

The Structure of Aqueous Solutions of Ammonium Nitrate

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An X-ray investigation of the structure of ammonium nitrate in aqueous solutions has been undertaken in connection with the structure determination of different aqueous solutions of nitric acid¹. The experimental method is the same as in earlier works². We have, however, reproduced the $\frac{\sigma(r)}{r}$ -curves³ instead of the $\sigma(r)$ -curves.

Our two solutions contain 60 and 48 g ammonium nitrate per 100 g solution. This corresponds to about 3 and 5 water molecules per molecule ammonium nitrate, respectively. The intensity curves, to-

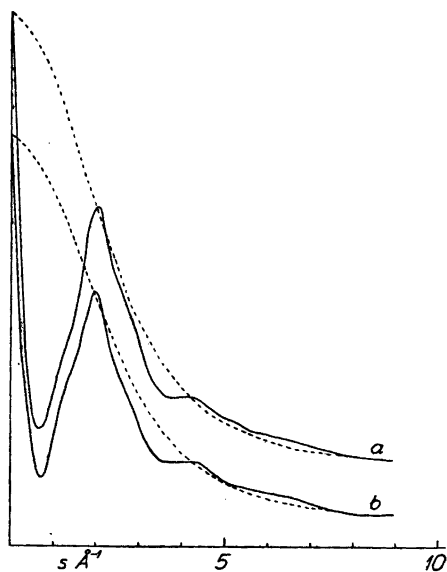


Fig. 1. Intensity curves (unbroken lines) and theoretical backgrounds (broken lines): a) 60% solution, b) 48% solution.

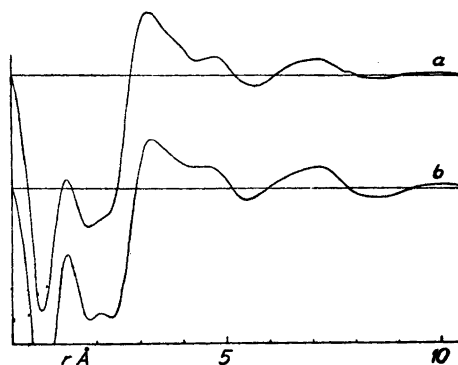


Fig. 2. $\frac{\sigma(r)}{r}$ -functions corresponding to Fig. 1.

gether with theoretical backgrounds, are given in Fig. 1, and the corresponding $\frac{\sigma(r)}{r}$ -curves in Fig. 2.

Both distribution functions have maxima at about 1.3 and 2.1 Å. In the nitrate ion, the average N—O distance is supposed to be 1.25 \AA^{4-7} , leading to about 2.2 Å for the average O—O distance. Accounting for a displacement of the maxima due to mutual interaction, our results agree well with these values.

For greater values of r , our distribution curves are similar to the corresponding curve for liquid water⁸. We find maxima at about 3.2, 4.7 and 7.2 Å. In addition, we see an indication of a maximum at about 4 Å for the most concentrated of our solutions, and no distinct minimum at this point for the other one. The curve for water has maxima at about 3.0 and 4.5 Å, with a sharp minimum between them, and a third maximum at about 7.0 Å.

Because of the limited content of ammonium nitrate in aqueous solutions, we can only expect to find the structure relative to the structure of water. The shift in position of the maximum at 3.0 Å (water) to 3.2 Å (ammonium nitrate) is easily explained (see Fig. 3): An ammonium group, or a water molecule, (A) is connected with

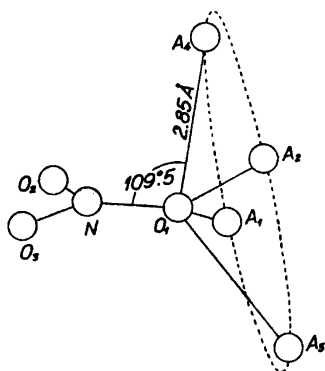


Fig. 3. Nitrate group (NO_3) with hydrogen bond to ammonium group or water molecule (A). The broken circle illustrates the rotation possibility of A.

an oxygen atom (O_1) of the nitrate ion by a hydrogen bond. With bond length 2.85 Å and bond angle 110° , the distance A—N in Fig. 3 is 3.47 Å. The distances A— O_2 and A— O_3 in Fig. 3 vary with the position of A on the broken circle in the figure. In positions A_1 or A_2 the hydrogen bond lies in the plane of the nitrate group and the distances are 3.2 and 4.7 Å. In positions A_3 or A_4 the hydrogen bond lies in a plane perpendicular to the nitrate group and both distances are about 4 Å. From the shape of our distribution curves in relation to that of water, we conclude that the latter structure is present, but evidently the presence of the first one cannot be eliminated. An equilibrium between the two and the intermediate positions, caused by a rotation around the bond N— O_1 , is not unlikely.

The displacements of the maxima at 4.5 and 7.0 Å (water) to 4.7 and 7.2 Å in the present case are explained by analogous reasoning.

However, we may mention that other possible arrangements may be partly responsible for the displacements of the maxima on the distribution curves: Water molecules packed around the nitrate group

give distances from 3.2 Å upwards. The ammonium groups may have greater packing radii than the water molecules. And lastly, the hydrogen bonds may be longer in the present case than in the case of liquid water. Investigations of crystal structures indicate that this is possible for hydrogen bonds between nitrate and ammonium ions⁷, but hardly between nitrate ions and water, where our value seems perhaps too great⁵.

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1. Michelsen, K. In publication.
2. Finbak, Chr. *Acta Chem. Scand.* **3** (1949) 1279, 1293.
3. Viervoll, H. *Acta Chem. Scand.* **1** (1947) 120.
4. Wyckoff, R.W.G. *Crystal Structures*. (1948). New York, Interscience Publishers, Inc.
5. Luzatti, V. *Acta Cryst.* **4** (1951) 120, 193.
6. Grison, E., Eriks, K., and de Kies, J. L. *Acta Cryst.* **3** (1950) 290.
7. Duke, J. R. C., and Llewellyn, F. J. *Acta Cryst.* **3** (1950) 305.
8. Finbak, Chr., and Viervoll, H. *Tids. Kjemi, Bergvesen, Met.* **5** (1943) 36.

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X-ray Crystallographic Data on Tetrathionates

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This note completes a preliminary X-ray survey on the crystal structure of polythionic compounds. Earlier reports give unit cell and space group data on salts of pentathionic, selenopentathionic and telluropentathionic acids¹, divalent sulphur, selenium and tellurium methanethiosulphonates², selenium and diselenium disulphates³, and divalent selenium and tellurium benzene- and *p*-toluenethiosul-