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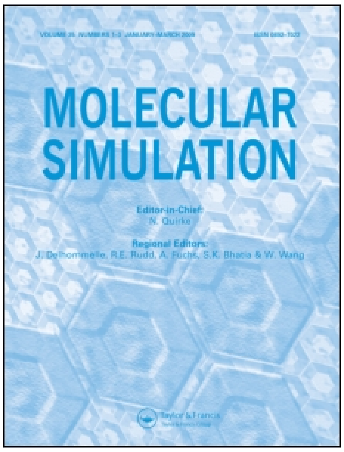

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Preliminary Communication

A SIMULATION STUDY OF AMMONIUM NITRATE IN AQUEOUS SOLUTION

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We present results from computer simulation studies of concentrated aqueous ammonium nitrate, and compare these with data obtained from neutron diffraction experiments. Our aim is to determine the structure, in order to improve our understanding of possible mechanisms of instability, in such systems.

KEY WORDS: Ammonium nitrate, neutron diffraction, instability.

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1 COMPUTERS AND NEUTRONS

Neutron scattering provides information on the structure of liquids. The scattering pattern can be related to a weighted linear combination of atom-atom pair distribution functions. In a molecular liquid mixture, some of the many contributions can be disentangled by the technique of isotopic substitution. This provides first-order difference functions which select structural features involving the labelled nuclei. An advantage of this technique is that contributions due to recoil effects and incoherent scattering tend to cancel, and so the associated corrections become less important in difference patterns. However, except in binary systems, the individual atom–atom correlations of interest can still not be resolved unambiguously. Thus, neutron scattering alone cannot provide a complete picture of the structure in a multicomponent molecular liquid.

Computer simulation predicts the structure of a liquid, given a model for molecular interactions. Simulation can provide all the individual atom-atom distribution functions, and show how they contribute to the total structure, as seen for example by neutrons. The crucial step in a simulation study is the development of realistic intermolecular potentials. If the results of computer simulation can be made consistent with experimental data, including those structural features which are directly inferred from neutron diffraction, this validates the choice of potential model. Then we may be confident in the more detailed picture of the structure provided by the simulation. Thus, computer simulation assists in the interpretation of neutron scattering experiments.

2 AMMONIUM NITRATE

Ammonium nitrate is a widely-used industrial chemical employed in both the manufacture of fertilizer and of explosives. It is known to be stable both as the anhydrous solid and in dilute aqueous solution. However, under other conditions, the system may explode, and there is considerable interest in methods of stabilizing systems of this kind. With this in mind, we wish to study the structure in concentrated aqueous solutions of ammonium nitrate.

In simple electrolytes, such as aqueous alkali halides, the ions are surrounded by well-defined hydration shells [1]. By contrast, ammonium ions and nitrate ions do not seem to produce such an obvious distortion of the surrounding water structure. Some authors have considered the ammonium ion to be indistinguishable from water molecules in its effect on the structure [2, 3]. Neutron diffraction studies of dilute solutions of ammonium chloride [4] show a broad hydration shell around the ammonium ion, no closer than 0.26 nm. It has been a matter of considerable debate as to whether or not a nitrate ion is hydrated at all, the situation seeming to depend strongly on the nature of the cation [5, 6, 7].

Recently, neutron diffraction studies of 12-molal aqueous ammonium nitrate [8] have been carried out. These show features in broad agreement with the results presented here, although the statistics are rather poorer.

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3 DISTRIBUTION FUNCTIONS

One of us (PAMW) has carried out neutron diffraction experiments on concentrated solutions of deuterated ammonium nitrate in heavy water. By altering the nitrogen isotopic composition, on both ammonium and nitrate species separately, first order difference patterns were obtained, which were used to give the local structure centred on these ions. These experiments will be described in more detail elsewhere [9].

The distribution function as seen in a neutron scattering experiment is a weighted sum of atom-atom correlations

$$\bar{G}(r) = \sum_{\alpha\beta} A_{\alpha\beta} g_{\alpha\beta}(r) \qquad (1)$$

The summation is over all the distinct pairs of atomic site types. Here there are six such types (remembering that atoms such as, for example, oxygen on nitrate ions and on water are chemically distinct) giving a total of twenty-one terms. The 'A' coefficients include a weighting factor for the isotope neutron scattering lengths and for the appropriate atomic fractions.

