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Preferential Solvation of Li^+ in 18.45 % Aqueous Ammonia: A Born−Oppenheimer ab Initio Quantum Mechanics/Molecular Mechanics MD Simulation

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A molecular dynamics simulation using a mixed ab initio quantum mechanics/molecular mechanics formalism has been performed in order to obtain refined structural properties for a Li(I) ion in 18.45% aqueous ammonia solution. Using a double-ζ valence basis set for the quantum mechanically described first solvation shell including the ion, a tetrahedral structure with three water and one ammonia ligand is observed, in contrast to the octahedral structure with three water and three ammonia ligands predicted by classical pair potential simulation. This can be considered as further proof for the importance of nonadditive *n*-body effects for a proper description of ions in solution, even if they are only single charged. Further structural data and the preference for water ligands are discussed on the basis of detailed simulation results.

Introduction

As a result of the continuous increase of computer capacity and performance, more sophisticated and accurate simulation techniques incorporating quantum mechanical algorithms have become accessible for the study of condensed systems.[1−7] A coupled semiempirical molecular orbital and molecular mechanics model has been applied for a wide range of neutral organic molecules in aqueous solution,[2] and the performance and suitability of combined quantum mechanical and molecular mechanical models concerning solvent effects in chemical reactions in solution have been discussed extensively.[3] Among these, the Born−Oppenheimer ab initio quantum mechanics/molecular mechanics approach has proven especially suitable for the study of structural and dynamic properties of solvated ions by molecular dynamics simulations.[4−7] This technique includes the crucial many-body contributions for the whole first solvation shell of the ions and has led to some major revision of previous results obtained for solvated ions by pair potential and even three-body corrected simulations. The many-body terms can effect drastic changes in the composition of the solvates, in particular concerning the coordination numbers, and have a strong influence on the orientation of the ligands as well.[4−7] Further, they are needed to reproduce well-known chemical properties of solvated ions as structure-making and structure-breaking effects.[7]

Since such properties and structural details have been successfully explored for some characteristic examples in pure solvents, analogous investigations for ions in mixed solvents have become of particular interest. Lithium ion in aqueous ammonia represents a very suitable example for such a study, as simulations of Li^+ solutions in water and liquid ammonia have already been carried out using the Born−Oppenheimer ab initio QM/MM technique,[4,6] resulting in a tetrahedral structure with four solvent molecules in the first solvation shell and thus contradicting the octahedral structure predicted for this shell in both cases on the basis of classical pair potential simulations. An earlier MC simulation of Li^+ in 18.45% aqueous ammonia[8] based on pair potentials led to a first solvation shell containing four water and two ammonia ligands and a second shell composed of eight water and four ammonia molecules. Although this result is in agreement with qualitative expectations of a preference for the "harder" ligand H_2O over the "soft" NH_3 by the "hard" ion Li^+, it seemed most worthwhile to examine the correctness of this prediction by the more accurate QM/MM molecular dynamics technique now available.

Methods

The system is partitioned into two regions: the QM/MM molecular dynamics technique treats the ion and its first solvation shell by means of Hartree−Fock level quantum mechanics for the evaluation of forces, whereas the forces between particles inside this region and "outside" solvent particles in the elementary box are computed on the basis of classical pair potentials. Likewise, the forces between molecules in the "outer" region are also treated by molecular mechanics.[5] The pair potential functions for Li(I)−water and Li(I)−ammonia have been obtained previously,[4,6] and flexible models for intra- and intermolecular interactions were employed for water[9,10] and ammonia.[11] The water−ammonia pair potential was also available from former work.[12] For the quantum mechanically treated region, a double-ζ valence basis set[13] was used, and long-range interactions were treated by the reaction field procedure.[14]

Initially, a classical MD simulation was performed whose equilibrium configuration was used as the starting point for the combined QM/MM simulation. The size of the QM region was selected as a sphere with 3.4 Å diameter, corresponding to the size of the first solvation shell resulting from the classical simulation. Within the interval from 3.4 and 3.6 Å, a smoothing function was applied to ensure a continuous transition between the QM and MM region.

