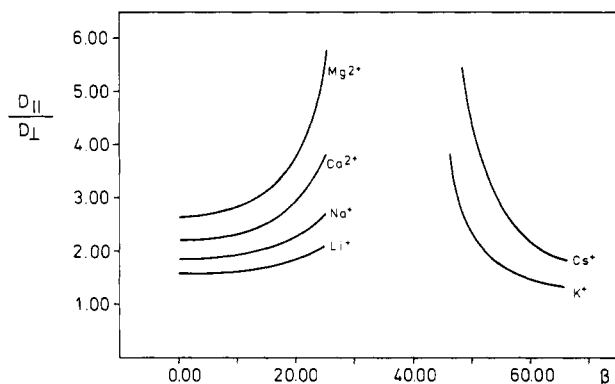


Figure 9. The degree of anisotropy, D_{\parallel}/D_{\perp} , of cationic hydration water of an infinitely diluted complex vs. the angle β .

It will therefore be assumed that the symmetry axis of the diffusion tensor is confined to the bisector plane of the water molecule (i.e., $\alpha = 90^\circ$) leaving only the angle β to be determined from the effective correlation times for the ^{17}O and D relaxation rates in the hydration shell.

From the two simultaneous equations for the effective correlation times τ_D^* and $\tau_{^{17}\text{O}}^*(\text{H}_2\text{O})$ it is possible to calculate the elements D_{\parallel} and D_{\perp} of the diffusion tensor for a given value of β . It was checked that small changes in the coupling constants as determined at 4 *m* salt solutions do not significantly change the results discussed below. As the coupling constants for hydration water in infinitely diluted salt solutions are unknown, the bulk water constants have been used. It turns out that physically acceptable solutions are only available in the range $0 < \beta \leq 30^\circ$ for Mg^{2+} , Ca^{2+} , Na^+ , and Li^+ , while in the case of the large cations Cs^+ and K^+ $\beta \gtrsim 40^\circ$ is found. For Mg^{2+} , Na^+ , and Cs^+ the possible solutions are displayed in Figure 8. As the angle β is defined with respect to the molecular plane of the water molecule, each value of β implies two possible orientations of D_{\parallel} with respect to the vector connecting the cation and the oxygen nucleus of the water molecule. From the symmetry of the cation-water interaction it seems reasonable to choose the D_{\parallel} orientation coincident with the direction of the electric field of the cation, which is nearly parallel to the cation-oxygen axis, as displayed in Figure 6. Thus the angle β characterizes the orientation of the water molecule with respect to the cation and it equals θ in Figure 6. Recent NMR experiments show the angle θ of the water orientation within the lithium hydration shell of a 0.2 *m* LiCl solution to be in the range 0 – 30° if an outer first hydration shell contribution to the ^7Li relaxation rate is accounted for.³⁰

It may be seen from Figure 8 that around the highly charged and small cations the water molecules are oriented with a small angle between their bisectrix and the ionic field. Concurrently these structure forming ions slow down the molecular motion of the neighboring water molecules and induce a certain amount of

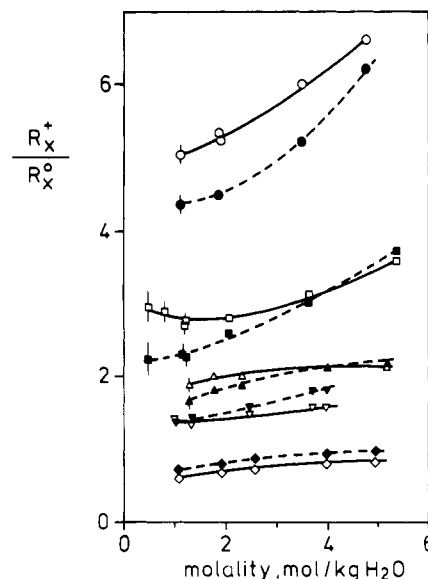


Figure 10. Cationic hydration water relaxation rates divided by the values of pure water vs. the molality. Cl^- was used as a reference. For the different nuclei the following notations are used: D, open symbols; ^{17}O , filled symbols. The symbols employed for the different cations are the following: Mg^{2+} , \circ ; Ca^{2+} , \square ; Li^+ , \triangle ; Na^+ , ∇ ; and Cs^+ , \diamond . Curves are drawn as an aid to the eye. Dashed curves denote ^{17}O relaxation, while for D relaxation rates solid curves are used.

