

## CHAPTER I

### INTRODUCTION



#### Review of Liquid State

Liquid state, including solutions, plays an essential role in most chemical processes in nature. Many chemical operations, for example, synthesis, mixing, purification and separation are carried out in the liquid state. The reactions in this state are much faster than in solid state, on the other hand, energetically cheaper and mechanistically more flexible than in gas state. There are many fascinating behaviours of liquids, for instance, the liquids flow, even when they are very viscous. They may be found in either bulk or tiny droplets. They may be vaporized or frozen. Life exists on the some of chemical reactions in the liquid state. Most biochemical and many environmental systems are in the liquid state or involve colloids or membrane boundaries between liquids.

The study of the liquid state of matter has a long and rich history, from both theoretical and experimental approaches. Based on the theoretical method by Bernal and Fowler (1), water was considered as individual molecules. Frank and Wen (2) presented a simple model to describe the structural aspects of ions in aqueous solutions.

Although the experimental approach has produced many reliable informations on structure of liquids and solutions, 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 be measured. In addition, the measurements concern mostly the study of a one-component solvent, while preferential solvation in mixed solvents is acceptably important phenomena, for which theoretical studies are also still quite rare; mostly due to the relatively high computational effort needed for the simulation of multicomponent systems.

### Computer simulation of liquids

Computer simulation is presently emerging as a powerful and increasingly popular computational means for the study of liquids and solutions. With knowledge of experimental testing, theoreticians have tried to develop simple models and to explain how liquids behave. A successful theory of the liquid state will be one that explains the bulk properties of the liquid from the knowledge of the intermolecular potentials.

In recent years a method has been developed for modeling liquids (3) which has been conceptually valuable and has proved capable of giving a quantitative interpretation of bulk properties. This method uses a modern computer with fast operation and large core storage to simulate the behaviour of a large number of atoms or molecules interacting under some assumed potential functions. No computer is large enough to