Both simulations were carried out in a canonical ensemble at 293 K with a time step of 0.2 fs. The cubic elementary box with a length of 18.56 Å contained one Li^+ ion, 37 ammonia,

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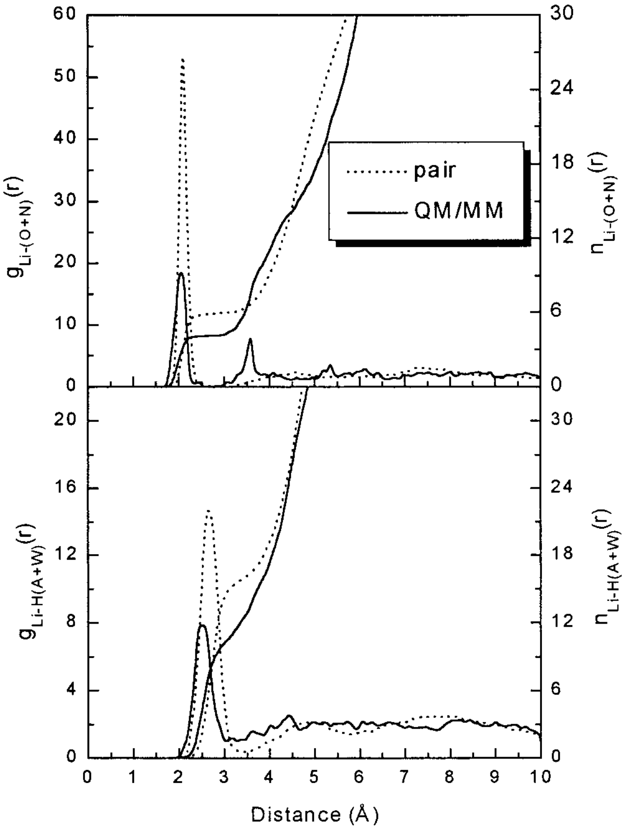

Figure 1. (a) Li−(N+O) and (b) Li−H(A+W) radial distribution functions and their corresponding integration numbers.

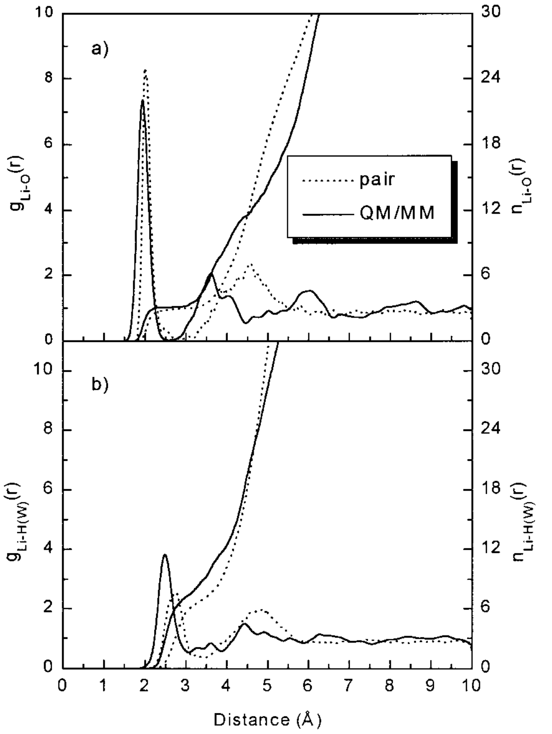

Figure 2. (a) Li−O and Li−H(W) radial distribution functions and their corresponding integration numbers.

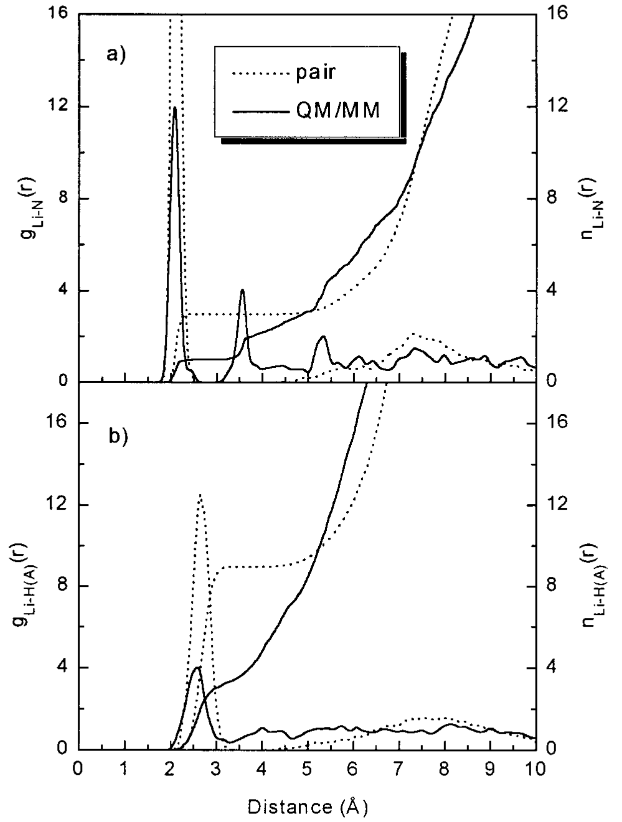

Figure 3. (a) Li−N and Li−H(A) radial distribution functions and their corresponding integration numbers.

