Hydration of the Ammonium Ion: Monte Carlo Simulation

R. Noto[a], V. Martorana[a], M. Migliore[a], and S. L. Fornili[a, b]

[a] C.N.R.-I.A.I.F., Via Archirafi 36, I-90123 Palermo, Italy
[b] Physics Department, University of Palermo, Via Archirafi 36, I-90123 Palermo, Italy

Z. Naturforsch. **46a**, 107–110 (1991); received August 3, 1990

Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

A Monte Carlo simulation of ammonium aqueous solution at infinite dilution shows that this ion is on the average rather loosely bonded to three of the fourteen water molecules present in its first hydration shell. This result agrees with conclusions suggested by recent experiments on the rotational mobility of ammonium in liquid water.

1. Introduction

Simulation of aqueous solutions give valuable information about the ionic hydration [1–8]. Thus, the results of a Monte Carlo (MC) simulation of the water-hydronium (H_3O^+) interaction [6] helped us to understand the discrepancies between experimental data and a simple theoretical model, and MC simulation applied to the study of the hydration of the hydroxide ion (OH^-) has evidenced a behaviour of the hydrogen-bonds (H-bonds) in the first hydration shell which might favor the mobility of the water molecules surrounding the ion through the same H-bond "catalytic action" found in a Molecular Dynamics (MD) simulation of low-density ST2 water [9].

These findings prompted us to use the same MC techniques to study aqueous solutions of NH_4^+, whose hydration presents some controversial features. Indeed, X-ray [10], Raman [11] and neutron diffraction [12, 13] data suggest that the structure of aqueous NH_4^+ solutions is similar to that of pure water. On the other hand, recent NMR experiments [14] provide evidence that the rotational mobility of this ion is higher than that of water, although NH_4^+ is strongly solvated [15]. Our aim was to ascertain if the structure of the first hydration shell of NH_4^+ presents features which can promote the ion mobility.

2. Computational Details

Our Metropolis Monte Carlo simulations have been accelerated by using a preferential sampling procedure [16]. The simulated system involved one fixed NH_4^+ ion and 215 water molecules confined in periodic cubes of 18.63 Å sidelength. Water-water and water-ion interactions were described by MCY [17] and Böhm and McDonald [5] *ab initio* potentials, respectively. The simulated temperature was 300 K. After equilibrium, $1.4 \cdot 10^7$ configurations were generated and stored for subsequent analyses, which were carried out by averaging over 20,000 configurations evenly spaced along the whole simulation "history".

Reprint requests to Dr. S. L. Fornili, Physics Department, University of Palermo, Via Archirafi 36, I-90123 Palermo, Italy.

3. Results and Discussions

a) Radial Distribution Function

In Table 1 we report data from the present and previous works for the radial distribution function $g_{NO}(r)$ and the running integration number $n_{NO}(r)$. As expected, since we use the same potentials, our results agree with those obtained by Böhm and McDonald [5] in MD simulation of the same system. Also, as these authors already pointed out, the position of the first minimum of $g_{NO}(r)$, r_{m1}, agrees well with that found

Table 1. Characteristic values of the nitrogen-oxygen radial distribution function, $g_{NO}(r)$: r_{M1} and r_{m1} represent the distances (in Å) of the first maximum and first minimum, respectively; $n_{NO}(r_{M1})$ and $n_{NO}(r_{m1})$ are the corresponding running integration numbers.

r_{M1}	$g_{NO}(r_{M1})$	$n_{NO}(r_{M1})$	r_{m1}	$n_{NO}(r_{m1})$	Ref.
3.05	6.85		3.68	8	[2]
2.9	4.0		4.4	13	[5]
2.9	3.9	2.9	4.4	14	this work
			4.35	10–11	[12]
2.85		4.4			[10]

0932-0784 / 91 / 0100-0107 $ 01.30/0. – Please order a reprint rather than making your own copy.

