

On the structure and dynamics of water in AlCl_3 solutions from H, D, ^{17}O , and ^{27}Al nuclear magnetic relaxation

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(Received 10 September 1986; accepted 11 December 1986)

The relaxation rates of ^{27}Al , H, D, ^{17}O , and the relaxation rate of H due to dipolar coupling to ^{17}O were obtained in a series of aqueous AlCl_3 solutions. From these data conclusions are reached about bulk water dynamics, the O–H bond distance, and the order within the Al^{3+} hydration shell. The bulk water dynamics is interpreted by a hydrodynamical model. For comparison viscosity data are presented. It is found that the change in the O–H distance of water molecules adjacent to Al^{3+} is significant and in agreement with reported theoretical results. The destruction of order within the Al^{3+} hexaquo complex with increasing concentration is indicated.

I. INTRODUCTION

The dynamical properties of water beyond the first hydration shell of ions have attracted renewed interest. Quasi-elastic neutron scattering experiments of Hewish *et al.* show a small influence on the dynamical behavior of bulk water in NiCl_2 and MgCl_2 solutions.¹ In the case of the monovalent ions Li^+ and Cs^+ , such an effect could not be detected. These results were interpreted in terms of a second hydration zone, an explanation which has recently been questioned by Friedman.² Friedman proposed a hydrodynamical long range effect to be responsible for the observed phenomena.

In Sec. III A the reorientational dynamics of bulk water in AlCl_3 solutions are discussed. At 298 K, the exchange time of water molecules between the Al^{3+} hydration site and the bulk is of the order 1 s. Hence, for ^{17}O NMR the slow exchange limit applies and the spectrum consists of two resonances.^{3,4} However, the hydration water resonance is located under the intense bulk water resonance. Because the relaxation rates of both resonances differ by a factor of 7, the bulk water relaxation time can be determined separately. The data will be analyzed by a hydrodynamical model. The result for the hydrodynamic radius of the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex is found to be in agreement with reported experimental data.

NMR investigations on the influence of monovalent ions⁵ and Mg^{2+} ⁶ on the O–H bond length and the D coupling constant of neighboring water molecules were reported recently. In Sec. III B these results will be summarized and extended with the result of the triple charged Al^{3+} ion. Comparison will be made to recent *ab initio* calculations of Newton *et al.*⁷ and MD simulations of Bopp employing the modified central force model.⁸

In Sec. III C results will be presented on the concentration dependence of the ^{27}Al quadrupolar relaxation and the hydration water deuterium relaxation. These data are in agreement with the hydrodynamical interpretation of bulk water dynamics, as presented in Sec. III A. An onset of internal motion and a diminished quenching of the field gradient within the Al^{3+} hydration shell with increasing concentration is indicated.

II. EXPERIMENTAL SECTION

A. Chemicals and solutions

All solutions were prepared by weight. All manipulations with isotopically enriched water were performed at 5 °C to minimize exchange with atmospheric humidity. Solutions prepared for proton measurements were shaken five times with argon to remove gaseous oxygen. NMR tubes (homemade, quartz) were heated in a NaHCO_3 solution, heated in an EDTA solution, and then stored for at least one week filled with deionized and filtered water.

Oxygen isotopically enriched water was obtained from Monsanto Research Corp., Miamisburg, containing 9.9% 0–16, 51.1% 0–17, and 39.0% 0–18 D_2O was obtained from Merck, Darmstadt. Distilled water was deionized and filtered by a Milli-Q water purification system (Millipore Corp.). The conductance did not exceed $1 \times 10^{-6} \text{ cm}^{-1} \Omega^{-1}$. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, gold label quality, originated from Aldrich. For viscosity experiments $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was obtained from Brocacef BV.

B. Viscosity experiments

The viscosity was determined with a Ubbelohde viscometer. The density was measured with a conventional pycnometer. Results are presented in Table I. The temperature was maintained at 25.0 ± 0.1 °C.

TABLE I. Density and viscosity data for AlCl_3 solutions at 298 K.

