

Chloride Ion in Liquid Hydroxylamine: Pair Potential Function and Monte Carlo Simulation

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An analytical pair potential function for the Cl^- – NH_2OH interaction energy surface has been constructed based on basis set superposition error corrected ECP/DZP *ab initio* calculations. The potential has been tested by Monte Carlo simulation of a solution of one chloride ion in liquid hydroxylamine at 32 °C, leading to the conclusion that under these conditions Cl^- forms a solvation shell of eight solvent molecules, coordinated via OH hydrogens.

Introduction

Hydroxylamine, chemically situated between water and ammonia, is a most interesting solvent for studying preferential coordination of ions, offering O and N site for cation and OH and NH hydrogens for anion binding. Unfortunately the pure solvent tends to decompose easily so that experimental structural investigations of electrolyte solutions by means of x-ray and/or neutron diffraction seem hardly feasible and have, to our knowledge, never been attempted so far. On the other hand, statistical simulation techniques based on *ab initio* derived potential functions provide a relatively easy and reliable tool to obtain information, and have been successfully employed already to study the solvation of Li^+ ion in liquid hydroxylamine [1]. For binding of the anion Cl^- , 3 hydrogen atoms are available for the formation of an H-bond, which represents an interesting example for preferential coordination. Further, the availability of a Cl^- – NH_2OH potential will allow the simulation of more “realistic” systems, where both cations and anions are present and for which – due to electroneutrality – long range corrections by Ewald summation become possible, improving the quality of the simulation results.

The work presented here extends these investigations to the anion Cl^- , in order to obtain data for the presumably hydrogen bonded solvate structure of this ion and to provide the preconditions for simulations

of more complex electrolyte solutions consisting of various salts and pure or aqueous hydroxylamine. For this purpose, a pair potential function was to be developed and tested by means of a Monte Carlo simulation.

Method

Construction of Potential Function

Ab initio SCF Calculations

The geometry of NH_2OH was kept rigid at the experimental values [2], and several hundred points of the interaction energy surface with a chloride ion were evaluated, with special emphasis on accurate representation of hydrogen bonded structures. The same ECP/DZP basis set as already tested and successfully employed in the construction of the $\text{NH}_2\text{OH}/\text{NH}_2\text{OH}$ potential function and previous simulations [3–5] was used for hydroxylamine, and for Cl^- the ECP/DZP basis set of Steven et al. [6] was taken. In contrast to the cation/ NH_2OH energy surface, larger basis set superposition errors (BSSE) had to be expected for these basis sets in the case of the anion. These errors were estimated therefore by the Boys-Bernardi counterpoise correction method [7], and the results of these investigations for the “ideal” NH- and OH-hydrogen bonded trajectories are summarized in Table 1. They indicate that the upper limit of BSSE at the respective minima amounts to 10% of the calculated binding energy; at shorter distances it increases further and

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Table 1. Basis set super position error of Cl–NH₂OH interaction energies for hydrogen bond trajectories.

| <i>r</i> [Å] | BSSE (kcal/mole) | |
|--------------|------------------|---------|
| | Cl–H(N) | Cl–H(O) |
| 2.0 | –5.79 | –4.77 |
| 2.2 | –5.13 | –4.34 |
| 2.5 | –4.24 | –3.67 |
| 2.8 | –3.08 | –2.63 |
| 3.0 | –2.50 | –2.09 |
| 3.7 | –0.87 | –0.66 |
| 4.2 | –0.30 | –0.16 |
| 5.2 | –0.02 | –0.02 |
| 7.2 | 0.00 | 0.00 |

becomes negligible only above 5 Å distance between the interacting species. For this reason, all energies corresponding to smaller distances than 5 Å were BSSE corrected by the counterpoise method.

Pair Potential Function

Based on the BSSE corrected interaction energy points of the *ab initio* calculations, an analytical function was constructed by means of a nonlinear Marquard-Levenberg fitting procedure [8]. Weighting of input data was performed to obtain fitting near the global and local energy minima. The trial functions contained, besides the Coulombic term based on the Mulliken partial atomic charges, an exponential term and some r^{-n} terms. The quality of the resulting function was tested by Beveridge's procedure [9], ensuring that the standard deviation remained constant after adding further SCF data to the fitting procedure.

Monte Carlo Simulation

A system consisting of 1 Cl[–] ion and 216 NH₂OH molecules at 32 °C was selected for the test simulation. From the experimental density of liquid hydroxylamine at this temperature (1.204 g cm^{–3}) the elementary box length resulted as 21.646 Å, and half of this box length was chosen as cut-off radius for exponential terms. Starting from a random configuration, equilibration was achieved after 2 million configurations, and another 2 million were used for sampling and data evaluation. During this procedure an acceptance ratio of 1/3 was maintained by automatic adjustment of translational and rotational displacement parameters. The simulation was carried out by the

Table 2. Mulliken charges and final fitting parameters.