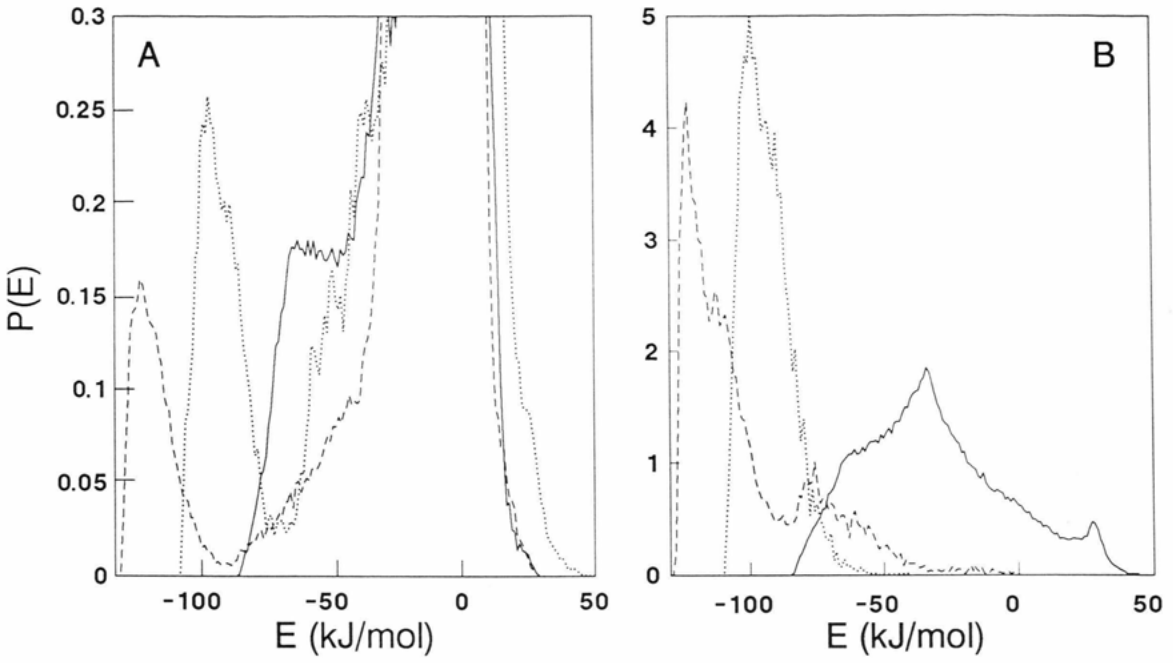

Fig. 1. Distributions of the ion-water pair interaction energy (A) and that of pairs within the first-hydration-shells (B) for NH_4^+ (full), OH^- (dotted) and H_3O^+ (dashed).

by neutron diffraction [12] while the number of water molecules present in the first hydration shell is slightly higher for the simulations.

The simulation performed by Szasz and Heinzinger [2] gave different results because they used the ST2 water model, empirical ion-water potentials and studied a high solute concentration (2.2 molal).

b) Pair Interaction and Average Energy Distribution Functions

In Fig. 1 we report ion-water pair interaction energy distribution functions (PDF). For comparison, analogous curves for H_3O^+ [6] and OH^- [7] ions are also shown. The PDF of NH_4^+ does not show the well defined peak to the left, present in the curves for H_3O^+ and OH^- ions, which corresponds to strong bonds between ions and the nearest water molecules. Instead, a shoulder is present in the range -70 to -60 kJ/mol.

We have also calculated the distribution of the ion-water interaction energy averaged over the first hydration shell (AEDF). The peak of this distribution, shown in Fig. 2, occurs at -31 kJ/mol, which is a rather high value, considering that the minimum of

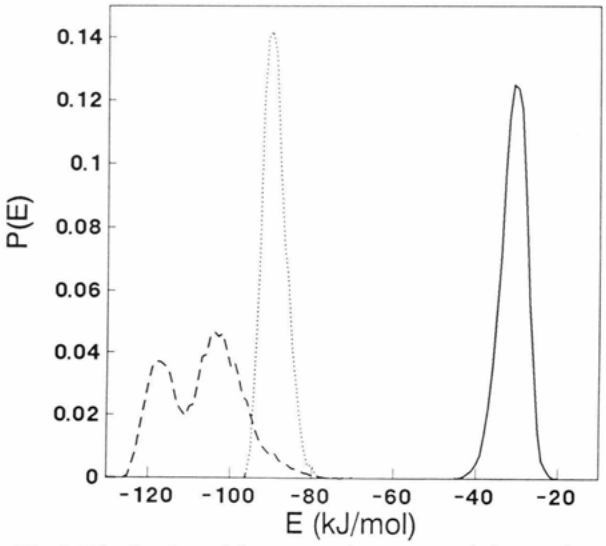

Fig. 2. Distribution of the average ion-water pair interaction energy within the first hydration shells for NH_4^+ (full), OH^- (dotted) and H_3O^+ (dashed).

the water-NH_4^+ potential function is -85.76 kJ/mol [5]. Again, the NH_4^+ behaviour is different from that for H_3O^+ and OH^-. This suggests that the water molecules surrounding NH_4^+ feel a weaker local charge density than those surrounding H_3O^+ and OH^-. In-

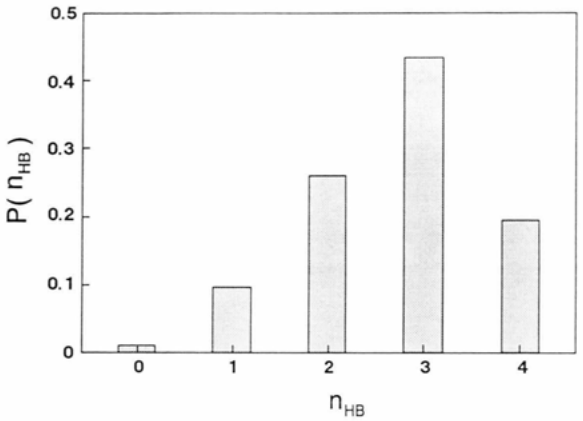

Fig. 3. Distribution of the number of water-NH_4^+ hydrogen bonds, n_{HB}.