Molarity, mol/l	Density, g/ml	Viscosity, cP
0.50	1.053	1.27
0.97	1.102	1.83
1.25	1.132	2.39
1.41	1.149	2.80
1.68	1.175	3.64
1.82	1.190	4.29
2.05	1.212	5.55
2.12	1.219	6.05
2.30	1.237	7.54
2.39	1.247	8.56
2.61	1.268	11.4

C. Determination of relaxation rates

All rates were measured on a homebuilt spectrometer equipped with a 2.1 T electromagnet (Bruker). The temperature was maintained at 25.0 ± 0.2 °C by a 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 the π and the $\pi/2$ pulses was alternated.⁹ In case of ^{17}O NMR, the collecting of data points started when a time interval of five times the hydration water relaxation time after the π pulse has elapsed. Within this interval, the hydration water resonance is sufficiently relaxed towards equilibrium. The hydration water ^{17}O transverse relaxation time was estimated by linewidth measurement, while the bulk water resonance was suppressed by inversion recovery.¹⁰ One hundred data points were collected and fitted to a single exponential by a nonlinear least-squares procedure. For H, D, and ^{17}O relaxation behavior pH dependence was not observed. For ^{27}Al relaxation measurements the samples were acidified with a droplet of HCl. Isotope effects on the relaxation rates were corrected as described before.⁵ The results are presented in Table II.

III. RESULTS AND DISCUSSION

A. Bulk water dynamics

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

$$R_{\text{O}}^b = \frac{3}{125} (2\pi\chi_{\text{O}}^b)^2 (1 + \eta_{\text{O}}^2/3) \tau_{\text{O}}^b. \quad (1)$$

The quadrupolar coupling constant and the asymmetry parameter are denoted by χ_{O}^b and η_{O}^b , respectively. The superscript b denotes that bulk water is referred to. The correlation time τ_{O}^b is the zero frequency Fourier component of the correlation function of the ^{17}O electric field gradient tensor. Because the relaxation process is completely intramolecularly determined, this correlation time refers only to reorientation dynamics.

The interaction constant and the correlation time are known reasonably well in pure water.^{6,11} Previous work shows the influence of monovalent ions on the quadrupolar interaction constants of their neighbors to be small.⁵ Therefore, a change of the bulk water interaction constant with respect to pure water will be neglected. Under this assumption the ratio bulk water rate to the pure water value may be expressed as

$$\frac{R_{\text{O}}^b}{R_{\text{O}}^o} = \frac{\tau_{\text{O}}^b}{\tau_{\text{O}}^o}. \quad (2)$$

In this equation R_{O}^o and τ_{O}^o denote the pure water ^{17}O relaxation rate and correlation time, respectively. For the ^{17}O relaxation rate in solvent medium H_2O at 25 °C one has¹²

$$R_{\text{O}}^o = 141.6 \pm 0.5 \text{ s}^{-1}. \quad (3)$$

The ratio $R_{\text{O}}^b/R_{\text{O}}^o$ is displayed in Fig. 1 as a function of the molarity. A remarkable influence on the reorientational dynamics beyond the first hydration shell of Al^{3+} is observed.

A possible explanation for the observed bulk water ^{17}O relaxation enhancement is a second hydration shell effect. The influence of Cl^- ions on the water dynamics is small and cannot account for the observed effect.⁵ Previous work shows a correlation between the hydration water relaxation rate and the electric field intensity on the surface of the ion.⁵ According to this correlation, the electric field on the surface of the Al^{3+} hexaquo complex is not intense enough to induce the observed relaxation enhancement in terms of a single layer second hydration zone. Radial distribution functions

TABLE II. Isotope effects corrected relaxation rates and isotopic composition of the samples.^a

Molality	n	$p17$	$p18$	$R_{\text{H}}, \text{s}^{-1}$	$R_{\text{D}}, \text{s}^{-1}$	$R_{\text{O}}^b, \text{s}^{-1}$	$R_{\text{Al}}, \text{s}^{-1}$
0.76	0.012	0.0032	0.0089	...	4.50	202	11.0
0.79	0.723
1.19	0.010	0.0028	0.0079	0.998	6.15	249	15.0
1.22	0.011	0.0029	0.0079	...	6.30	252	...
1.26	1.015
1.70	0.005	0.0016	0.0051	...	8.97	331	22.9
1.73	1.43
2.09	0.006	0.0018	0.0054	...	11.29	418	30.3
2.12	1.83
2.50	0.005	0.0016	0.0051	...	15.27	523	43.0
2.53	2.45
1.13	0.012	0.0032	0.0088	...	5.78	235	...
1.12	0.920
1.15	...	0.1430	0.1104	1.10
1.17	...	0.2302	0.1767	1.26
1.20	...	0.3419	0.2615	1.40
1.20	...	0.4449	0.3398	1.50