Fractional atomic charges:

| Atom | Charge (a.u.) |
|----------------|---------------|
| Cl | –1.000 |
| N | –0.482 |
| H _N | 0.301 |
| O | –0.525 |
| H _O | 0.405 |

Fitting parameters:

| Cl– <i>i</i> | <i>A</i> ₁ (kcal.Å ⁴) | <i>A</i> ₂ (cal.Å ⁵) | <i>A</i> ₃ (kcal) | <i>A</i> ₄ (Å ^{–1}) |
|--------------|----------------------------------------------|---------------------------------------------|------------------------------|------------------------------------------|
| Cl–HN | –1421.366 | 1826.340 | 1281.625 | 2.01397 |
| Cl–N | –2849.103 | 8625.442 | 137.119 | 0.61021 |
| Cl–O | –2142.729 | 6523.416 | 0.73468 | 0.30704 |
| Cl–HO | –898.081 | 1569.668 | –0.4327 | 0.02244 |

program MC 91 [10] on the DEC 3100 and IBM 6000/530 workstations of the Austrian-Thai Centre for Computer Chemistry at Chulalongkorn University, where also all *ab initio* calculations have been performed with the program HONDO 7 [11].

Results and Discussion

Pair Potential

Optimal fitting was obtained by the potential form

$$\Delta E = \sum_i \frac{q_{\text{Cl}} q_i}{r_i} + \frac{A_{1i}}{r_i^4} + \frac{A_{2i}}{r_i^5} + A_{3i} \exp(-A_{4i} \cdot r_i),$$

where q_i is the partial charge of the *i*-th atom of NH₂OH, r_i the distance of this atom to Cl[–] and A_{ni} are the fitting parameters, listed in Table 2. The standard deviation obtained with this function was 1.52 kcal/mole, but for the most stabilizing region of the energy surface agreement is considerably better, as can be seen from the scatterplot in Figure 1.

The Mulliken charge for the atoms obtained with the basis set employed here lead to an increased dipole moment of the ligand molecule, about 20% above the experimental value [3]. This is a desirable effect, however, since ion-solvent polarization induces such an increase in the effective dipole moment.

The two r^{-n} terms cannot be given a simple physical interpretation; they should be considered mainly as convenient fitting devices which represent the aver-

