CHAPTER I

Introduction

1.1 General about liquid state and solutions

Elements and chemical compounds may exist, under suitable conditions of temperature and pressure, in three different physical states called, respectively, the solid, liquid and gaseous states. The solid state is stable at low temperature and/or high pressure; the liquid state is stable in an intermediate range of temperature and pressure, and the gaseous state is stable at high temperature and low pressure. The solid state is characterized by high cohesion and rigidity; the liquid state by high cohesion, lack of rigidity and comparatively low resistance to flow; and the gaseous state by low cohesion, lack of rigidity and low resistance to flow. On the molecular level the solid state exhibits a regular crystalline structure and the gaseous state has complete molecular disorder, while the liquid state is intermediate between these extremes. Solutions are homogeneous mixtures of solid, liquid or gaseous state in which all parts of the mixture have the same composition. They all consist of two or more components which remain mixed in solution and have no tendency to separate from the solution. The properties of a solution depend on the type of solute and solvent which are the components of the solution.

Solutions and liquid state have been performing an essential role in many chemical process in nature. Most chemical systhesis is carried out in the liquid state because reactions are on the one hand faster than in solid state and on the other hand energetically cheaper and mechanistically simpler than in gaseous state. Most methods of purification involve either a distribution of solutes between immiscible solvents or the partition of mixtures in solid-liquid or liquid-gas equilibria. Most biochemical and many environmental systems are in the liquid state or involve colloids or membrane boundaries between liquids.

Some decades ago, investigation of liquid and solution structure was mainly based on spectroscopic methods such as x-ray scattering technique. The information which can be derived from this technique can be summarized in the so-called "radial distribution function", which describes the distribution of molecules around a given central molecule or atom selected for consideration. Clearly this function contains a good deal of information about the structure of liquid and solution. From the intensity $I(\theta)$ of the x-ray scatter by a liquid in a direction making an angle θ with the incident beam, the radial distribution function $g(r)$ can be computed and used to determine the structure of liquid. The experimental approach to liquid and solution structure, although it has produced many reliable informations on a wide range of systems, it encounters, however, some difficulties to produce data when the sample is very dilute or when the interaction is so weak that the input energy from the spectroscopic apparatus exceeds that of the interaction energy which should detected.

1.2 Theoretical approaches to the description of liquids and solutions

The attempts that have been made to formulate a theory of liquids fall into two broad classses. Theories of one class start from a description of the structure, usually a simplified and approximate description, leaving the question of how the structure is determined by the molecular properties to be answered after the fact. These theories are called "lattice" theories because the proposed structure often bears some relation to the regular lattice structure of a crystalline solid. Theories of the other class place emphasis initially on the process by which the intermolecular forces determine the structure, in the hope that a correct mathematical description of this process will lead to equations whose solutions describe the actual structure. Theories of these class are called "distribution function" theories because the equations involve distribution functions specifying the probability of finding sets of molecules in particular configurations. Both of these approaches have respectable antecedents. The first develop logically from methods found to be successful in the theory of solids, while the second draws its ideas to some extent from the equally successful

kinetic theory of gases.

For solutions, a concept used in the treatment of the behavior of ions existing in is the so-called "solvation" or "hydration number". The discussion of hydration numbers over the years has given some insight into the question of short and long range interaction of ions with solvents and the problem of coordination of ions by solvent molecules in the bulk. The hydration number is conventionally defined as the number, n, of water (or solvent) molecules that are "associated" with the ion in the solution. In order to have a quantitative definition of n, Bjerrum (1) has defined the hydration number as the number of water molecules which have an energy of interaction with the ion greater than kT, where k is the Boltzmann constant and T is the absolute temperature. The distance from the ion at which this condition limitingly obtains could be called the hydration radius. Due to some difficulties of calculation the number n resulting from an estimated ion-solvent inteaction energy on this basis, an alternative definition was proposed by Azzam(2). He regarded n as being defined as the number of water molecules around an ion which have an energy of interaction with the ion greater than or equal to that with other water molecules in the bulk. This approach is obviously more satisfactory than the first as it attempts to base the definition of hydration number on the distinguishable properties of water molecules near an ion in comparison with those of water molecules associated with other water molecules in the bulk.