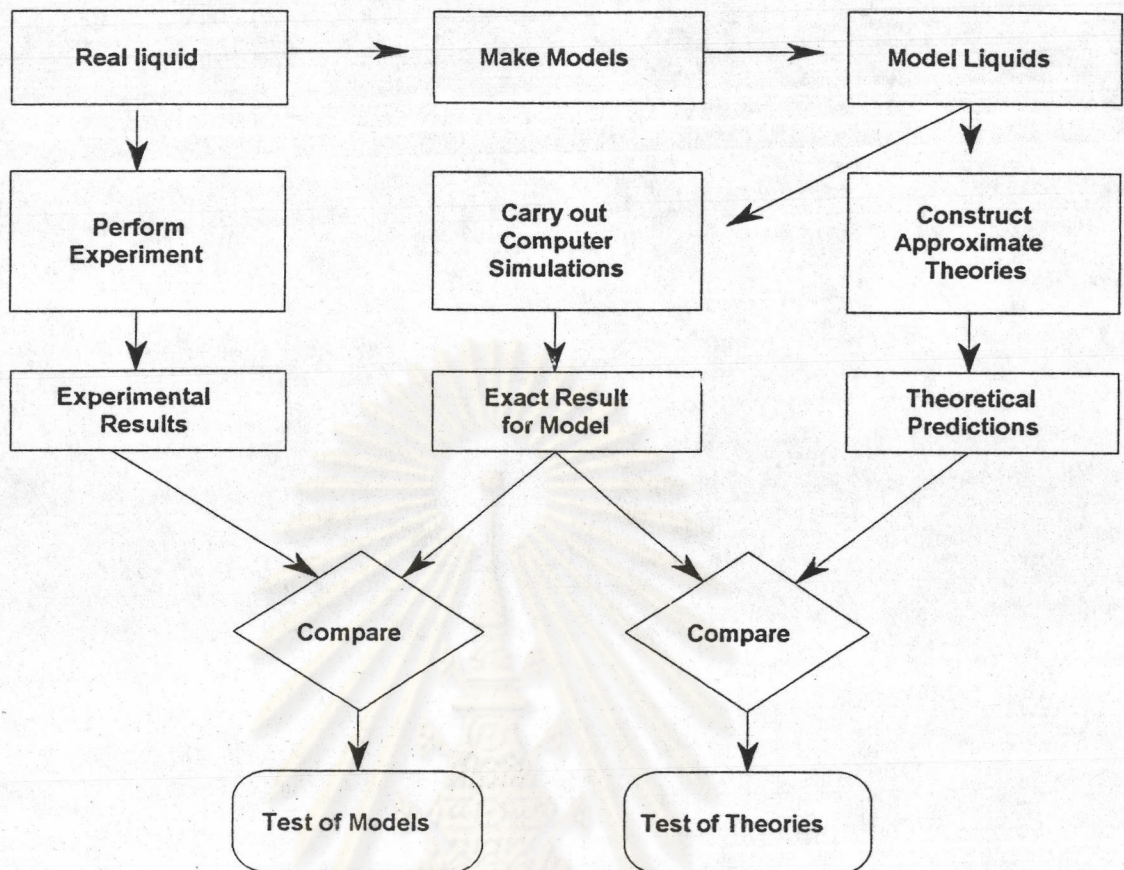


handle directly the interaction of one mole ( $10^{23}$  particles) but techniques exist for dealing with much smaller numbers ( $10^2$ - $10^3$ ) which will give results not significantly different from the true bulk. This mathematical method has been known as "*computer simulation*", whose technique has been developed in two different ways, Monte Carlo (MC) and Molecular Dynamics (MD). They are widely applicable now to large molecular systems and to solutions of practical chemical interest, especially for investigation of microstructures formed in solution.

It is now about 40 years since the first computer simulation of a liquid was carried out at the Los Alamos National Laboratories in the United States. Due to the rapid development of computer technology, computer simulations have been expanded at a tremendous speed (4) and application of these and other simulation methods have penetrated almost every field of physics, chemistry, biosciences and engineering sciences. Results of the simulations may also be compared with those of real experiments. In the first place, this is a test of the underlying model used in a computer simulation.

The connection between experiment, theory and computer simulation is exhibited in Figure 1.1. If the model is a good one, the simulator hopes to offer insights to the experimentalist, as a bridge between models and theoretical predictions on one hand, and between models and experimental results on the other. Because of this connecting role, and the way in which simulations are conducted and analysed, these techniques are often termed "*computer experiments*".





**Figure 1.1** The connection between experiment, theory and computer simulation.

The availability of powerful 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. The Monte Carlo and Molecular Dynamics methods have overcome some limitations of the first approaches and made it possible to simulate the statistical and dynamical behaviour 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 and numerous studies based on these methods for solution have been published (5-9). Most of the investigations were, however, based on the structure and dynamic properties of pure liquids or the first solvation shell of ions in pure solvents.

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 perceptual contribution of various coordination numbers to the average solvation 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.

#### **The hydroxylamine - water system**

Huge amount of experimental and theoretical data on aqueous electrolyte solvation have been collected over the last hundred years because of their importance in physics, chemistry and biology. Much of chemistry and virtually all biochemical system pertain to solutions and involve ionic species. Mixed aqueous-organic solvents is not only



used for the study of electrochemical processes and for carrying out analytical procedures, but also for synthesizing compounds by reaction paths that involve ionic intermediates.

In all of these systems, the ions interact with solvent molecules and these interactions are of importance for the chemist and biochemist. The extent of these interactions and the rate of any reactions in which the ions take part depend strongly on the nature of ion-ion, ion-solvent and solvent-solvent interactions. Understanding the rate of solvent, effecting the interactions and reactions that ions undergo in solution, can help us to optimize the variables in their reaction system to achieve their purpose, and also to rationalize the phenomena underlying experimental observation. The main idea to study the system of hydroxylamine-water mixtures treated here is to understand the fairly complicated processes in systems offering various coordination site to ions, as it also happens in numerous biosystems.

### The present work

The solvation structure of water ( $\text{H}_2\text{O}$ ) and hydroxylamine ( $\text{NH}_2\text{OH}$ ) mixtures of different composition containing  $\sim 0.5$  M lithium chloride have been examined. Four different mixtures containing 195+5, 169+31, 129+71 and 75+125 water + hydroxylamine molecules have been considered by introducing constantly 2  $\text{Li}^+$  and 2  $\text{Cl}^-$  into these systems.



The mixture of these two solvents seem of particular interest, since  $\text{NH}_2\text{OH}$  chemically situates between water and ammonia and offers at the same time 2 hydrogen bonding regions and 2 coordination sites for the cation. Further, the relatively weak hydrogen bonding framework between  $\text{NH}_2\text{OH}$  molecules is easy to break (10) and hence allows easy orientational adaptation of these molecules as ligands in the first solvation shell of any central ion or molecule.

The simulation of solutions containing cations and anions simultaneous is an important extension of previous studies treating only one isolated ion in a mixed solvent (5,11,12). It is a further step towards the "reality" of the corresponding electrolyte solution. Experimental data for  $\text{LiCl}$  in aqueous hydroxylamine are unfortunately not available, but results of the theoretical approach will hopefully stimulate some experimental studies on this system.

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