X-Ray Diffraction Study of a Concentrated $Al(NO_3)_3$ Solution

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The scattering of X-rays from a concentrated $Al(NO_3)_3$ aqueous solution has been measured and analyzed at 25 °C. Good agreement with experimental data is achieved through a model in which $Al^{3+}(H_2O)_6$ interacts with twelve water molecules through short and linear H-bonds. The water molecules which are the nearest neighbors to the Al^{3+} ions have trigonal orientation and each 0 atom in the nitrate ion gives rise to about 2 weak hydrogen bonds with water molecules.

Introduction

In recent investigations on the structure of aqueous electrolyte solutions [1–3] it has been shown that the characteristics of the hydrogen bonds depend on the strength of the cation-OH bond. In particular, if we express this strength by the quantity $t = Z/CN$ (where Z is the formal cation charge and CN is its coordination number), it can be predicted that the water molecules nearest to the cation (W_1) will form strong and linear (H-bonds (shorter than 2.73 Å) with external water molecules (W_2) when $t > 0.4$ valence units. In this case the W_1 water molecules are generally oriented in such a way that they point with the negative end of their electric dipoles towards the metal ion (trigonal orientation), and their angle H–O–H greatly widens with respect to the tetrahedral value. These expectations have been confirmed in diffractometric investigations of $CrCl_3$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, and $AlCl_3$ aqueous solutions [4–6].

On the basis of these results we decided to extend our systematic research on the structure of aqueous electrolytes to a concentrated solutions of $Al(NO_3)_3$. A dilute solution of this salt (0.5 M) has already been investigated with X-ray diffraction by Bol and Welzen [7]. However, they inquired into the description of the cation contributions, while no information was given about the anion.

The aims of our work were to determine the behavior of the nitrate ion in circumstances different from those studied earlier [4, 5, 8–11] and to check whether the behavior of Al^{3+} is the same in this solution. The hexa-coordination of the Al^{3+} ion in solutions has already been demonstrated by X-ray diffraction [6, 7, 12], NMR spectroscopy [13, 14] and theoretical studies [15].

Evidence was also found for the existence of a second hydration shell of about 12 molecules around the Al^{3+} ion [7, 15]. In a previous work [6] we suggested a detailed model for the second coordination shell of Al^{3+}. The same model was used for Cr^{3+} and Fe^{3+}. As far as the anion is concerned, the diffractometric studies generally result in the conclusion that the NO_3–H_2O interactions are weak. In presence of trivalent cations, as in solutions of $Cr(NO_3)_3$ and $Fe(NO_3)_3$, they can be totally masked by the strong cationic contributions, while in solutions of NH_4NO_3 they can be seen clearly. For $NaNO_3$ [11] and $LiNO_3$ [8] solutions it was found necessary to introduce discrete interactions between the NO_3^- and the solvent. Indeed, the nitrate ion can be very sensitive to the structure formed around the counterion because of its geometry, its tendency to create ion pairs and its capability to form H-bonds even if they are weak; moreover, it can be very sensitive to variations in concentration.

Experimental

X-ray scattering measurements on a 2.53 M $Al(NO_3)_3$ solution were carried out in a $\theta - \theta$ dif-

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fractometer thermostated at 25 ± 1 °C. MoK_α radiation with $\lambda = 0.7107$ Å was diffracted on the horizontal surface of the sample and then monochromated by reflection from a curved quartz crystal. The observed range of scattering angles (2θ) was from 3° to 123°, corresponding to the range

$$0.5\ \text{Å}^{-1} \leqq s \leqq 15.53\ \text{Å}^{-1},$$

where $s = 4\pi \sin\theta/\lambda$ is the scattering variable.

The measured intensities were corrected for background, polarization, and absorption [16] and smoothed by fourth differences [17]. The Compton contribution was evaluated by a semiempirical method [18] in order to account for the monochromator discrimination. The corrected intensities were scaled to the independent scattering factor for the solution using both the analytical method [19] and visual comparison.

The structure function was then constructed according to

$$i(s) = \left[I_{\text{e.u.}} - \sum_{i=1}^{m} x_i f_i^2\right] \Big/ \left[\sum_{i=1}^{m} x_i f_i\right]^2, \qquad (1)$$

where f_i are the atomic scattering amplitudes corrected for anomalous dispersion, x_i are the stoichiometric coefficients in a structural unit containing m kinds of atoms and $I_{\text{e.u.}}$ is the intensity in electron units. The scattering factors were computed according to an analytical formula using the coefficients proposed by Hajdu [20] for water molecule, by Cromer and Mann [21] for Al^{3+} and Cromer and Waber [22] for the other species.

