

## WATER AND ALUMINIUM SELF-DIFFUSION IN AQUEOUS $\text{AlCl}_3$ SOLUTIONS

J.R.C. VAN DER MAAREL and J. DE BLEIJSER

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

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Self-diffusion coefficients of  $^{27}\text{Al}$  and  $\text{H}_2\text{O}$  were determined by the NMR pulsed-field-gradient method in a series of  $\text{AlCl}_3$  solutions. From these data, bulk water self-diffusion coefficients are derived. It is shown that the relative influence on the bulk water translational motion agrees reasonably with the relative influence on the reorientational motion as reported in previous work. The bulk water self-diffusion is interpreted using a hydrodynamical model.

### 1. Introduction

An NMR investigation on the structure and dynamics of water in  $\text{AlCl}_3$  solutions was reported recently [1]. At 298 K, the exchange time of water molecules between the  $\text{Al}^{3+}$  hydration site and the bulk is of the order of 1 s. Hence, for  $^{17}\text{O}$  NMR the slow exchange limit applies and the bulk water  $^{17}\text{O}$  relaxation time can be determined separately. These experiments show an influence on the water reorientational dynamics beyond the  $\text{Al}^{3+}$  hydration.

As an extension of these results, self-diffusion coefficients of  $^{27}\text{Al}$  and  $\text{H}_2\text{O}$  were determined by the NMR pulsed-field-gradient technique in a series of aqueous  $\text{AlCl}_3$  solutions. The water self-diffusion coefficient is decomposed into contributions from  $\text{Al}^{3+}$  hydration water and bulk water. Identifying the hydration water self-diffusion coefficient with the  $^{27}\text{Al}$  diffusion coefficient then yields the bulk water self-diffusion coefficient. The influence on the bulk water translational motion is compared to the influence on the reorientational motion. Finally, the bulk water self-diffusion is analyzed using a hydrodynamical model.

### 2. Experimental

For chemicals and solutions see ref. [1]. A 3 molal stock solution was acidified with a drop of HCl to

avoid hydrolysis ( $\text{pH}=0.7$ ). Samples were prepared by dilution. Concentrations are presented in table 1.

Self-diffusion coefficients were determined by the NMR pulsed-field-gradient technique with a steady background gradient. For a description of the method ref. [2] may be consulted. All coefficients were determined 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 gradient pulses the lock was disabled. The temperature was maintained at  $298 \pm 0.2$  K by a fluid thermostat using Fluorinert grade FC-43 (3M Co.).

Water self-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.  $^{27}\text{Al}$  self-diffusion coefficients are quantitatively measured, i.e. without the use of a reference compound. For this purpose the magnitude of the pulsed gradient  $\bar{g}$  and the steady gradient  $\bar{g}_0$  were determined through the use of an intentional mismatch of gradient pulses [2]. The magnitude of  $\bar{g}_0$  was determined by fitting the shape of the spin echo. The value was typically 0.8 G/cm. The magnitude of the pulsed gradient  $\bar{g}$  ranged from 5 to 400 G/cm. The diffusion time between gradient pulses was 14 ms for both  $^{27}\text{Al}$  and protons. Water and  $^{27}\text{Al}$  self-diffusion coefficients ( $D^w$  and  $D^{\text{Al}}$ , respectively) are collected in table 1.

Table 1  
Concentrations and diffusion data for  $\text{AlCl}_3$  solutions at 298 K

Molality ( $\text{mol kg}^{-1}$ )	Molarity ( $\text{mol l}^{-1}$ )	$D^{\text{Al}}$ ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	$D^{\text{w}}$ ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	$D^{\text{b}}$ ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )
0.87	0.847	0.309	1.470	1.590
1.30	1.25	0.227	1.079	1.219
1.47	1.42	0.196	0.946	1.088
2.12	1.99	0.117	0.552	0.681
2.90	2.66	0.0613	0.279	0.378

### 3. Results and discussion

Aluminium and water self-diffusion coefficients are displayed in fig. 1. For comparison water self-diffusion data obtained by Hertz et al. are also displayed in fig. 1 [3]. There is excellent agreement. The  $\text{Al}^{3+}$  diffusion is extremely slow, comparable to the  $\text{La}^{3+}$  self-diffusion in  $\text{LaCl}_3$  solutions [4].