TABLE 1: Comparison of Solvation Parameters for Li$^+$ in 18.45 mol % Aqueous Ammonia Solution, Obtained from Pair Potential and QM/MM Simulations; r_{max} and r_{min} Denote the First Maximum and Minimum of the Radial Distribution Functions in Å, and n_{min} Is the Average Number of Ligand Molecules Obtained by Integration up to r_{min}

	r_{max}	r_{min}	n_{min}	method	ref
Li−O	2.00	2.83	2.9	pair potential MD	this work
	1.94	2.58	3.1	QM/MM MD	this work
	1.95	2.75	4.0	pair potential MC	8
Li−H(W)	2.76	3.26	6.3	pair potential MD	this work
	2.48	3.07	7.4	QM/MM MD	this work
	2.60	3.10	8.2	pair potential MC	8
Li−N	2.10	2.74	3.0	pair potential MD	this work
	2.08	2.69	1.0	QM/MM MD	this work
	2.50	2.85	0.5	pair potential MC	8
splitting peak	3.35	3.80	1.9	pair potential MC	8
Li−H(A)	2.65	3.42	9.0	pair potential MD	this work
	2.58	3.30	3.2	QM/MM MD	this work
	3.15	4.20	6.5	pair potential MC	8

and 164 water molecules, corresponding to the experimental density of 18.45% aqueous ammonia solution (0.9307 g cm^{-3}). Starting from a random configuration, the classical simulation required 30 000 time steps for equilibration, and was continued for another 60 000 time steps for data collection performed at every 10th step. The combined QM/MM MD simulation needed 15 000 time steps for reequilibration and another 30 000 time steps were used to collect data at every 5th step. The requirement of computation time for a QM/MM simulation is approximately 200 times higher than that of the classical MM formalism.

Results and Discussion

Figure 1 shows the radial distribution functions (RDF) for Li$^+$−(N+O) and Li$^+$−H (from both water and ammonia molecules) together with the corresponding integration numbers

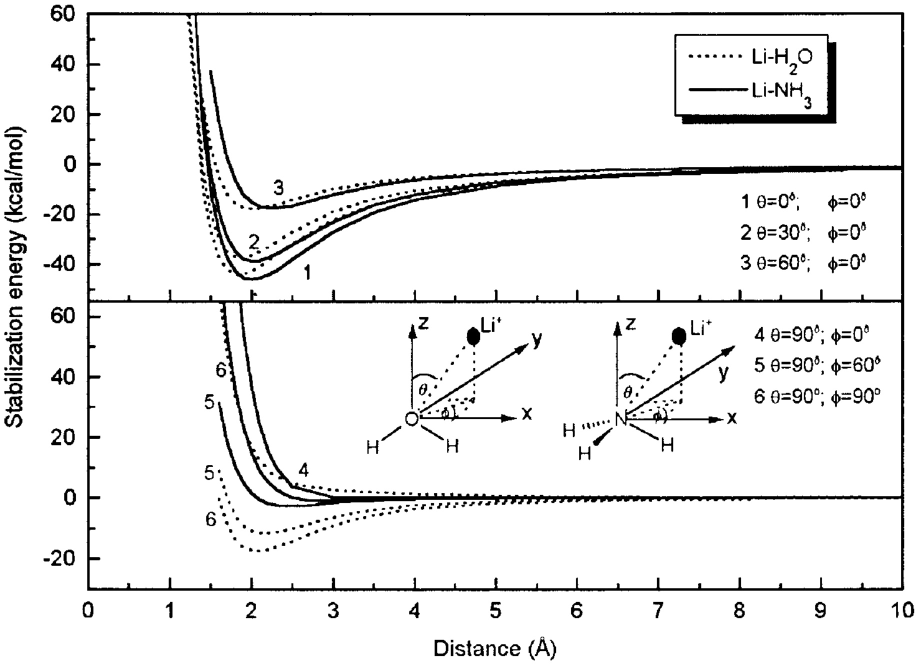

Figure 4. Comparison of the Li^+-H_2O and Li^+-NH_3 interaction energies for some values of θ and ϕ, obtained from the ab initio calculations with double-ζ valence basis set.