Consider subtracting scattering patterns from samples differing only in the nitrogen isotope on the ammonium ion. Only those six terms in the equation which involve the substituted nucleus survive. The resulting difference function gives information about the structure around the ammonium ion. A similar argument applies if we subtract patterns obtained with different nitrogen isotopes on the nitrate ion, to give the structure around nitrate. In each case, the remaining six individual atom-atom distributions are not resolved from each other.

4 SIMULATION PARAMETERS

We have carried out molecular dynamics simulations of 20-molal aqueous ammonium nitrate, using the CCP5 library program MDMPOL. The concentration was

Table 1 Simulation parameters

Ammonium ion		*Nitrate ion*	
Lennard-Jones radius, σ (nm)	0.325	Lennard-Jones radius, σ (nm)	0.3154
Lennard-Jones well depth, ε(J)	1.1819×10^{-21}	Lennard-Jones well depth, ε(J)	1.0772×10^{-21}
Charge at hydrogen sites (e)	0.35	Charge at oxygen sites (e)	−0.5533
Charge at centre (e)	−0.4	Charge at centre (e)	0.66
Bond length, N–H (nm)	0.104	Bond length, N–O (nm)	0.123
Bond angle, H–N–H (deg)	109.5	Bond angle, O–N–O (deg)	120
Water molecule			
Lennard-Jones radius, σ (nm)	0.3154		
Lennard-Jones well depth, ε(J)	1.0772×10^{-21}		
Charge at hydrogen sites (e)	0.52		
Charge at lone pair (e)	−1.04		
Bond length, H–O (nm)	0.09572		
Bond angle, H–O–H (deg)	104.52		
Displacement of lone pair charge from centre of mass (nm)	−0.007534		

chosen to match that of the neutron diffraction studies. Our system consisted of 23 ion pairs and 62 water molecules in cubic periodic boundary conditions.

The water molecules were modelled using the standard TIP4P potential [10, 11, 12], wherein each water molecule is represented by a single Lennard-Jones unit with three embedded point charges. The ammonium ions were modelled in a similar way, with Lennard-Jones parameters obtained from the literature [13], and a charge distribution which has also been used previously [14]. For the nitrate ion, we used three Lennard-Jones sites to represent the oxygen atoms. Each oxygen carries a negative charge and there is an additional central positive charge [15, 16]. The usual Lorentz-Berthelot mixing rules are employed for the Lennard-Jones interactions between unlike atoms.

In the simulations, the short-range forces were calculated with the usual spherical cutoff imposed at half the box length, and long-range Coulomb interactions were handled using the Ewald sum. Using artificially increased hydrogen masses, and the proper masses for the other nuclei, we found a timestep of 2 fs to be satisfactory. After equilibration, production runs of 6000 timesteps were used to generate the distribution functions.

5 RESULTS

The simulation results appear in Figure 1. We give those individual atom-atom distribution functions which relate to the structure around the ammonium ion and around the nitrate ion respectively. We observe some well-defined atom-atom correlations involving the ammonium ion, whereas correlations around the nitrate ion are not so distinct.

Predicted first-order difference functions, obtained as weighted sums of the above distribution functions, are compared with the results of the neutron scattering experiments, in Figure 2. For both ammonium and nitrate ions, the predicted position of the hydration shell agrees roughly with that seen experimentally.

