



CHAPTER 5

DISCUSSION

5.1 Zn(II)-NH₃ Intermolecular Pair Potential

In Table 4.2, the standard deviation of the fit decreases only slightly when the number of SCF data points are increased from 475 to 575. The low value of 0.409 kcal/mol indicates that the interaction of Zn(II) and ammonia is well represented by the function. A comparison of the stabilization energies obtained from SCF calculation and fitted function at various orientation, as shown in Fig. 4.2, are in good agreement, especially for the vitally important region, the minima.

Fig. 4.1 indicates that the function can represent the attractive interactions very well, while it is somewhat less accurate for the repulsive interactions. However, the interactions will never reach those points when the simulations are performed at normal temperatures.

5.2 Zn(II)-NH₃ Intermolecular Potential with Three-body Correction

5.2.1 Non-Additivity of Zn(II)-NH₃ Pair Potential

From Table 4.3, the ion-nitrogen distance is found to increase and the stabilization energy per ammonia molecule, ΔE_{av1} , to decrease as expected, for the larger clusters. Since no literature data available for the metal-ammonia system, these

results can only be compared to the cation-water system. Since most of small cations prefer octahedral coordination under normal conditions, the calculations for $n=6$ are the most interesting. The increase of the Zn(II)-N distance of 0.33 Å from $n=1$ to $n=6$ is quite large, whereas the corresponding values for Na(I), Mg(II) and Al(II) complexes with water are 0.22 Å, 0.16 Å and 0.13 Å, respectively [75]. The accompanying drop in the interaction energy per solvent molecule is 28% ($\%E_1$) for the Zn(II)-NH₃ cluster and more than 40% for the corresponding Zn(II)-water clusters. The main reason for the smaller loss of complex stability despite of the larger increase of Zn(II)-ligand distance in the case of NH₃ should be due to the "softer" character of nitrogen as coordination site, allowing a good stabilization even at the increased distance.

Table 4.3 also demonstrates that the assumption of pairwise additivity of the Zn(II)-NH₃ interaction energy leads to an error of 18% for Zn(II)-(NH₃)₆, while these discrepancies for Na(I), Mg(II) and Al(III) in water are 8%, 15% and 21%, respectively. Since this percentage of non-additivity for Zn(II)-NH₃ is quite high, neglect of three-body corrections in the computer simulations would most probably lead to errors in radial distribution functions and their running integration numbers which are otherwise not very sensitive to the interaction potential.

5.2.2 Three-body terms

The three-body correction ΔE_{3b} is slightly attractive at short distances ($r_1, r_2 \leq 1.8$ Å) and repulsive at intermediate distances between 2 Å and 3 Å before decaying to zero at about 6-7 Å. A simple analytical expression cannot properly model this unusual three-body behaviour observed for the Zn(II)-ammonia system. Therefore, in

the fitting procedure, it was decided to omit about 300 attractive SCF data points in the region of $r_1, r_2 < 1.8 \text{ \AA}$.

An unusual behavior of the three-body correction similar to our has been observed by Lybrand and Kollman, who found that three-body interactions for the hydration of Mg(II) are attractive at short distances ($< 2 \text{ \AA}$) and repulsive at medium distances. The same behaviour has been reported by Ortega-Blanke et al. [76] for Mg(II) and Ca(II) water-clusters and by Kockanski [77] for $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ system.

The omission of these attractive three-body terms at distances $< 1.8 \text{ \AA}$ in the fitting should not cause any problem for the quantitative behaviour of the three-body function since they would occur only within the area where the two-body terms are already highly repulsive.

A strong three-body effect is clearly recognized, especially when both ammonia molecules are coordinated in the first solvation sphere (Figure 4.4 (a) and 4.4 (b) where $r_2=1.95 \text{ \AA}$ and 2.00 \AA , respectively). The three-body interaction energies are less than 0.5 kcal/mol when the first ammonia situates at 5.0 \AA from Zn(II) and vanish when both ammonia are more than 5.0 \AA far from Zn(II).