and compares MM and QM/MM simulations. The pair potential simulation gives a first Li−(N+O) peak at 2.10 Å, for which a, less pronounced, correspondence is found at 2.04 Å in the QM/MM simulation. In the latter, a well-recognizable second peak is found at 3.5 Å, whereas the classical simulation displays a rather broad peak in the region from 3.5 to 6.0 Å. This second shell is well separated from the first one in both cases, but the coordination numbers differ greatly, being four in the QM/MM and six in the MM simulation, respectively. Figures 2 and 3 detail these findings by separately displaying Li−O, Li−H(W), Li−N, and Li−H(A) RDFs and their corresponding integration numbers. In addition, Table 1 gives a comparison of the structural parameters of this work with data from a previous Monte Carlo simulation. The first Li−O and Li−N peaks of our classical simulation, culminating at 1.98 and 2.10 Å, contain on average 2.9 and 3.0 ligand molecules, respectively. The QM/MM approach shortens the peak distances from the ion to 1.93 and 2.08 Å, leads to a better separation of first and second shell, and delivers average coordination numbers of 3.1 and 1.0 for water and ammonia, respectively. A similar trend is recognized in the relatively shorter Li−H(W) and Li−H(A) distances, and the corresponding average number of H atoms in the QM/MM simulation results as ∼10 (3 from the one ammonia ligand and 7 for the three water ligands). The additional 10th H atom is supposed to belong to a second shell ligand, establishing a hydrogen bond to one of the first shell ligands and thus reaching into the region limited by $r_{\min}$ (a slight shoulder in Li−H {A + W} RDF supports this assumption). The total coordination number of four ligands is in clear contrast to the value of six obtained with the assumption of pairwise additivity of interactions and once more proves the enormous importance of *n*-body effects for structural data of solvates. The QM/MM simulation also clearly indicates the preference of Li^+ for water as a ligand, similar to that found in the previous Monte Carlo simulation based on pair potentials,[8] and interpretable in the chemical concept of “hard” and “soft” ions and ligands.

Looking at the pair interaction energies for Li^+−water and Li^+−ammonia obtained from ab initio calculations for some selected reaction coordinates (Figure 4), one can recognize that the global minima are not too different with 44.1 and 46.2 kcal mol^{-1} and would even slightly favor ammonia as a ligand. However, deviations from the ideal (dipole-oriented) configuration lead to much stronger repulsion forces in the case of ammonia than for water, as can be seen from Figure 5, where the angle θ is fixed at 90° and Φ is varied. In addition to this, an investigation of three-body effects in the system $NH_3-Li^+-NH_3$ showed that considerable repulsive three-body effects appear at short Li−N distances, which are strongly depending on the N−Li−N angle.[15] This finding seems to give another good reason for the preference of water over ammonia ligands in the first solvation shell.

Figure 6 shows the O−Li−O, N−Li−N, and N−Li−O angular distributions, calculated up to the first minimum of the respective RDFs. The octahedral geometry of the solvate resulting from the classical simulations is clearly revealed by distinct peaks in the range 80°−110°and smaller peaks between 160° and 180°. The broad peak between 80° and 140° in the plot of the QM/MM simulation data corresponds to the tetrahedral arrangement expected for four ligands. Additional information on this arrangement is available from the orientational distribution of solvent molecules in the first shell, presented in Figure 7 by the distribution of the angle θ, defined by the dipole vector of the solvent molecules and the Li···O and Li···N vectors, respectively. In both the classical and the QM/MM simulations, ammonia ligands stick more rigidly to the dipole-oriented configuration, whereas a shoulder between 120° and 150° for Li−O in the QM/MM simulation indicates a higher flexibility of the water ligands’ orientation, most probably influenced by their binding to solvent molecules in the second shell.

Inspecting the second solvation shell of Li^+, a corresponding peak is found around 4.5 Å in the Li−O RDF of the MM simulation, whereas the second Li−N RDF peak at 7.3 Å cannot be assigned to the second sphere. This would lead to the conclusion that the second shell consists exclusively of water molecules. In contrast to that, the QM/MM simulation shows