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

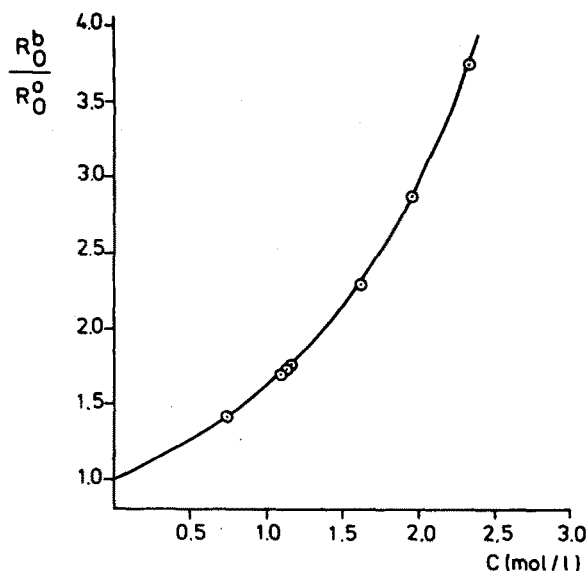


FIG. 1. Relative bulk water ^{17}O relaxation rate vs molarity. The line gives the fit obtained using Eqs. (5)–(7) together with the values given in Table III for ϕ_m and s .

for Nd^{3+} and Dy^{3+} interactions obtained by neutron diffraction do not show a second hydration zone.^{13,14} The very little bump beyond the first hydration shell is more probably due to cation–chloride interactions.¹⁵ Therefore, a hydrodynamical interpretation will be presented, as was proposed by Friedman to interpret bulk water dynamics in NiCl_2 and MgCl_2 solutions.²

When a water molecule reorients, a flow in the surrounding fluid is produced. This flow is spatially nonuniform, and hence there is a viscous dissipation of momentum and energy. As was recently stressed by Zwanzig *et al.*, this dissipation and the reorientational correlation time are proportional to the first power of the viscosity of the fluid.¹⁶ The presence of ions in solution causes an increase of this dissipation. As a consequence, the effective relative viscosity of bulk water η_r^b is increased. Accordingly, the ratio of the bulk water reorientational correlation time to the pure water value should be proportional to η_r^b . Hence, according to Eq. (2) one obtains

$$\frac{R_O^b}{R_O^o} = \eta_r^b. \quad (4)$$

A failure of hydrodynamics is usually regarded to be due to the short ranged solute–solvent interactions. However, in AlCl_3 solutions these interactions seem to be less important. The $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex is rather big and the boundary consists of water molecules. The dynamical influence of Cl^- on water is known to be small.⁵ As a consequence hydrodynamics is expected to work well. To allow a comparison between the microscopic bulk viscosity η_r^b as probed by ^{17}O NMR and the macroscopic relative viscosity η_r^m , the latter data are displayed in Fig. 2. A difference between the macroscopic viscosity and the microscopic bulk water viscosity is observed.

From hydrodynamic theory, Bedeaux proposed the fol-

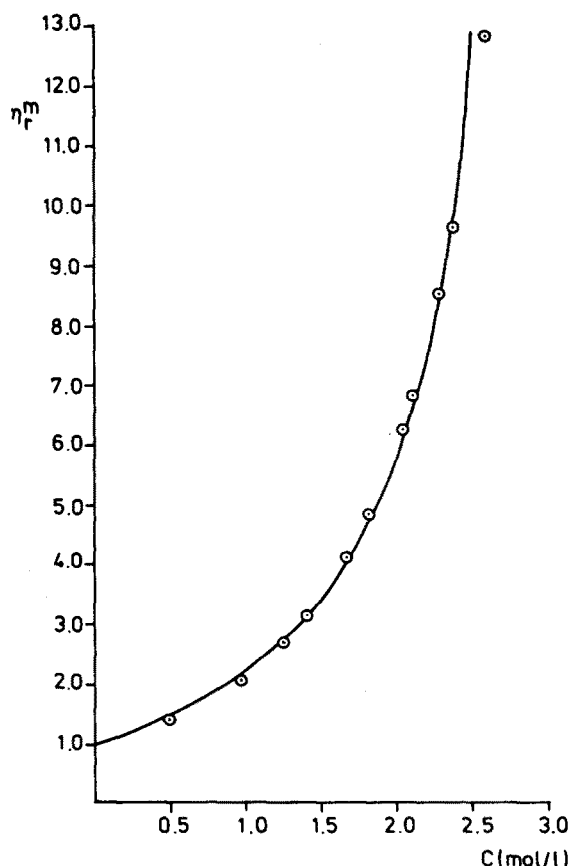


FIG. 2. Relative macroscopic viscosity vs molarity. The line gives the fit obtained using Eqs. (5)–(7) together with the values given in Table III for ϕ_m and s .