The experimental correlation function $G(r)$ was obtained from $i(s)$ by Fourier transformation according to

$$G(r) = 1 + (2\pi^2 \varrho_0 r)^{-1} \int_{s_{\min}}^{s_{\max}} si(s) \sin(sr)\, ds, \qquad (2)$$

where r is the interatomic distance, $s_{\min}$ and $s_{\max}$ are the lower and upper limits of the experimental data and ϱ_0 is the bulk density of the stoichiometric units.

Before calculating the final correlation function, the structure function si(s) was corrected for residual systematic errors by means of a procedure described by Levy, Danford and Narten [18]. In this case, following a procedure used elsewhere [9], also the peak due to the N–O distance was removed, since the contribution arising from the NO_3^- is mainly weighted by its 0–0 interactions.

Discussion

The experimental structure function si(s) and the resulting pair correlation function are plotted in Figs. 1 and 2 (dots). In the experimental $G(r)$, four well-resolved peaks can be distinguished with their maxima centered at about 1.85, 2.15, 2.7 and 4.0 Å. A small peak at about 3.4 Å is also observed.

The to interpretation of the maxima at 1.85 and 2.7 Å can follow the same arguments as in the case of the 2M $AlCl_3$ solution [6], giving the Al-O and W_1–W_2 distances, respectively. In the fairly complex composition of the large peak at about 4.0 Å we can also see some contribution from Al–W_2 distances.

The assignement of the peak at 2.15 Å is easy, too; it is due to the O–O distance within the NO_3^-. The small peak at 3.4 Å can be ascribed to the N—H_2O interactions since its value is not too different from that expected for the N—H_2O pair supposing that the water molecules around the anion occupy positions directed by tetrahedral angles. This feature of the $G(r)$ function indicates the existence of a hydration sphere around the NO_3^- ion.

As a general conclusion, the experimental pair correlation function is mainly characterized by cationic hydration. The influence of the anion on cationic hydration appears to be rather weak.

In order to get more detailed information than it can be deduced directly from the experimental $G(r)$, we used the usual analysis based on the calculation of a model structure function, the parameters of which were determined by a systematical refinement against experimental data. The general characteristics of this procedure, as well as the formulae used have been treated elsewhere [23, 24]. The contribution of discrete interactions to the structure function is accounted for by using the Debye formula so modified that a Gaussian type distribution of distances can be introduced, while a uniform distribution of distances is described by the formula proposed by Narten and Levy [25].

For calculating the theoretical si(s) we used a structural model based on the hypothesis that the first and second-neighbor water molecules to the cations have a discrete structure. The hydrated ions were considered spatially non-correlated. The discrete structure of anions extends up to the first neighbors only. Dividing the water molecules between the hydration shells, no free water remains.