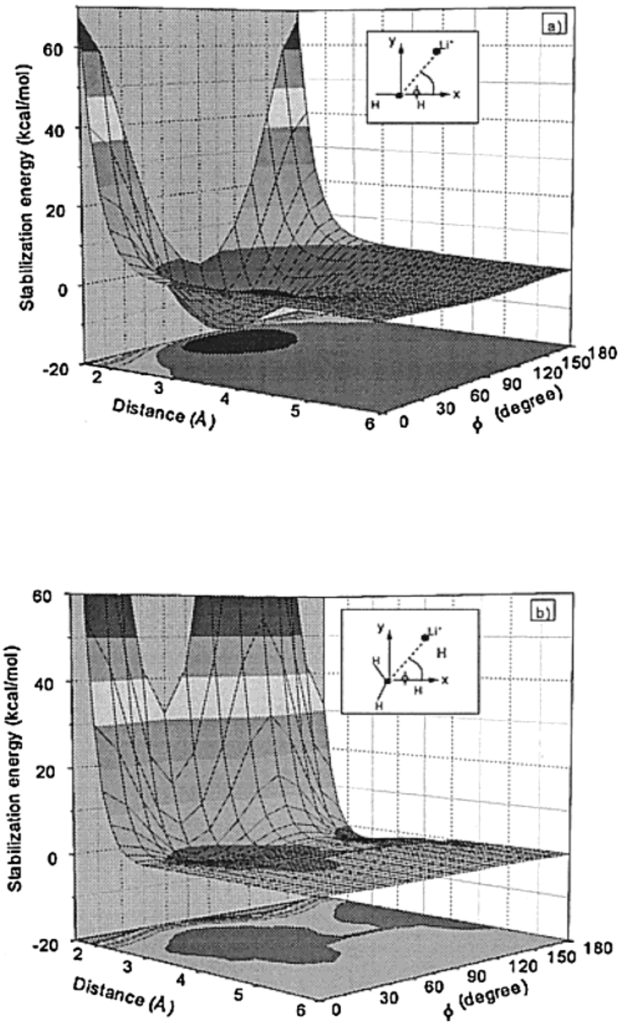

Figure 5. Selected parts of the potential energy surface obtained from ab initio calculations with respect to movements of Li^+ around (a) water and (b) ammonia molecules, where θ is fixed at 90° and ϕ is varied.

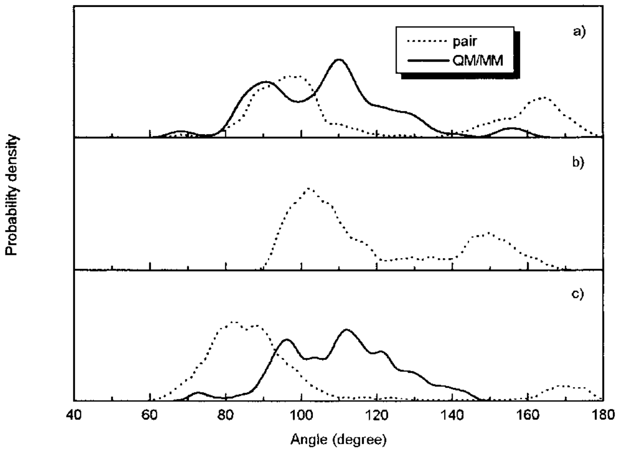

Figure 6. (a) O−Li−O, (b) N−Li−N and (c) O−Li−N angular distributions, calculated up to the first minimum of the Li−(N+O) RDFs.

second peaks for both RDFs around 3.5 Å, proving a significant participation of NH_3 molecules in this solvation sphere as well.

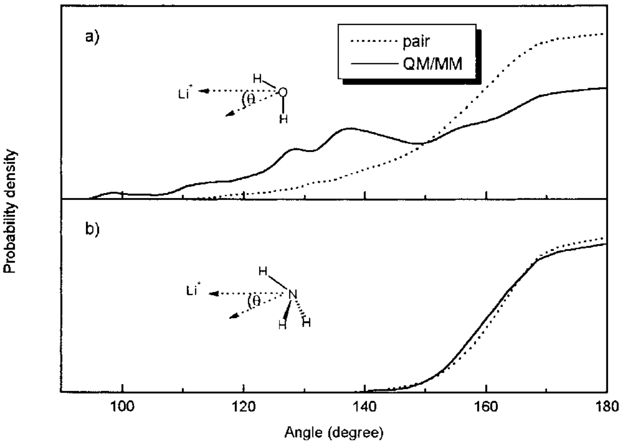

Figure 7. Distribution of θ in the first solvation shell of Li^+ for (a) water and (b) ammonia ligands.

Conclusions

The results presented in this study seem to justify fully the increased computational effort related to the more accurate QM/MM simulation technique. The use of pair potentials leads to distinctly wrong predictions for the geometrical structure of the solvated ion, and also to errors in the composition of first and second solvation shell. It can be expected that these errors would, as a consequence, strongly effect the evaluation of all other physicochemical data on the basis of the simulation. It is concluded, therefore, that nonadditivity of interactions due to *n*-body effects play an even more important part for the correct treatment of electrolyte solutions than recognized so far.

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