lowing formula for the effective viscosity of a suspension of spheres¹⁷:

$$\eta_r = \frac{1 + 3/2\phi[1 + S(\phi)]}{1 - \phi[1 + S(\phi)]}. \quad (5)$$

The volume fraction ϕ is expressed in the molarity c of the solution

$$\phi = \phi_m c \quad (6)$$

in which ϕ_m denotes the solute volume per mole. The term proportional to $S(\phi)$ takes into account the interactions and correlations between the spheres. This term may be expanded in powers of ϕ . Any dielectric dissipation due to the motion of water molecules in the electric field of ions has been neglected.

As displayed in Figs. 1 and 2, Eq. (5) describes both the bulk water ^{17}O relaxation data and the macroscopic viscosity data well. In case of the macroscopic viscosity, one obtains an acceptable fit with the term proportional to $S(\phi)$ equal to zero. It should be borne in mind, that there is only one adjustable parameter left. In case of the bulk water relaxation data one should expand $S(\phi)$ to first order in ϕ :

$$S(\phi) = s\phi. \quad (7)$$

However, even if one neglects this term, Eq. (5) still describes the ^{17}O relaxation data well. Values of the parameters s and ϕ_m , resulting from the fit of Eqs. (5)–(7) to the data displayed in Figs. 1 and 2, are collected in Table III.

TABLE III. Parameters resulting from the fit of Eqs. (5)–(7) to the data displayed in Figs. 1 and 2, and some derived quantities.

	ϕ_m , ℓ/mol	s	r_c^h , Å	τ_c^h , ps
η_r^m	0.33 ± 0.01	0	4.82	102
$R_D^0/R_D^0(=\eta_r^0)$	0.1756 ± 0.0004	0.70 ± 0.01	3.73	47.0

At this moment an interpretation of the parameter s is not feasible. However, the solute volume fraction may be used to derive the hydrodynamic radius of the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex. These values, as obtained from the fitted volumes ϕ_m and after subtracting the volume of Cl^- , are also collected in Table III. The volume of Cl^- has been estimated from the radius 1.81 Å. The hydrodynamic radius as derived from the bulk water ^{17}O rates agrees reasonably with the radius estimated from the relevant minimum in the neutron diffraction radial distribution functions for, e.g., Nb^{3+} and Dy^{3+} .^{13,14} Comparing these data one must bear in mind a difference in ionic radii between these ions. The result as derived from the macroscopic viscosity data is somewhat too high.

To allow further comparison with experimental data, the reorientational correlation time of the Al^{3+} hexaquo complex will be estimated. According to the Stokes–Einstein relation this correlation time is expressed in terms of the hydrodynamic volume

$$\tau_c^h = \frac{4}{3} \pi r_c^h{}^3 \eta / kT \quad (8)$$

(stick boundary conditions are assumed). By inserting the pure water viscosity ($\eta = 0.8904$ cP) and the hydrodynamic radius as presented in Table III, one obtains the hydrodynamic reorientational correlation time of a infinitely diluted complex. These values are also presented in Table III. Hertz *et al.* obtained for the correlation time of the Al–H vector the result: $\tau_c = 53 \pm 13$ ps ($c \rightarrow 0$).¹⁸ For Cr^{3+} by the study of the frequency dependence of the proton relaxation one has: $\tau_c = 49 \pm 3$ ps ($c = 1.4 \cdot 10^{-3}$ mol/ ℓ).¹⁹ The crystal radius of Cr^{3+} is 0.63 Å and comparable to the value of Al^{3+} (0.51 Å). The correlation time as obtained from the hydrodynamical interpretation of bulk water ^{17}O relaxation agrees well with these reported values. Hence, it is concluded that this interpretation is acceptable. Further experimental support will be presented in Sec. III C. The interpretation using the macroscopic viscosity, η_r^m , yields too large values for the radius and therefore the correlation time of the hexaquo complex. An explanation connecting the macroscopic viscosity and NMR data can not be given at present.