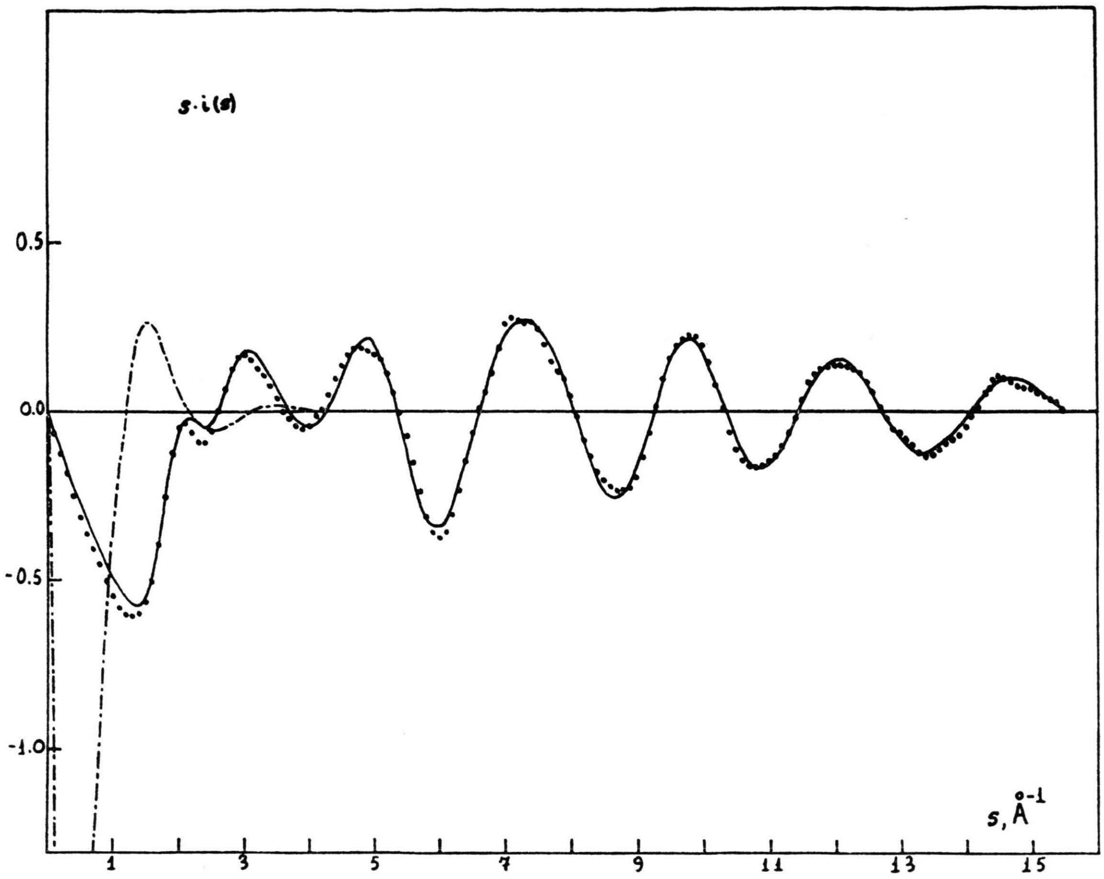

Fig. 1. Experimental (........) and model (———) structure function for the 2.53 M $Al(NO_3)_3$ solution. The (-·-·-·-) curve shows the overall contribution of "continuum" terms.

According to these assumptions, the model used has the following features:

a) The Al^{3+} ion has six water molecules as first neighbors, arranged in octahedral geometry. The $Al(H_2O)_6^{3+}$ is surrounded by twelve water molecules in the second hydration shell. The refinement procedure for the cationic hydration is nearly the same as for the $AlCl_3$ solutions [6], with the exception that the angle $\widehat{\text{Al–W}_1\text{–W}_2}$ is not fixed.

b) For the NO_3^- ion, the usual planar structure is supposed [9], with the O–O distance and the corresponding σ as parameters to be refined.

c) Since the H-bonds between the anion and the surrounding water molecules must be weak, the assumption of symmetry for the hydration shell is dropped, and the number n for the frequency of $N-H_2O$ interactions is introduced as independent parameter for describing the anion hydration, together with the distances and mean square deviations for the $O-H_2O$ and $N-H_2O$ interactions.

d) To calculate the contributions of uniform distributions, only terms of higher weights are introduced with their corresponding r_{0ij} and σ_{0ij} parameters, i.e.the $Al-H_2O$, $N-H_2O$ and H_2O-H_2O type continuum parts. For mathematical reasons we have to distinguish the O^--H_2O and $O-H_2O$ from that of H_2O-H_2O.

This model deviates in some respects from the original concept of the first neighbor models FNM1 and FNM2, analyzed by Pálinkás et al. [24]. The introduction of second neighbor interactions with the cations, appropriate for the trivalent cations, strengthens the model, as structural information on the second hydration shell, can be derived, while the structure of the first shell becomes more rigor-