Due to the fast H exchange [5] and the long life-

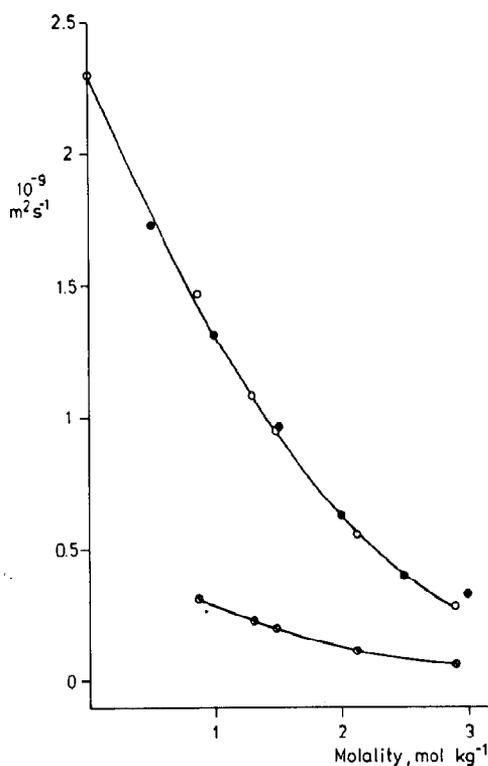


Fig. 1. Self-diffusion coefficients versus molality. Aluminium coefficients,  $\odot$ ; averaged water coefficients,  $\bullet$  and  $\circ$ . Open symbols, this work; filled symbols, ref. [3]. Lines are drawn as an aid to the eye.

time of the hydration shell [6], one can decompose the water self-diffusion coefficient into the contributions of  $\text{Al}^{3+}$  hydration water and bulk water

$$D^{\text{w}} = fD^+ + (1-f)D^{\text{b}}. \quad (1)$$

In eq. (1)  $D^+$  and  $D^{\text{b}}$  denote the hydration water and bulk water self-diffusion coefficients, respectively. The fraction of hydration water,  $f$ , is expressed in the molality  $m$

$$f = 6m/55.5. \quad (2)$$

The hydration water self-diffusion coefficient may be identified with the  $\text{Al}^{3+}$  diffusion coefficient

$$D^+ = D^{\text{Al}}. \quad (3)$$

Bulk water self-diffusion coefficients, obtained by inserting  $D^{\text{Al}}$ ,  $D^{\text{w}}$ , and the molality  $m$  into eqs. (1)–(3) are also presented in table 1.

The ratio of the pure water self-diffusion coefficient  $D^0$  to the bulk water diffusion coefficient  $D^{\text{b}}$  is displayed in fig. 2. For comparison, the ratio of the previously reported bulk water  $^{17}\text{O}$  relaxation rate to the pure water value  $R_{\text{b}}^{\text{b}}/R_{\text{b}}^0$ , is also shown in fig. 2. This ratio equals the corresponding ratio of the reorientational correlation times,  $\tau_{\text{b}}^{\text{b}}/\tau_{\text{b}}^0$ . In the range 0–1.5 molar, the relative influence on the bulk water self-diffusion equals the relative influence on the reorientational dynamics. At higher concentrations a small difference of approximately 10% is observed. This indicates a somewhat more restricted translational compared to reorientational motion. A possible explanation may be restricted self-diffusion due to the solute excluded volume.

As discussed in ref. [1], a hydrodynamical interpretation of bulk water dynamics in  $\text{AlCl}_3$  solutions prevails over an interpretation in terms of a second hydration zone effect. Accordingly, the ratio of the

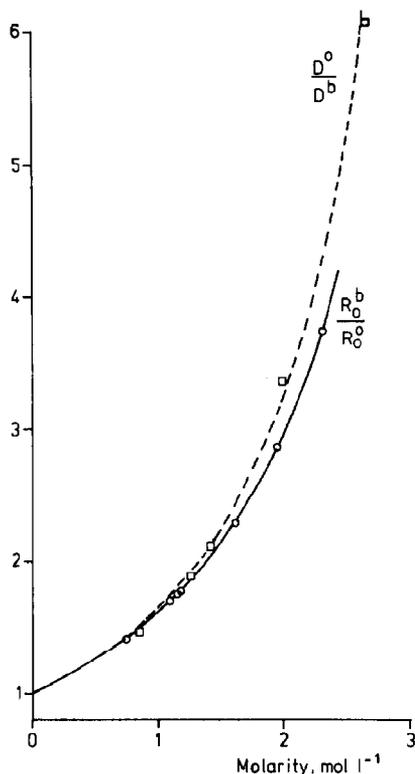


Fig. 2. The ratio  $D^0/D^b$  and the ratio  $R_0^b/R_0^0$  versus molarity. The bulk water  $^{17}\text{O}$  relaxation rates originate from ref. [1]. The lines are drawn according to the fit of eqs. (4)–(7) together with the values of the parameters  $s$  and  $\phi_m$  given in table 2.