In Sec. III B the hydration water O–H bond length and the D quadrupolar coupling constant will be evaluated. For this purpose the contribution of oxygen-17 to the proton relaxation was determined experimentally to allow a comparison with the deuterium relaxation rate.

B. Hydration water interaction constants

The D relaxation rate is determined intramolecularly by the quadrupolar interaction, with rate

$$R_D = \frac{3}{8} (2\pi\chi_D)^2 (1 + \eta_D^2/3) \tau_D \quad (9)$$

in which the definitions of the symbols correspond to those given below Eq. (1) for ^{17}O relaxation. The intramolecular part of the H– ^{17}O dipolar interaction contribution to the H relaxation rate is given by

$$R_{\text{OH}}^{\text{intra}} = \frac{35}{3} (\gamma_{\text{H}}^2 \gamma_{^{17}\text{O}}^2 \hbar^2) / r_{\text{OH}}^6 \tau_{\text{OH}} \quad (10)$$

in which r_{OH} denotes the O–H bond length. To evaluate the correlation times, knowledge is needed about the interaction constants. This problem may be solved due to the fact that the correlation times τ_{OH} and τ_D are in fact equal. To obtain the O–H bond length, D coupling constant, and the correlation time, the following method will be applied. This method is applicable to both hydration water as well as pure water.

For both the quadrupolar and the dipolar interaction mechanism the lattice part of the coupling Hamiltonian is given by the second order spherical tensor elements $V_k^{(2)}$.²⁰ In the principal axis system of the dipolar interaction one has

$$V_k^{(2)} = \delta_{0k} (2/3)^{1/2} r_{\text{OH}}^{-3}. \quad (11)$$

In the principal axis system of the quadrupolar interaction these elements are defined as

$$V_0^{(2)} = (3/2)^{1/2} \text{eq}, \quad (12a)$$

$$V_{\pm 1}^{(2)} = 0, \quad (12b)$$

$$V_{\pm 2}^{(2)} = -\frac{\eta}{2} \text{eq}. \quad (12c)$$

The principal axis of the H– ^{17}O dipolar interaction tensor coincides with the principal axis 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 components are very small with respect to the main $V_0^{(2)}$ component. These two features combined then lead to an approximate equality of the effective correlation times for these relaxation mechanisms, irrespective of the details of the motion. In case of isotropic reorientation, this equality holds within 0.6%, as was recently confirmed in pure water.⁶ This equality is exact when η_D is neglected. As the correlation times of water molecules within the complex are mainly determined by the overall reorientational motion, a D solute isotope effect¹² has been neglected.

Quantum chemical calculations show the main factor determining χ_D is the O–D bond length, while the bond angle is of minor importance.^{21–23} Recently a semiempirical correlation connecting χ_D and r_{OH} was proposed⁶:

$$\chi_D = \frac{595 \pm 11}{r_{\text{OH}}^3} - (390 \pm 9) r_{\text{OH}}. \quad (13)$$

This relation reproduces experimental data and theoretical results quite well. A small difference between the O–H and the O–D bond length has been neglected. Now from Eqs. (9), (10), and (13), and the equality of the effective correlation times, one can obtain r_{OH} , χ_D , and τ_D ($=\tau_{\text{OH}}$).

In case of D and H NMR only one resonance is observed, because of the fast L ($=\text{H}$ or D) exchange between the Al^{3+} hydration complex and the bulk.^{24,25} There is no

exchange contribution to the longitudinal relaxation rates, as was confirmed by an independence of the rates on pH. The deuterium relaxation rate R_D of a 1.13 m solution is shown in Table II. Proton relaxation rates R_H are displayed in Fig. 3 as a function of the ^{17}O mole fraction. All rates are interpolated to molality 1.13. In view of the observed linearity one has

$$R_H = R_{HH} + p_{17} R_{OH} \quad (14)$$

in which R_{HH} and R_{OH} denote the H–H and H– ^{17}O , respectively, dipolar interaction contribution to the H relaxation. The intermolecular contribution to R_{OH} is unknown, but will be taken to be 2% of the total H– ^{17}O dipolar interaction contribution, as it is in pure water.¹² From the fit of Eq. (14) to the data displayed in Fig. 3 and after subtracting the 2% intermolecular interaction contribution, one obtains

$$R_{OH}^{\text{intra}} = 1.190 \pm 0.027 \text{ s}^{-1}. \quad (15)$$

Due to the fast L exchange the D relaxation rate and the H– ^{17}O dipolar interaction contribution to the H relaxation rate may be decomposed into the contributions of Al^{3+} hydration water and the bulk

$$R_x = R_x^+ f^+ + (1 - f^+) R_x^b \quad (16)$$

in which the subscript x can be D or OH. The fraction hydration water f^+ is expressed in the molality m ,

$$f^+ = \frac{6m}{55.5}. \quad (17)$$

A homogeneous distribution of D and ^{17}O between hydration water and the bulk is assumed.

