C H A P T E R   I

INTRODUCTION

Solutions and the liquid state , especially aqueous solutions play an important role in many chemical processes in nature. According to advantages for energy exchange and reaction mechanisms, most of the chemical operations such as synthesis , mixing , purification and separation are performed in the liquid state in laboratory and industry.

Nevertheless, a proper mathematical approach to describe the structure of the liquid state has long been a problem. It is comparatively simple to develop a mathematical treatment describing the gaseous and the solid state because of the long distances of molecules and the regular arrangement of atoms or molecules, respectively. In the liquid state, however, a continuous consideration of most the other variable intermolecular interactions is required , without the regularity but at the density of the solid state.

Based on the theoretical approach by Bernal and Fowler (1), in which water was considered as individual molecules , Frank and Wen (2) presented a simple model to describe the structural aspects of ions in aqueous solutions. They proposed three different regions A,B , and C of water molecules surrounding ions. In region A, water molecules are strongly oriented by the powerful short-range forces acting between solute and solvent , and the influence of Coulombic forces is significant as well. The water structure in region C is the

same as in bulk water. Region B, which interfaces regions A and C, is assumed in order to allow a continuous transition between these struc- tures. It is generally called " region " , according to macroscopic observations. The most interesting area is of course the region A, which is called " solvation shell " , where spectroscopic measurements can provide structural data.

The concept of solvation is often used in general to describe the structure of a solution where the geometrical arrangements are significantly different from the bulk structure of the solvent itself. The dynamical stability depends on the combination of forces acting between homogeneous or heterogeneous molecules of which the solution consists. On one hand , a discrete solvation shell can be based on a solute - solvent interaction which is so strong that the exchange rate is much lower in the first solvation shell than that among solvent molecules. On the other hand, a shell structure can also be detected even when the interaction between solute and solvent is weaker than the solvent-solvent interaction. In this case density and mobility effects in the solution are the dominant factors rather than the binding forces between particles.

Some decades ago, investigation of solution structure was mainly a domain of spectroscopical methods such as X-ray , neutron diffraction and NMR etc. They encounter, however, some difficulties to produce data when the sample is very dilute , or when solvent exchange takes place very fast , or when the interaction is so weak that the input energy from the spectroscopic apparatus exceeds that of the interaction which should be detected.

Especially solvation numbers for ions depend on methods being used for their determinations (78,79) and have to be based, in addition, on an arbitrary separation of anionic and cationic contributions to the overall-effect being measured. Diffraction data seem to supply the most well-defined results. The capacity of these methods seems to be limited however, by the complexity of the system being investigated and the impact of energy exerted during the measurement, in comparison with the interaction energies determining the formation of structural units in solutions.

Quantum chemical investigations, which still have strong limits in the size of molecular system and the related computational time , have been a useful tool to predict configurations of molecules, stabilization energies, excitation energies , force constants , and other physical data. Although they often produce data in good agreement with experiment , this approach can not reflect all properties of a condensed system with large amounts of particles.

The availability of electronic computers with high processing capacities has changed the situation most favourably within the past twenty years. Numerical solutions for the n-electron systems have become feasible at ever increasing levels of accuracy and complexity, and statistical mechanics has made a remarkable progress with the help of computer technology , and can be applied by simulations of Monte Carlo or molecular dynamics types, originally introduced by Metropolis et al. (3) and Adler et al. (4). These methods have overcome some limitations of first approaches and made it possible to simulate the statistical and dynamical behaviors of rather large ensembles of molecules based on accurate potentials derived from

quantum chemical calculations. Therefore, theoretical investigations of the liquid state and solutions have rapidly developed.

Numerous studies based on Monte Carlo and molecular dynamics simulations for solution have already been plublished (5-30). Most of the discussions were , however, based on the structural and dynamical properties concerning the first hydration shell structure. It is also interesting to obtain data how far the influence of an ion acts beyond this first solvation shell , as this gives interesting information about the further structure and the microscopic properties of solutions.

Monte Carlo simulation allows not only to evaluate solvation numbers and solute-solvent distances from computed radial distribution functions , but give also access to data not available from any experimental technique so far, as for example an analysis of the percentual contribution of various coordination numbers to the average solvation number of ions or solvent molecules. The access to the angular distribution of neighbour molecules is also an important means of these methods for the evaluation of structural factors in solution.

Most of computer simulations being presented focus only on pure liquids (5,8-9,13,18,20) and ions in water (15,19,21,24-28) , while computer simulations of solvent mixtures are relatively rare (6,10,14,21,22,29,30). Solutions consisting of two different kinds of solvent are particularly interesting, as they behave as both solvent and solute to each other.

There exist so far only a few Monte Carlo simulations, concerning mixed solvents (6,10,14,21,22,29) , and only one dealing

with the solvation of an ion in mixed solvent (30), namely sodium ion in aqueous ammonia. Considering the size of ions and the property of " hardness " and " softness " (31) of solvent molecules and ions, it seems of particular interest, therefore to compare sodium with the smaller and " harder " lithium ion. As an analysis of the solvation shell structure by any experimental means is almost impossible, especially for very dilute solutions and ligands as similar as ammonia and water, statistical mechanic simulations of the Monte Carlo type represent the most appropriate tool to gain access to such data (29).

In the first part of this thesis, therefore , the potential function of lithium ion/ammonia has been determined. The ab-initio LCAO-MO-SCF (Linear Combination of Atomic Orbitals to form Molecular Orbitals establishing a Self-Consistent Field) method is presented in chapter II and the fitting procedures of the potential function are contained in chapter III. The second part, Monte Carlo simulations of a lithium ion in 18.45 mole % aqueous ammonia solution have been performed based on ab-initio LCAO-MO-SCF pair potentials. The details of simulation is given in chapter IV. Simulation results and discussion are presented in chapter V in form of radial distribution functions and other structural and energetical properties. The results are compared with those for aqueous ammonia solution (29) and sodium ion in this solution (30). In the last chapter, characteristics of the preferential solvation of lithium ion in 18.45 mole % of aqueous ammonia solution are summarized.