5.2.3 Monte Carlo Simulations : Radial Distribution Functions and Running Integration Numbers

According to the Zn(II)-N radial distribution functions and the corresponding integration numbers displayed in Fig. 4.5 for both simulations, without and with three-body correction, the solvation structure of Zn(II) in ammonia is strongly influenced by the non-additivity correction, both for radius of solvation shell and the corresponding coordination number. Without the use of the three-body correction, the first solvation sphere of Zn(II) is represented by a sharp Zn(II)-N peak

at 2.10 Å, followed by a small pronounced peak centered at 2.85 Å. Integration up to the local minimum between them leads to a number of 6.0 ammonia molecules and over both peaks up to 3.50 Å to a number of 9 ammonia molecules. Inclusion of the three-body terms causes a single distinct peak for the first solvation shell whose maximum is shifted to 2.22 Å. The small peak at 2.85 Å has disappeared, and thus an unambiguous coordination number for the first shell of exactly 6 is obtained.

The second peaks of $g_{ZnN}(r)$, centered at 4.35 and 4.40 Å without and with 3-body correction, respectively, are well recognized. The number of ammonia molecules contained in this second solvation shell is 19 and 17, respectively.

Although no experimental data are available for the structure of Zn(II) in liquid ammonia, it seems that the potential function including three-body interactions offers a far more reliable result than the conventional pair potential. The assumption of a realistic description of Zn(II) solvation in NH_3 by means of simulation with this corrected potential is supported by some recent results of aqueous solutions of $ZnCl_2$ [78,79] and $CuCl_2$ [80,81], where 3-body corrections were introduced in an approximate form. For these systems, conventional pair potentials had failed to predict structural data observed by experimental investigations, but the approximate 3-body correction was sufficient to establish full agreement with experimental results.

5.3 Molecular Dynamics Simulation Using Zn(II)- NH_3 Intermolecular Pair Potential Without Three-body Correction

Section 5.2 has shown how much the three-body effects influence the structural properties. The Molecular Dynamics simulations using the

Zn(II)-NH₃ intermolecular potential excluding three-body terms were performed in order to compare the results with the Monte Carlo data of section 4.2.3 .

The $g_{ZnN}(r)$ of MD simulations for the two temperatures (Fig. 4.6) show sharp peaks at 2.10 Å in agreement with MC results, followed by a number of local peaks around 2.6-3.6 Å. Although the MD RDFs do not show the well-pronounced second peak as MC, all the peaks of MD and MC approach zero about 3.5 Å. In addition, integrations up to the first local minimum at 2.5 Å, and up to 3.5 Å, lead to the same values of 6 and 9, respectively. These accordances of MD and MC mean that the conventional pair potential definitely fails to represent the interactions between Zn(II) and NH₃ in condensed state. Therefore, all further simulation work was carried out with the Zn(II)-NH₃ intermolecular potential including three-body corrections.

5.4 Static Properties

5.4.1 Solution Structure

(a) Solvent Structure

Due to the fact that there is only one ion per 215 ammonia molecules, the observed solvent properties are within the limits of statistical error identical with those of pure liquid ammonia. The N-N RDF from the X-ray measurements by Narten [73] at 277 K (see Table 4.5) exhibits a maximum at 3.37 Å and minimum at 5.3 Å leading to the coordination number of 12. The MD results agree well with these X-ray data, especially for the coordination number and height of the first RDF peak. The

N-N nearest neighbour distances resulting from four other simulations [33,76-78] agree within methodical limits with the ones found in this work and the X-ray measurement, while those reported in [79] and [80] are smaller by about 0.2 Å. All coordination numbers calculated range from 12 to 13. The N-H and H-H RDFs show only a small deviation from a uniform distribution and they are not significantly different for the two temperatures (Fig. 4.8 and 4.9). The shoulder in the N-H RDF (Fig. 4.8) at approximately 2.3 Å corresponds to the first maximum of the O-H RDF in water [81]. The fact that, contrary to the water case, the first and second peak in the N-H RDF are not separated and the shoulder is only weakly pronounced, shows the relatively low contribution of hydrogen bonding to the structure of liquid ammonia. This is in agreement with the value of 12 for the coordination number which also favours the picture of a closely packed structure rather than that of a hydrogen bonded network.