anisotropy in their motion, as depicted in Figure 9. For large ions such as Cs^+ and to a lesser degree K^+ the dipole-ionic field interaction is relatively less important. In this context it is of interest to note that, if the angle θ increases to 52° , the hydration water molecule may form hydrogen bonds with surrounding water molecules. It is seen in Figure 9 that, for $\beta = 52^\circ$, the structure-breaking ions still induce some motional anisotropy.

From these NMR data regarding the cationic influence on the water molecules at infinite dilution it is seen that this influence on the dynamical behavior is limited. If we assume bulk water to reorient isotropically a distinct but moderate anisotropy is induced even by Mg^{2+} and Li^+ .

Effects of Electrolyte Concentration. After this discussion of the influence of ions with a common counterion on water molecules in the hydration shell of these ions at infinite dilution of the salts, attention may now be directed to the concentration dependence of the water nuclear relaxation rates as depicted in Figures 1 and 2.

As the dependence of the relaxation rates on the salt molality is nonlinear it must be concluded that the rates in the hydration shell, in bulk water or in both phases, depend on the molality. Now it should be noted that the ratio of the D and ^{17}O relaxation rates can only change due to a change of the diffusion tensor, because a sufficient change in the ratio of the coupling constants for these nuclei is not to be expected. From Figures 1 and 2 it is seen that the ratio R_x^+/R_x^0 is clearly concentration dependent. In view of the moderate anisotropy of the dynamical behavior of the hydration water molecules it is improbable that significant anisotropy will be induced outside the first hydration shell. Therefore, the concentration dependence of R_D^0 , $R_{^{17}\text{O}}^0$, and $R_D^0/R_{^{17}\text{O}}^0$ will be assigned to the first hydration shell. Indeed neutron scattering pair correlation functions for water nuclei around Ni^{2+} and Li^+ show a concentration dependence of the orientation within the first hydration shell.²⁶ Relative hydration water relaxation rates R_x^+/R_x^0 calculated with the model discussed in the Introduction are displayed in Figures 10 and 11.

The concentration-dependent dynamic behavior of the cation hydration shell may now be discussed. According to the rotation diffusion model used here, the effective D correlation time is longer than the effective ^{17}O correlation time if the angle $\beta \leq 30^\circ$ (Figure 7). If the orientational angle β of the diffusion tensor increases to $\beta \gtrsim 40^\circ$ the ^{17}O correlation time becomes the larger of the two. According to eq 19 the relative relaxation rates R_x^+/R_x^0 should

(30) R. Mazitov, K. J. Müller, and H. G. Hertz, *Z. Phys. Chem. (Frankfurt am Main)*, **140**, 55 (1984).

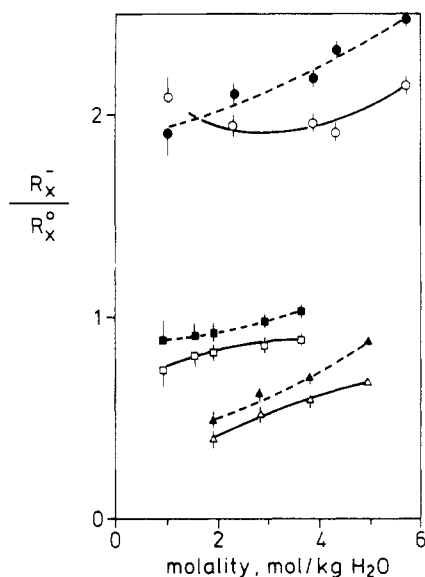


Figure 11. As in figure 10, but for anionic hydration water. K^+ was used as a reference. The symbols employed for the different anions are the following: F^- , \circ ; Cl^- , \square ; and I^- , Δ .