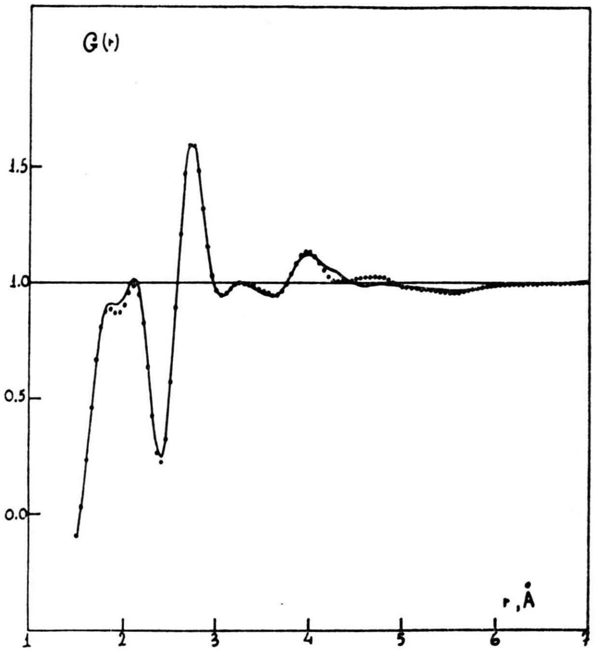

Fig. 2. Experimental (.......) and model (———) correlation function for the 2.53 M Al$(NO_3)_3$ solution.

ous, thus passing the question of uncertainty to the second neighbors. Obviously, this version can not be called FNM any more. The exclusion of any symmetry in the hydration shell of NO_3^-, will surely weaken the model, and will lead to less exact information on its structure. But this procedure seems to be justified because of the weak NO_3^-—H_2O interaction. Since there is no "free" water in this model at such a concentration, the distinction between FNM1 and FNM2 disappears.

The very good compatibility of the model with experimental data is demonstrated Figs. 1 and 2, where the structure function and the pair correlation function obtained from the best fit, are compared with the experimental data. The final values of the distances and mean square deviations describing the hydration of Al^{3+} and NO_3^- ions are given in Table 1. For comparison the values for the hydrate structure of Al^{3+} from a previous study of a 2M $AlCl_3$ solution [6] are given. The agreement confirms not only the validity of the model proposed, but also the fact that in both solutions the cations are the main structure-forming centers.

The distances and σ parameters obtained for the NO_3^- ion are also very similar to those expected from earlier results [11]. From r_{O-O} and the geometry of NO_3^- a value of 1.25 Å is derived for the distance N—O, in agreement with the literature data.

The values of 3.39 Å for the N—H_2O distance corresponds to the position of the fourth peak in the experimental $G(r)$, thus indicating the presence of a hydration sphere around NO_3. The n-value, of six seems to indicate that each O atom has two water molecules in its neighborhood. An exact geometry can not be derived because of assumption c) in our model. A calculation for the $\widehat{\mathrm{N{-}O{-}H_2O}}$ angle, based on the obtained distances will result in about 102 degrees, which is less than that for a tetrahedral arrangement. This deviation is not surprising if we take into account that a tetrahedron around the O atoms defines three free positions, and filling them up needs 9 water molecules instead of 6. The tetrahedral structure was reported in a recent study on a concentrated NH_4NO_3 solution [9]. In that case, however, there was no possibility to distinguish between NH_4^+ ions and H_2O molecules, and, as a consequence, between the hydration and ion-pairing phenomena.

In $LiNO_3$ solutions [8] the NO_3^- ion was found to be hydrated by five water molecules, with three

Table 1. Values of the parameters [r: distance (Å); σ: mean-square deviation (Å); n: frequency factor] used in the final calculation of the synthetic structure function.

CATION							
Parameters	r_{Al-W_1}	σ_{Al-W_1}	$r_{W_1-W_2}$	$\sigma_{W_1-W_2}$	r_{Al-W_2}	σ_{Al-W_2}	$\widehat{\mathrm{Al{-}W_1{-}W_2}}$
Present work	1.87	0.15	2.70	0.09	3.99	0.25	119.2°
$AlCl_3$	1.88	0.09	2.69	0.08	4.02	0.25	120°
ANION							
Parameters	r_{O-O}	σ_{O-O}	r_{O-H_2O}	σ_{O-H_2O}	r_{N-H_2O}	σ_{N-H_2O}	n
Present work	2.17	0.10	2.91	0.13	3.39	0.22	5.9

equatorial and two axial ones. In $NaNO_3$ solutions [11] a hydration number of six for NO_3^- was also found but no definite structure of the hydration shell proposed.

The results for Li^+, Na^+ and Al^{3+} cations agree in that direct cation-nitrate contacts are excluded and that with $n=6$ the hydration geometry deviates from the tetrahedral arrangement. Since the structures formed around the cations are fairly different and the $NO_3^- — H_2O$ interactions rather weak, a counter ion independent structure of the hydration shell of NO_3^- can not be expected.

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