(b) Solvation Shell Structure of the Zn(II)

In Fig. 4.7 the Zn-N RDF and the corresponding running integration numbers for the two temperatures are depicted. A well pronounced first solvation shell can be seen from the sharp peak with maximum at 2.23 Å and 2.21 Å for 235 K and 266 K, respectively. The first peak in Zn-N RDF is lower than that of Zn-O RDF in water at 277 K [74] (Table 4.5). Integration of the Zn-N RDF over the first solvation shell yields 6 ammonia molecules indicating favourization of an octahedral structure, which is in agreement with the result of our Monte Carlo simulation (see 4.2.3). Difference in the Zn-N RDF between the two temperatures are found only in the heights of the first peak and the distances of the second maxima. The higher first maximum of the RDF and shift of the second solvation shell to shorter distance for

266 K show the effect of pressure (about 5 bar) on the solvation structure. In the case of aqueous solutions [82-84], increase of pressure does not significantly influence the hydration shells but only hydrogen bond structure of bulk water.

5.4.2 Intramolecular Geometry

Intramolecular geometry is a time-averaged property available only from MD and MC simulations with a flexible model. As shown in Fig. 4.10, the most probable N-H bond length of ammonia in the solvation shell of Zn(II) is longer than that of ammonia in the bulk since N-H bonds of ammonia in the solvation shell are weakened by the interaction between Zn(II) and nitrogens. In comparison with Li(I) and Na(I) [33,76], Zn(II) has a much stronger effect on the intramolecular geometry of ammonia in the solvation shell. Shifts of the most probable H-H distances and HNH angles to lower values (Fig. 4.11 and 4.12) for ammonia in the solvation shell indicate the repulsive force between Zn(II) and hydrogens.

The effect of temperature on bulk ammonia by broadening of the N-H, H-H and HNH peaks at increased temperature can be explained by simple kinetic theory. In contrast to bulk ammonia, these peaks for ammonia in the solvation shell are more narrow when the temperature increases. According to the effect of pressure on the solvation structure (see section 5.4.1 (b)), solvating ammonia gets closer to Zn(II) which leads to more restrictions in the movement of the hydrogen atoms.

5.5 Dynamic Properties

Normalized velocity autocorrelation functions (VACFs) allow the investigation of translational motion of Zn(II) and of translational motion, vibrational

motion and rotational motion of ammonia molecules. Due to the cost of simulations, more illustrative data by Fourier transformation could not be provided. Therefore, it is difficult to distinguish rotational and vibrational motion by the VACF itself.

In Fig. 4.13 the normalized VACFs are plotted versus time up to 1.8 ps. The strong oscillation of the Zn(II) VACF, also observed for Ca(II) [85] shows tightly bound movement of Zn(II) within the ammonia solvation shell. In comparison with VACF of singly charged cations [33,86,87], the translational motions of doubly charged cations are much more hindered.

In Fig 4.14 the normalized center-of-mass VACF of bulk ammonia decays to zero over a time range about 0.8 ps and remains zero except for statistical noise. There are some small oscillations before approaching zero which were not observed in the simulations reported by Hannongbua [33]. These fluctuations indicate the influence of Zn(II) on ammonia beyond the solvation shell. Large oscillations in the normalized center-of-mass VACF of ammonia in the solvation shell indicate that these ammonia experience strong vibrations.

The normalized VACFs of nitrogen and hydrogen atoms (Fig. 4.15 and 4.16) give some informations of intramolecular dynamic properties. Nitrogen VACFs, show after smoothing the same behavior as the center-of-mass VACF of ammonia molecules. This implies that the translational motions of the whole ammonia molecules are dominated by these of nitrogen atoms. A series of pronounced local peak in nitrogen's VACFs and large oscillations in the hydrogen's VACFs give evidence of internal vibrations of ammonia.

Without Fourier transformed data, unavailable for aforementioned reasons, the effect of temperature on dynamic properties, rotational motion and intramolecular vibration can not be clearly visualized.