deed, while on the latter ions the distribution of the net charge is rather asymmetric, on NH_4^+ the net charge distribution is tetrahedral. Thus, the ionic radii being similar (Goldschmidt's values are 1.40, 1.43 and 1.45 Å for H_3O^+, NH_4^+ and OH^-, respectively [18]), the ion-water interaction would be stronger and more localized for H_3O^+ and OH^- than for NH_4^+. This is consistent with the PDF curve for the first hydration shell (Fig. 1 b), which shows a broad distribution being remarkably different from the H_3O^+ and OH^- curves.

c) H-bond Number Distribution

Figure 3 shows the distribution of the number of the H-bonds between NH_4^+ and water molecules present in its first hydration shell under the assumption that a H-bond exists if the distance $H_N \cdots O$ between a hydrogen atom belonging to the NH_4^+ ion and the oxygen atom of water is less than 2.1 Å. It turns out that the most frequent configurations are those featuring three bonds. This result is rather unexpected, since on the basis of simple energetic and geometric considerations one would expect that all four hydrogen atoms of NH_4^+ are engaged in H-bonds with nearby water molecules. On the contrary, only 20% of the MC configurations show four ion-water bonds (Figure 3).

d) Water Molecule Arrangement Around NH_4^+

To gain some insight into the geometric arrangement of the water molecules closest to NH_4^+, we have selected from the simulation history ca. one hundred evenly spaced configurations, whose ion-water energy value, averaged over the first hydration shell, is around -31 kJ/mol, which corresponds to the peak of the AEDF curve for NH_4^+ (Figure 2). The general impression is that the molecules surrounding NH_4^+ are arranged in a rather disordered way and that the pattern of the ion-water bonds is unstable and flickering.

4. Conclusions

We can draw the following main conclusions from the analysis of the present MC simulation: i) although the first hydration shell of the ammonium ion consists of fourteen water molecules, only three of them on the average are H-bonded to the ion, rather than four. ii) Such bonds are, on the average, surprisingly weak (-31 kJ/mol) with respect to the energy minimum (-85.76 kJ/mol) of the ion-water potential. Thus, the general picture which emerges also by direct inspection of statistically representative configurations is that in liquid water, ammonium is surrounded by a disordered arrangement of rather loosely bonded molecules. This agrees with and confirms conclusions suggested by recent NMR experiments [14], which show a surprisingly high rotational mobility of ammonium in water in spite of its strong solvation.

Acknowledgements

This work has been carried out at C.N.R.-I.A.I.F. General indirect support from Italian M.P.I.-60% and C.R.R.N.S.M. are acknowledged. We thank Mr. M. Lapis, Mr. G. La Gattuta and S. Pappalardo for technical assistance.

[1] E. Clementi, Lecture Notes in Chemistry, Vol. 2, Springer-Verlag, Berlin 1976.
[2] Gy. I. Szasz and K. Heinzinger, Z. Naturforsch. **34a,** 840 (1979).
[3] M. Mezei and D. L. Beveridge, J. Chem. Phys. **70,** 622 (1981).
[4] R. W. Impey, P. A. Madden, I. R. McDonald, J. Phys. Chem. **87,** 5070 (1983).
[5] H.-J. Böhm and I. R. McDonald, J. Chem. Soc. Faraday Trans. 2 **80,** 887 (1984).
[6] S. L. Fornili, M. Migliore, and M. A. Palazzo, Chem. Phys. Lett. **125,** 419 (1986).

[7] G. Andaloro, M. A. Palazzo, M. Migliore, and S. L. Fronili, Chem. Phys. Lett. **149,** 201 (1988).
[8] K. Heinzinger, in: Computer Modeling of Fluids Polymers and Solids (C. R. A. Catlow et al., eds.), Kluwer Academic Publ., London 1990, p. 357.
[9] A. Geiger, P. Mausbach, and J. Schnitker, in: Water and Aqueous Solutions (G. W. Neilson and J. E. Enderby, eds.), Hilger, London 1986.
[10] A. H. Narten, J. Phys. Chem. **74,** 745 (1970).
[11] P. M. Vollmar, J. Chem. Phys. **39,** 2236 (1963).
[12] N. A. Hewish and G. W. Neilson, Chem. Phys. Lett. **84,** 425 (1981).
[13] P. A. M. Walker, D. G. Lawrence, G. W. Neilson, and J. Copper, J. Chem. Soc. Faraday Trans. I **88,** 1365 (1989).
[14] a) C. L. Perrin and R. K. Gipe, J. Amer. Chem. Soc. **108,** 1088 (1986). – b) C. L. Perrin and R. K. Gipe, Science **238,** 1393 (1987).
[15] M. Meot-Ner, J. Phys. Chem. **91,** 417 (1987).
[16] J. C. Owicki and H. A. Scheraga, Chem. Phys. Lett. **47,** 600 (1977).
[17] O. Matsuoka, E. Clementi, and M. Yoshimine, J. Chem. Phys. **64,** 1351 (1976).
[18] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, Oslo 1923–1927.