A useful operational definition of hydration number and distinction of n values into two classes was given by Bockris (3). He defined a *primary solvation number, n_1,* as the number of water molecule which are relatively permanently associated with the ion and move with it as an entity in the kinetic behavior of the ion. The corresponding distance within which such water molecules are associated with the ion is called the *"primary hydration shell"*. Secondary hydration, corresponding secondary hydration numbers, n_2, describe the situation of the large number of water molecules that are in some way affected by the ion but do not move with it as a

kinetic entity. There are a number of methods to obtain a hydration number of solutions but the most suitable one is to obtain it via the radial distribution functions. Thus, the hydration number based on the number of nearest neighbour water molecules to an ion is defined as :

$$n \quad = \quad 4 \pi \rho_0 \int_0^{r_{ml}} g_{IO}(r) . r^2 dr$$

(1.1)

where ρ_0 is the mean number density of water molecules, $g_{IO}(r)$ the ion (I)-oxygen (O) radial pair distribution functions and r_{ml} the position of the first minimum in $g_{IO}(r)$.

The usage of quantum chemical calculations in solution chemistry extends from investigations on various aggregates and/or complex species formed in solution to the development of intermolecular potential functions describing the interaction between species present in a consensed (liquid) system. Typical applications of the first type are calculations of solvated solutes (e.g. hydrated ion structures) or of various hypothetical species expected to be formed according to potentiometric or spectroscopic investigations of solutions.

The availability of fast computer in the past decade has, however, opened solution chemistry to yet some other computational research tools, formerly restricted to limited applications, only simple chemical model systems and specialized theoretical chemists. These tools - mainly quantum chemical calculations and statistical simulations of the Monte Carlo and Molecular Dynamics type - are widely applicable now to larger molecular systems and to solutions of practical chemical interest. Especially for investigation of microstructures formed in solution, these tools are nowadays sometimes even superior to experimental methods, and for many systems, where experiments cannot be performed (e.g. infinite dilution), these computer simulations can be employed.

The quantum chemical evaluation of intermolecular potential functions has become a more and more important application of such methods, as the availability of such potential functions is a precondition for the performance of simulations, either of the Monte Carlo or Molecular Dynamics type. This application therefore deserves some more detailed attention, especially since the quality of such functions is essential for obtaining correct structural and other data from the simulations.

Although the importance of 3-body terms for the accurate description of intermolecular interactions in condensed systems is well-known (4-6), most of Monte Carlo and Molecular Dynamics simulations of aqueous salt solutions have been performed assuming additivity of pair potentials (7-11). For monovalent and some divalent metals ion, most of the structural data obtained appeared to be correct. When, however, water is strongly bound to divalent ions at comparatively short distances, the neglected 3-body terms become significant enough to alter crucial structural data such as the first shell coordination number. For example, inclusion of 3- body effects was needed to correct the first hydration shell numbers 6 and 8 as predicted for Be^{2+} and Cu^{2+} by pair potential functions, to 4 and 6 respectively.(12,13)

In this work, a Monte Carlo simulation of Zn^{2+} ion in water using a conventional pair potential also encountered the same problem as in the case of Cu^{2+}, due to the lack of three-body terms in the potential function it resulted in the wrong hydration number of 8. Inclusion of (at least) 3-body effects was inevitable therefore. Since the usual evaluation of a suitable function including 3-body terms is very demanding in time as well as computational effort, thus a new approach which has been used successfully in the case of Cu^{2+}(13) is performed and tested for the case of Zn^{2+} in water. The procedure is refered to as "Nearest Neighbour Ligand Correction (NNLC)". This improved potential will be employed to simulate Zn^{2+}-water system at infinite dilution and, in order to compare simulation results to more experimental data, simulations will be also performed for 1 M, 3 M and 5 M

solution of zinc chloride in water.

Within this thesis, the ab-initio LCAO-MO-SCF (Linear Combination of Atomic Orbitals to form Molecular Orbitals establishing a Self-Consistent Field) method and analytic forms of intermolecular potential functions are presented in chapter II. The theory of Monte Carlo and some reviews of MC simulations of electrolyte solutions are contained in chapter III. In chapter IV, the results for Zn^{2+}-water pair potential function from MC simulation are given and in chapter V, the results for Zn^{2+} - chloride pair potential function including NNLC correction. Chapter VI contains the results from MC simulations of $ZnCl_2$ solutions at 1, 3 and 5 M concentration. The results are also compared with various experimental data (46,54-57). The thesis is concluded by a summarizing discussion.