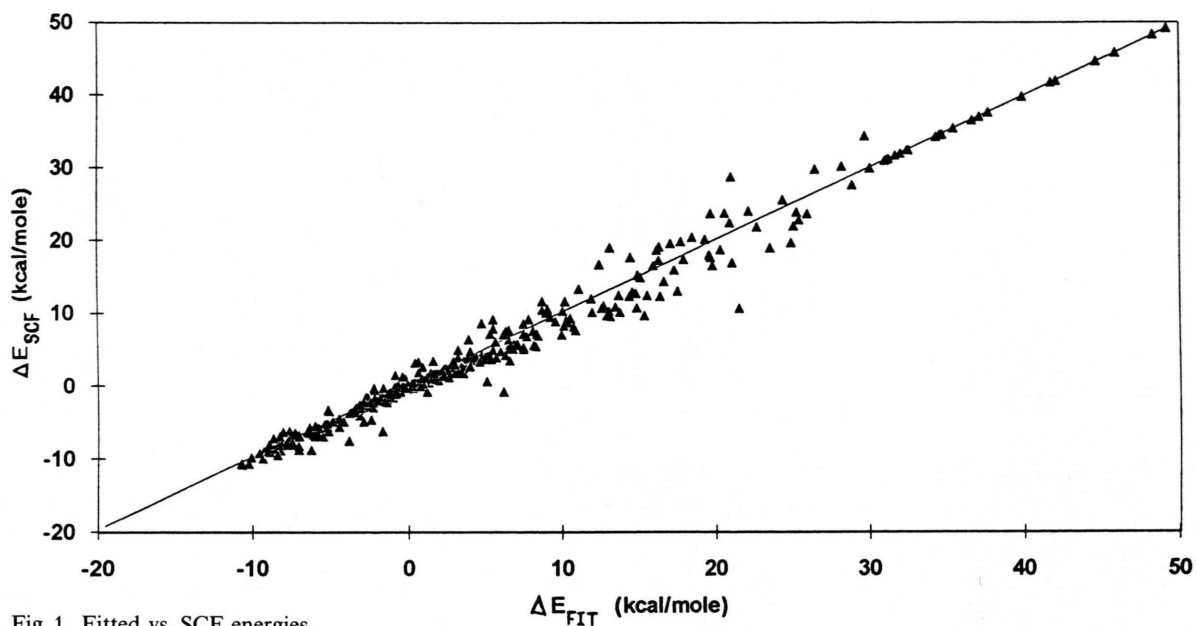
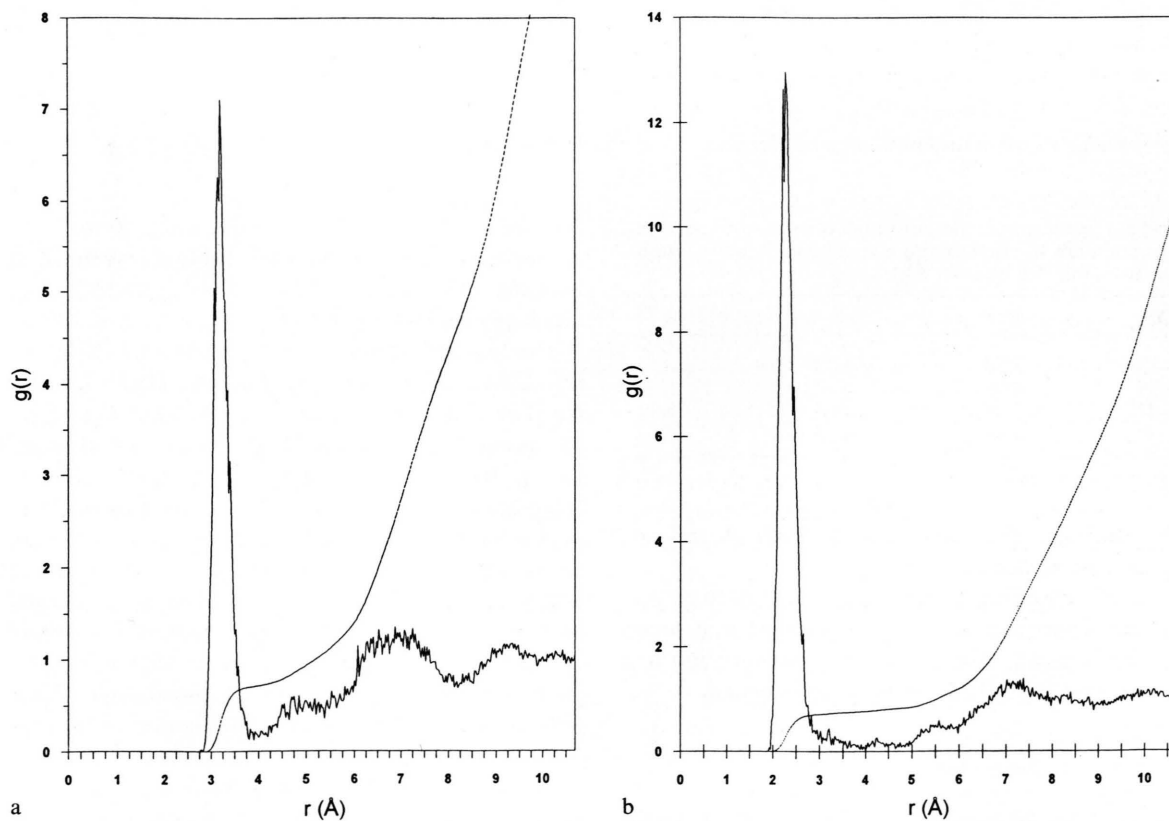


Fig. 1. Fitted vs. SCF energies.

Fig. 2. Radial distribution function and integration/10. a) Cl-O; b) Cl-H_O.