The bulk water rates, R_D^b and $R_{OH}^{b,\text{intra}}$, can be estimated from bulk water ^{17}O relaxation. The experimental ratio R_D^b/R_O^b reflects the ratio of the bulk water correlation time to the pure water value. By multiplying this ratio with the pure water values for D relaxation and H– ^{17}O dipolar relaxation, R_D^o and $R_{OH}^{o,\text{intra}}$, respectively, one can obtain the bulk water rates: R_D^b and $R_{OH}^{b,\text{intra}}$. A change of bulk water interaction constants with respect to the pure water values is explicitly neglected.

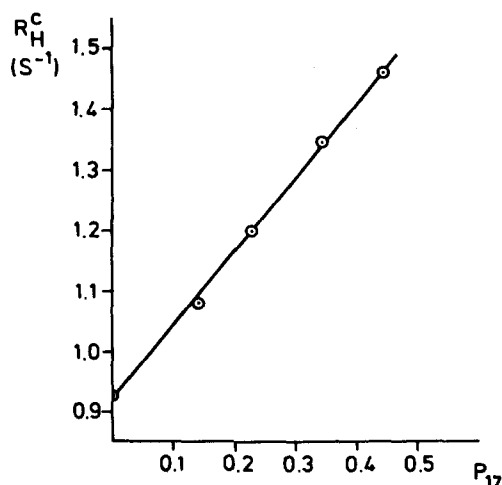


FIG. 3. Proton longitudinal relaxation rates, corrected for oxygen isotope viscosity effects (Ref. 5), as a function of the ^{17}O mole fraction in 1.13 m AlCl_3 solutions. The line is drawn according to the linear least-squares fit: $R_H = (0.921 \pm 0.008) + p_{17}(1.214 \pm 0.027)$.

citly neglected. Also a possible induced anisotropy in the bulk water reorientational motion with respect to pure water is ignored. For the D relaxation rate in solvent medium H_2O one has¹²

$$R_D^o = 1.944 \pm 0.004 \text{ s}^{-1} \quad (18)$$

and for the H– ^{17}O dipolar interaction

$$R_{OH}^{o,\text{intra}} = 0.270 \pm 0.011 \text{ s}^{-1}. \quad (19)$$

For the hydration water rates, calculated according to Eqs. (16) and (17) with the experimental rates, R_{OH}^{intra} and R_D , and the estimated bulk water rates, R_D^b and $R_{OH}^{b,\text{intra}}$, one obtains

$$R_D^+ = 23.54 \pm 0.24 \text{ s}^{-1} \quad (20)$$

for D relaxation, and for the intramolecular H– ^{17}O dipolar interaction contribution to the H relaxation

$$R_{OH}^{+,\text{intra}} = 6.43 \pm 0.15 \text{ s}^{-1}. \quad (21)$$

These hydration water relaxation rates refer to molality 1.13.

Hydration water values of the O–H bond length and the D coupling constant, as obtained from Eqs. (9), (10), (13), (20), and (21), and the equality of the effective correlation times, $\tau_D^+ = \tau_{OH}^+$, are presented in Table IV. For the discussion of the correlation times see below. Previously reported values of hydration water of monovalent ions,⁵ Mg^{2+} ,⁶ as well as pure water,⁶ are also collected in Table IV. In Ref. 5 somewhat different values were reported. This is because a somewhat different relation connecting χ_D and r_{OH} has been applied. However, the difference in reported values is less than 0.7%. Hydration water O–H bond lengths as well as the pure water value are displayed in Fig. 4 as a function of the electric field intensity on the surface of the ion. A linear correlation is observed

$$r_{OH} = (0.980 \pm 0.001) + (0.0034 \pm 0.0002)z/r_{\text{ion}}^2. \quad (22)$$

For comparison, results of recent *ab initio* calculations of ion–water clusters by Newton *et al.*⁷ and MD simulations of Bopp employing the modified central force model⁸ are also depicted in Fig. 4. All results are in agreement with our data within experimental error (1%). A possible small D isotope effect on the O–H bond length will shift the reported distances to a somewhat lower value in a systematic manner.