behave in exactly the same way as the effective correlation times. Thus it is concluded from Figure 10 that the angle β in the hydration shell of Mg^{2+} should remain below $\sim 30^\circ$ in the range of concentrations studied. This contrasts with the behavior around Ni^{2+} where θ reaches a value of 42° at $1.5\ m$.²⁶ Alternatively this might indicate that in the Mg^{2+} hydration shell $D_{||}$ is not completely coincident with the direction of the ionic electric field (i.e., $\beta \neq \theta$). The results for Ca^{2+} and Li^+ show that the relative D and ^{17}O relaxation rates cross in the $4\ m$ range. Here β is seen to increase from values $\beta \lesssim 30^\circ$ at low concentration to $\beta \gtrsim 40^\circ$ at high concentration, definitely indicating a change in the hydration water properties as a function of the salt concentration. For Na^+ ions the increase of β to the region $\beta \gtrsim 40^\circ$ occurs at relatively low concentration ($1\text{--}2\ m$) while in the limit $m \rightarrow 0$ β is found to be less than 30° . In the hydration shell of the larger ions, K^+ and Cs^+ , $\beta \gtrsim 40^\circ$ is found in the whole concentration range.

Thus one arrives at the following view of the orientation of water molecules in the first hydration shell of cations if β equals θ . In the case of small highly charged cations (Mg^{2+}), there is a clear orientation of the water molecule in the direction of the ion ($\beta \lesssim 30^\circ$) even at high concentrations. For Ca^{2+} , Li^+ , and Na^+ a perturbation of the orientation at infinite dilution occurs at concentrations that increase with the electric field at the ionic

surface. This trend continues with K^+ and Cs^+ where, even at infinite dilution, one finds $\beta \gtrsim 40^\circ$.

Rotation diffusion constants have not been calculated as a function of concentration, because the exact values of β are of course unknown. The degree of anisotropy will be quite moderate anyway, as was already found for infinite dilution.

The concentration dependences of the relative D and ^{17}O anion hydration water relaxation rates, as displayed in Figure 11, differ outside experimental error. As discussed in the preceding section the anion and hydration water molecule are expected to be coplanar, as displayed in Figure 5. If the $D_{||}$ axis of the diffusion tensor is positioned in the molecular plane, i.e. $\beta = 0$, the effective D correlation time has to be longer than the ^{17}O correlation time. The relative anion hydration water relaxation rates, as displayed in Figure 11, however, show a longer ^{17}O effective correlation time in the whole concentration range and for all anions studied (see eq 19). The motion within the hydration shell is clearly anisotropic, but the values for α and β depend on the ratio $D_{||}/D_{\perp}$. No solutions are, however, obtained for $\beta \lesssim 45^\circ$. The $D_{||}$ axis is not positioned in the molecular plane. As in case of cationic hydration water the degree of anisotropy is moderate. The anisotropy of the motion within the anionic hydration shell at higher concentrations supports the expectation of anisotropic motion in the limit of infinite dilution.

Conclusions

Magnetic relaxation rates of the nuclei of the water molecules yield structural and dynamical information about hydration water that is complementary to neutron diffraction results. The influence of the ions on the O-H bond length and on the D quadrupole coupling constant is found to be significant but moderate for the ions investigated here.

The orientational mobility of the water molecules decreases in the proximity of the structure-making ions and it increases near the structure-breaking ions. A moderate anisotropy is observed in the reorientational motion.

For the cation hydration water the major axis of the molecular diffusion tensor may consistently be taken to lie in the bisectrix plane of the water molecule. For the anionic hydration water this axis does not lie in the plane of the water molecule.

The increasing amount of structural information from neutron diffraction and the application of NMR may allow the investigation of more detailed dynamical models in the near future. In such a model the approximate description in terms of free anisotropic rotational diffusion should probably be extended to include interaction potentials.

Registry No. $MgCl_2$, 7786-30-3; KCl , 7447-40-7; $CsCl$, 7647-17-8; $LiCl$, 7447-41-8; $NaCl$, 7647-14-5; $CaCl_2$, 10043-52-4; KI , 7681-11-0; KBr , 7758-02-3; H_2O , 7732-18-5; ^{17}O , 13968-48-4; D_2 , 7782-39-0.