It should be emphasised that the work reported here is of a preliminary nature. In

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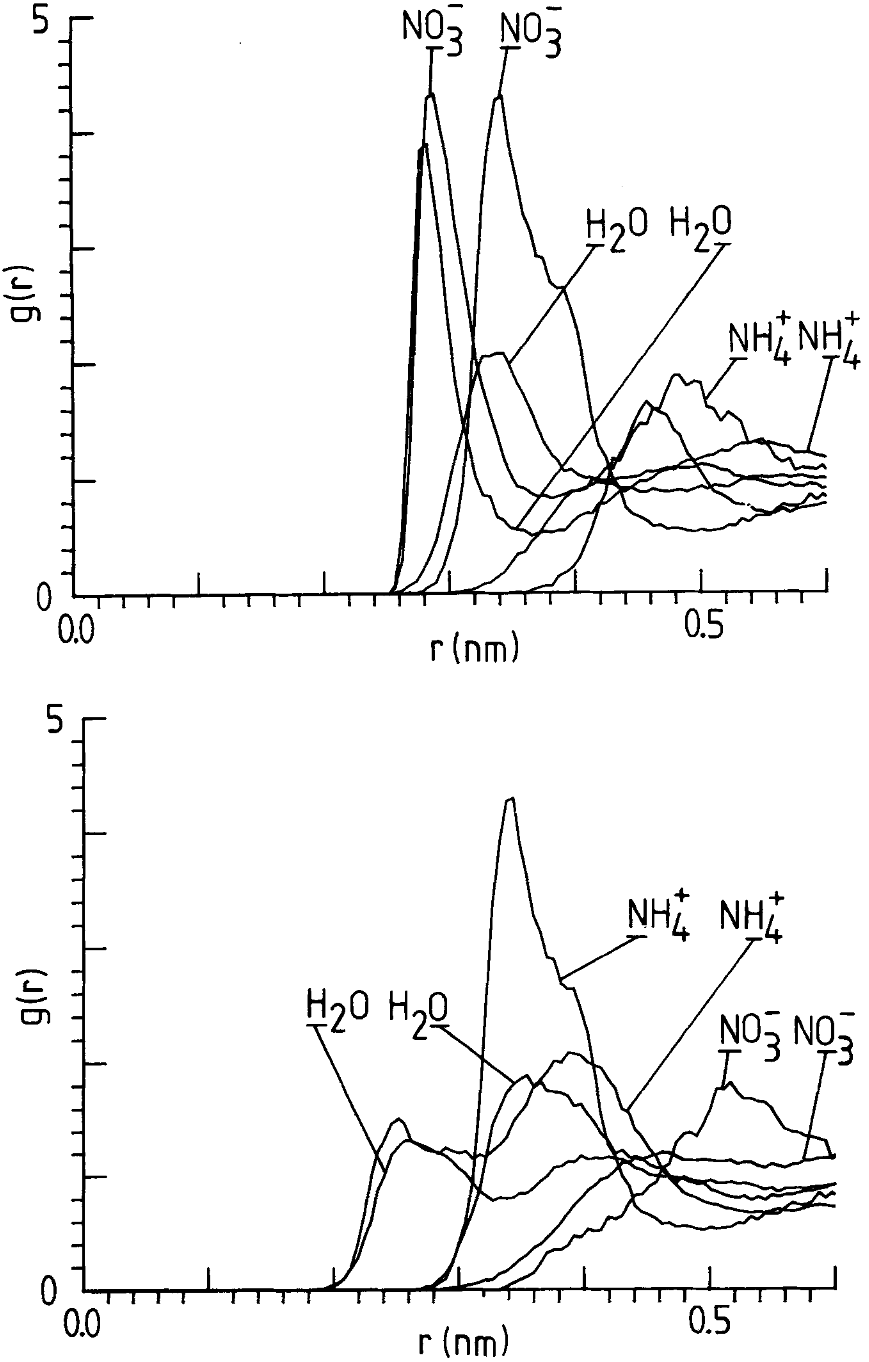

Figure 1 Atom-atom correlation functions which contribute to the total distribution functions around (a) the ammonium ion and (b) the nitrate ion, as derived from the simulation. In each case the curve refers to the correlation between the central nitrogen atom and the underlined atom.