In Sec. III C the dynamics within the Al^{3+} hexaquo complex will be evaluated. To this end hydration water D

TABLE IV. Hydration water O–H bond length and D coupling constant. The value of pure water is also included.^a

Ion	Molality	χ_D^+ , kHz	r_{OH} , Å	Reference
Al^{3+}	1.13	164	1.019	This work
Mg^{2+}	1.00	213	0.996	6
	4.00	217	0.994	6
Li^+	3.96	236	0.986	5
Na^+	4.00	236	0.986	5
F^-	4.00	223	0.992	5
H_2O	...	254	0.978	6

^aThe estimated errors in r_{OH} and χ_D are, respectively, 1% and 3%.

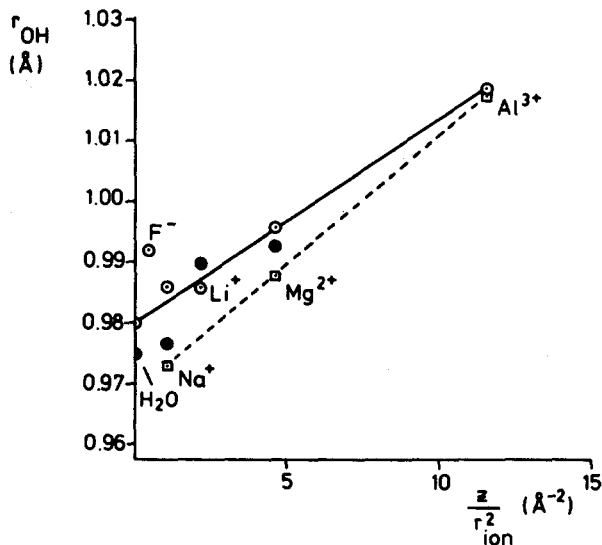


FIG. 4. Hydration water O-H bond length vs the electric field intensity on the surface of the ion. The electric field intensities are calculated using the Pauling ionic radii. The solid line is drawn according to a linear least-squares fit. The NMR results refer to concentrations as presented in Table IV. The following notation is used: experimental results, \circ ; *ab initio* results of Newton *et al.* (Ref. 7) \square ; MD results of Bopp (Ref. 8), \bullet . The MD result of Li^+ refers to a 13.9 m LiCl solution.

correlation times and ^{27}Al quadrupolar relaxation rates will be discussed.

C. Destruction of order within the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex with increasing concentration

As discussed in Sec. III B the hydration water D relaxation rate can be calculated according to Eqs. (16) and (17), and the estimated bulk water rate R_D^b . By inserting these values into Eq. (9) together with the D coupling constant as presented in Table IV, one obtains the hydration water D correlation time τ_D^+ . The value of the D asymmetry parameter η_D is of the order 0.1 and is in this context immaterial. The ratio of the hydration water D correlation time τ_D^+ to the relative bulk water viscosity η_r^b is displayed in Fig. 5 as a function of the concentration.

The hydration water D correlation time of a diluted complex can be derived by linear extrapolation of the ratio τ_D^+/η_r^b to zero concentration

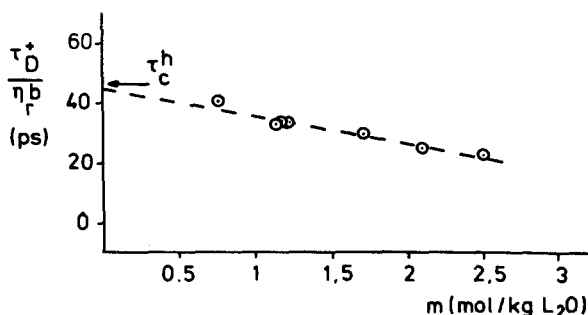


FIG. 5. The ratio hydration water D correlation time to the microscopic bulk water viscosity vs molality. The line is drawn to extrapolate to zero concentration.

$$\tau_D^+(m \rightarrow 0) = 45 \pm 2 \text{ ps.} \quad (23)$$

This value agrees with the value as derived from the hydrodynamical interpretation of bulk water dynamics (see Table III). There is also agreement with reported experimental data, as discussed in Sec. III A. Hence, it is concluded that in the limit of infinite dilution the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex reorients as a rigid body on the time scale of the overall reorientational motion.