pure water self-diffusion coefficient to the bulk water value should be proportional to the effective relative microviscosity of bulk water

$$D^0/D^b = \eta_r^b. \quad (4)$$

From hydrodynamic theory, Bedeaux proposed the following formula for the effective viscosity of a suspension of spheres [7]:

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

in which  $\phi$  denotes the volume fraction. This fraction can be expressed in the molarity  $c$  of the solution

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

in which  $\phi_m$  denotes the solute volume per mole. The term proportional to  $S(\phi)$  takes into account the interactions and correlations between the spheres and may be expanded to first order in  $\phi$ :

Table 2

Parameters resulting from the fit of eqs. (4)–(7) to the data displayed in fig. 2, and some derived quantities. The  $^{17}\text{O}$  relaxation data originate from ref. [1]

	$\phi_m$ ( $\ell \text{ mol}^{-1}$ )	$s$	$r_c^h$ ( $\text{\AA}$ )	$\tau_c^h$ (ps)
$D^0/D^b$	$0.17 \pm 0.01$	$1.0 \pm 0.4$	3.7	46
$R_0^b/R_0^0$	$0.1756 \pm 0.0004$	$0.70 \pm 0.01$	3.73	47.0

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

It should be borne in mind that eq. (5) was derived on the basis of purely hydrodynamical arguments. Any dielectric dissipation due to the motion of water molecules within the electric field of ions has been neglected.

In ref. [1] it was shown that eqs. (5)–(7) describe the macroscopic viscosity and the bulk water reorientational dynamics well. However, the interpretation using the macroscopic viscosity yielded too large a value for the solute volume fraction. A qualitative relation connecting the NMR data and macroscopic viscosity cannot be given. As displayed in fig. 2, eqs. (4)–(7) describe the bulk water self-diffusion as well. The curve gives the fit obtained using eqs. (4)–(7) together with the values given in table 2 for  $\phi_m$  and  $s$ . For comparison, the corresponding fit for bulk water  $^{17}\text{O}$  NMR data is also displayed in fig. 2. The two sets of values for  $\phi_m$  and  $s$  resulting from the fit to self-diffusion and  $^{17}\text{O}$  NMR data are equal within experimental accuracy.

An interpretation of the parameter  $s$  is not feasible. However, the solute volume fraction  $\phi_m$  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  $\phi_m$  and after subtracting the volume of  $\text{Cl}^-$ , are also presented in table 2. The volume of  $\text{Cl}^-$  has been estimated from its radius 1.81  $\text{\AA}$ . The hydrodynamic radii derived from the bulk water self-diffusion and  $^{17}\text{O}$  relaxation are equal and agree reasonably with the radius estimated from the relevant minimum in the neutron diffraction radial distribution functions for, e.g.  $\text{Nb}^{3+}$  and  $\text{Dy}^{3+}$  [8]. Comparing these data one must bear in mind the difference in ionic radii between these ions.

According to the Stokes–Einstein relation the reorientational correlation time of the  $\text{Al}^{3+}$  hexa-aqua

complex can be 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 given in table 2, one obtains the reorientational correlation time of an infinitely diluted complex. These values are also shown in table 2. There is agreement with reported experimental data, as discussed in ref. [1].

#### 4. Conclusions

The present self-diffusion experiments, together with previously reported  $^{17}\text{O}$ ,  $^{27}\text{Al}$ , and hydration water deuterium magnetic relaxation results [1], are in agreement with a hydrodynamical long-range effect on the dynamical behaviour of bulk water. It is shown that eq. (5) describes the dynamics well, although it has been derived for the effective viscosity of a suspension of uncharged spheres. However, the fitted volume fraction and the reorientational correlation time of the  $\text{Al}^{3+}$  hexa-aqua complex are in

agreement with reported neutron diffraction and magnetic relaxation data, respectively. It should be noted that the bulk water microviscosity as probed by  $^{17}\text{O}$  NMR and self-diffusion, differs substantially from the macroscopic viscosity. Therefore, for this kind of solution, one cannot evaluate microscopic transport quantities from macroscopic viscosity data.

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