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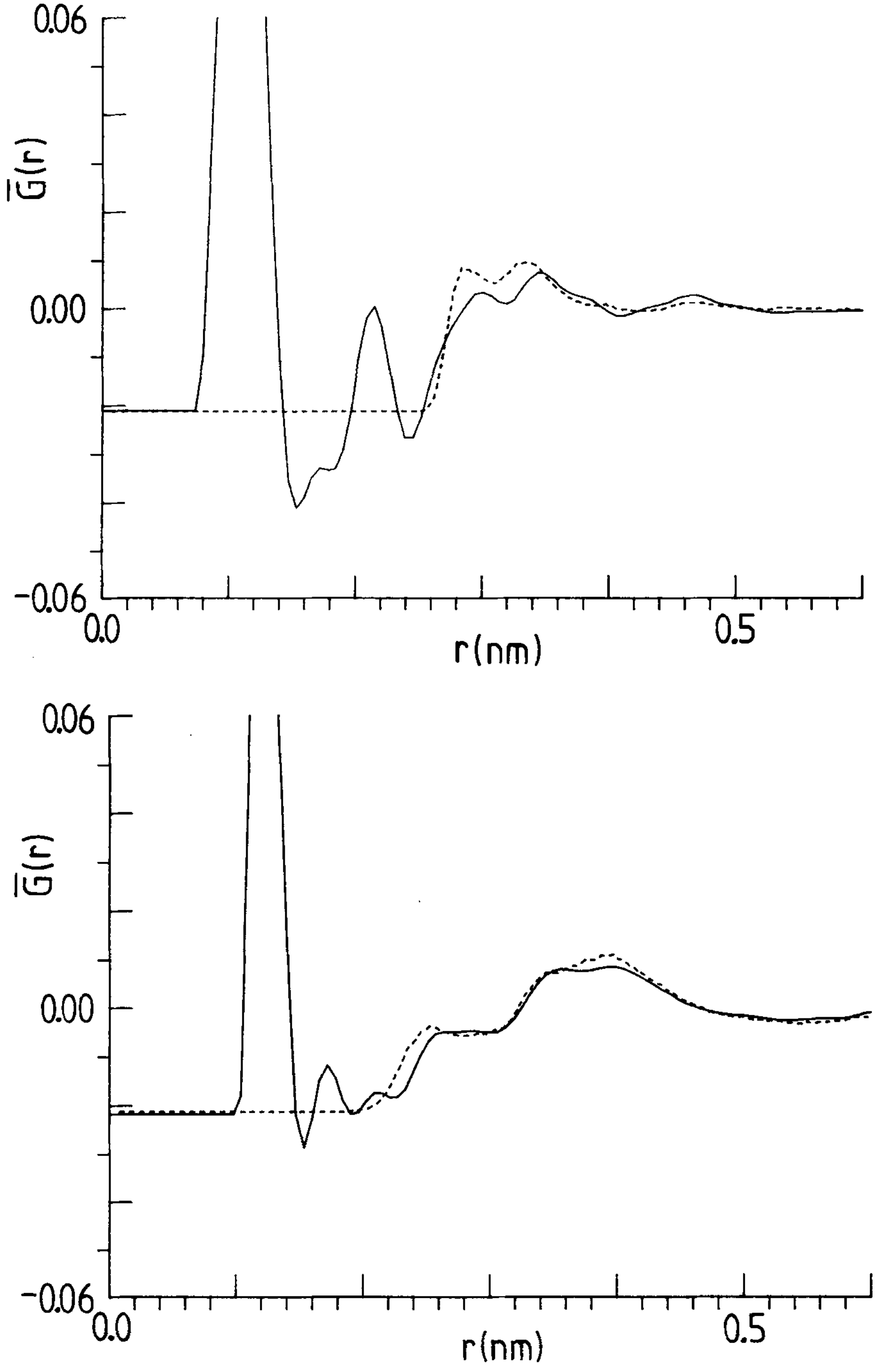

Figure 2 The first-order difference function predicted by simulation (dashed line) compared with the experimentally determined structure (solid line) around (a) the ammonium ion and (b) the nitrate ion. (*Note that short-range peaks due to intramolecular coordination, and Fourier transform truncation, appear in the experimental curves*).

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particular, we have used a rather small system for potential development. The ionic potentials used here appear to be a reasonable starting point; however, further refinement is clearly necessary. Our intention is to compare the results of simulations with solid state lattice properties of anhydrous ammonium nitrate. It is expected that this will be a sensitive test of the potential model. This work is now in progress.

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