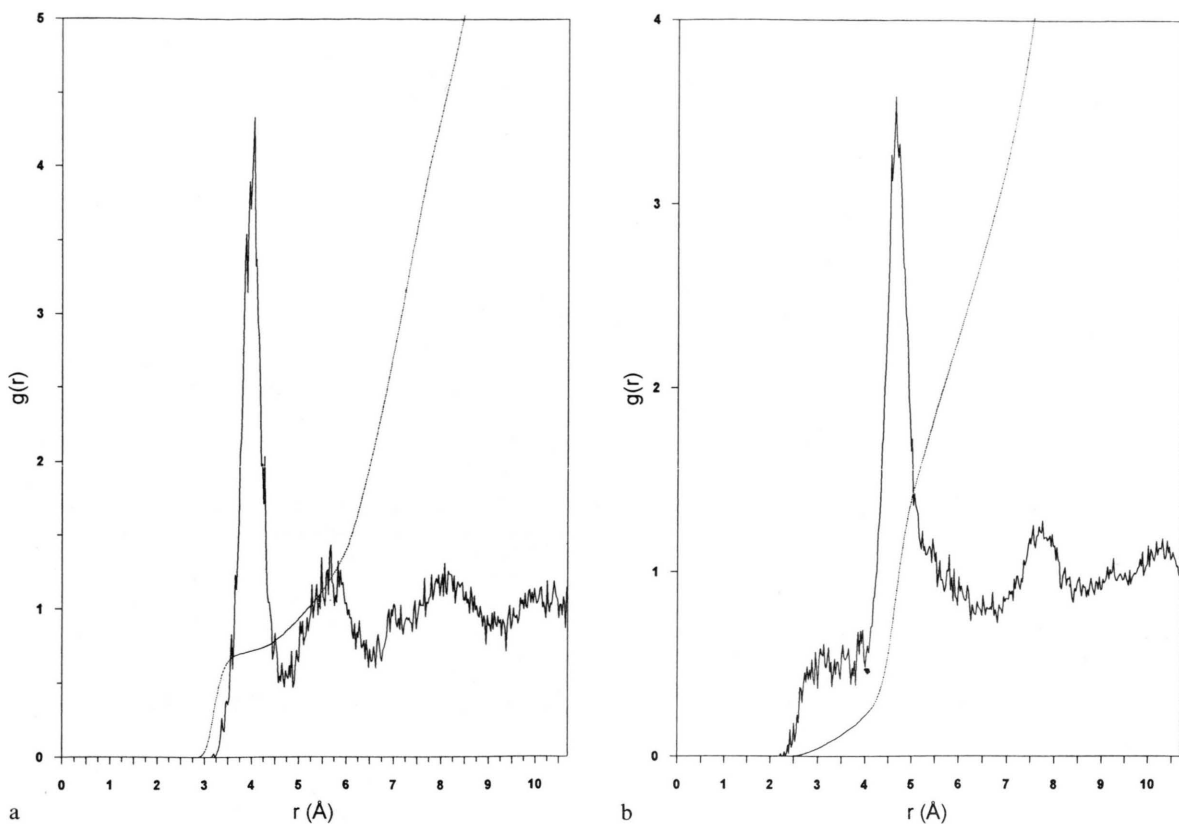


Fig. 3. Radial distribution function and integration/10. a) Cl-N; b) Cl-H_N.

Table 3. Characteristic data of radial distribution functions; first maximum R_1 , first minimum r_1 and integration number n up to r_1 (all distances in Å).

| RDF | R_1 | r_1 | n |
|-------------------|-------|-------|-----|
| Cl-O | 3.20 | 4.00 | 8 |
| Cl-N | 4.00 | 4.70 | 8 |
| Cl-H _O | 2.28 | 4.60 | 8 |
| Cl-N _H | 4.63 | 6.50 | 25 |

age influence of various effects, such as induced dipole- and higher interactions.

Three-body effects could be expected not to play an important part due to the relatively weak interaction and the large equilibrium distance between ion and ligands, and have thus not been investigated.

Monte Carlo Simulation

Structural information was collected from the sampled configurations in the form of radial distribution

functions (RDF) and their running integration. Their characteristic data are shown in Table 3, and the most relevant RDFs, Cl-O, Cl-N, Cl-H_O and Cl-H_N, are displayed in Figs. 2 and 3.

The first maximum in the Cl-O and Cl-N RDFs is located at 3.2 and 4.0 Å respectively, clearly indicating that hydrogen-bonding of the solvent ligands to Cl⁻ occurs to O of NH₂OH. This is confirmed by the Cl-H_O RDF, showing a single sharp peak at 2.28 Å. Integration of this peak as well as of the first peaks of the Cl-O and Cl-N RDFs leads to 8 NH₂OH molecules located in the first solvation shell of the chloride ion. The Cl-H_N RDF shows a shoulder first, followed by a larger peak extending up to almost 7 Å, where integration already reaches a value above 20. This RDF indicates that the angular orientation of the solvent molecules in the first shell is not uniform so that a few of the NH hydrogens can be found within the area of the first shell. The majority of them are located at the far side of the anion, where some NH hydrogens of the outer region can be found already.

A second solvation layer is not well defined, but according to the Cl–N and Cl–O RDFs, nitrogen atoms are closer to the solvent molecules in the first shell than oxygens. Since all NH_2OH – NH_2OH RDFs are identical to those of the bulk solvent [2–4], this second layer can be considered rather as a perturbation of the bulk structure by the solvate and not as ion-oriented second solvation shell.

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