At high concentration, the reorientational correlation time of the Al^{3+} hexaquo complex is expected to be proportional to the bulk water viscosity. As a consequence, if there is absence of internal motion, the hydration water D correlation time τ_D^+ is expected to be proportional to η_r^b . However, as observed in Fig. 5, the ratio τ_D^+/η_r^b shows a decrease as a function of the concentration. This might indicate the increasing influence of internal motion with increasing concentration, presumably around the O- Al^{3+} axis. Recent proton NMR experiments at low temperatures show a similar behavior.²⁶

Further experimental support for the destruction of order within the hydration shell originates from ^{27}Al quadrupolar relaxation. The general expression for the ^{27}Al relaxation rate is given by²⁷

$$R_1 = \frac{3}{125} \left(\frac{eQ}{h} \right)^2 \cdot \frac{2}{15} \int_0^\infty \langle V^{(2)}(0) \odot V^{(2)}(t) \rangle dt \quad (24)$$

in which $V^{(2)}(t)$ denotes the electric field gradient tensor. The quadrupolar relaxation rate depends both on the mean squared field gradient fluctuation and the temporal duration. In Ref. 27 more elaborate expressions are given. In case

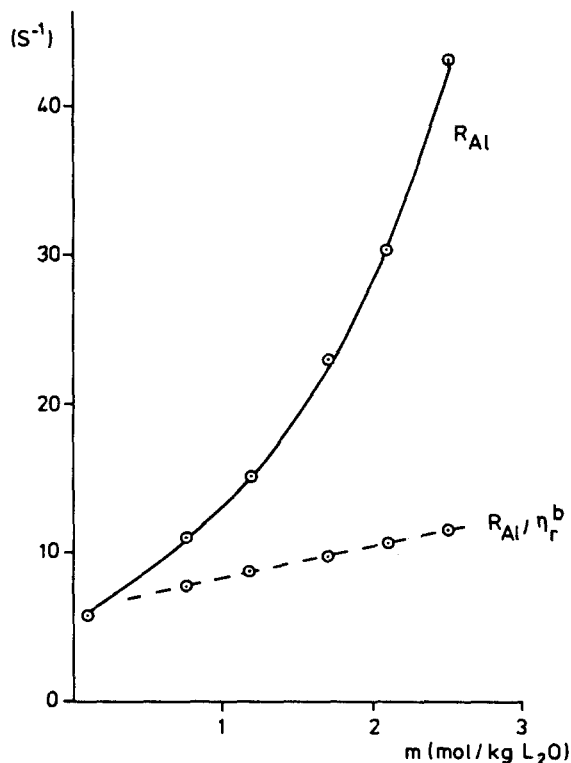


FIG. 6. The ^{27}Al relaxation rate and the ratio to the microscopic bulk water viscosity vs molality. Curves are drawn as an aid to the eye.

of Al^{3+} this electric field gradient is mainly caused by the first hydration shell. The main contribution originates from the distortion of the octahedral symmetry around the ion, which is modulated by reorientational motion of the complex. Also fluctuations arise due to internal motion of water molecules within the complex and ion-ion interactions.

The ratio of the ^{27}Al quadrupolar relaxation to the relative bulk water viscosity as a function of the concentration is displayed in Fig. 6. A linear relation is observed with a slightly positive slope. This indicates the reorientational motion of the complex indeed to be proportional to the relative bulk water viscosity, as probed by ^{17}O NMR. The slight increase as a function of the concentration is possibly due to an increase of the mean squared field gradient caused by an increased distortion of the octahedral symmetry of the complex.

IV. CONCLUSIONS

Bulk water ^{17}O NMR shows an influence on the bulk water dynamics in AlCl_3 solutions, which was interpreted by a hydrodynamical model. Comparison of the D relaxation and the H relaxation due to dipolar coupling to ^{17}O shows an increase of the hydration water O-H bond length. Finally, the destruction of order within the Al^{3+} hydration shell with increasing concentration was indicated by hydration water D relaxation data and the ^{27}Al quadrupolar relaxation.

Note added in proof: In Ref. 7 the H/D fractionation factor for trivalent ions was theoretically estimated to be 0.85. Taking this effect into account, one obtains $r_{\text{OH}} = 1.011 \text{ \AA}$ instead of 1.019 \AA for Al^{3+} hydration water.

These figures differ just within the uncertainty margin of 1%.

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