Determination of the structural properties of the aqueous electrolyte $\text{LiCl}_6\text{H}_2\text{O}$ at the supercooled state using the Reverse Monte Carlo (RMC) simulation

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Abstract. A structural study of an aqueous electrolyte whose experimental results are available. It is a solution of $\text{LiCl}_6\text{H}_2\text{O}$ type at supercooled state (162K) contrasted with pure water at room temperature by means of Partial Distribution Functions (PDF) issue from neutron scattering technique. The aqueous electrolyte solution of the chloride lithium LiCl presents interesting properties which is studied by different methods at different concentration and thermodynamical states: This system possesses the property to become a glass through a metastable supercooled state when the temperature decreases. Based on these partial functions, the Reverse Monte Carlo method (RMC) computes radial correlation functions which allow exploring a number of structural features of the system. The purpose of the RMC is to produce a consistent configuration with the experimental data. They are usually the most important in the limit of systematic errors (of unknown distribution).

1. Introduction

Aqueous electrolyte solutions are of great interest in physicochemistry of materials, they possess the property of forming a glass through a metastable supercooled liquid state when the temperature decreases [1, 2, 3, 4, 5, 6]. Many properties of aqueous electrolyte solutions are due to the hydrogen bridge between molecules of water, resulting from orientations and interactions of water molecules and from the other interactions between water-ion and ion-ion, under influence of the salt concentration [2, 3, 7, 8, 9, 10, 11, 12, 13, 14]. Understanding of thermodynamic liquid and glass states is, in our view, advanced enough compared to the inevitable metastable supercooled state which ensures the passage between the two states. Several persuasive theoretical and experimental studies have been proposed over the last decades to explain and spell out the behaviour of this state. The purpose of this article is to add a piece in the puzzle of understanding anomalies of water and aqueous electrolyte solutions by studying the solution of LiCl in water (R=6) at the supercooled state (162K). The aim is to complement previous works by displaying all of pair distributions functions and computing some of physical properties such as numbers and the average positions of coordination.
We use the Reverse Monte Carlo (RMC) simulation in conjunction with neutron diffraction (ND) data [15]. This technique has the advantage to be applied without any specified interatomic and/or intermolecular interactions, it can be also, hybridized by introducing interactions potentials as additional constraint [9, 11, 16, 17]. RMC simulation allows the construction of a 3-dimensional model on the atomic level based on both experimental data and some geometric constraints. This simulation method completes the experiment by computing the pair correlation functions between each two components of the studied system.

Implementation method and details of the simulation performed here are described in Section 2. In Section 3 we give obtained results and their discussion. Finally in Section 4, conclusion is drawn.

2. Simulation details

The aim of the RMC simulation [18, 19, 20] is to produce three dimensional structural models of ordered or disordered systems consistent with the available experimental data (in particularly those of diffraction ) within fixed standard deviation. This technique is based on the same principle of the metropolis Monte Carlo (MMC) method [21], but instead of minimizing the potential term, the difference between the computed and the experimental total or partial distribution functions $G(r_i)$ is the quantity to be minimized $\chi^2$, which is given by

$$\chi^2 = \sum_i (G^{RMC}(r_i) - G^{Exp}(r_i))^2 / \sigma(r_i)^2$$

Where $G^{RMC}(r_i)$ and $G^{Exp}(r_i)$ are the total or partial distribution functions obtained from the RMC configurations , $\sigma(r_i)$ is an estimate of the experimental error.

The initial configuration depends on the type of the simulated materials; when studying ordered samples, atoms are positioned in the average crystallographic positions, and several unit cells are used to produce the simulation box. If studying disordered materials, a random distribution of atoms without unreasonably short inter-atomic distances is generated by using an initial code. A new configuration is obtained by random choices and moves of atoms, after each move, the atoms without unreasonably short inter-atomic distances is generated by using an initial code.

$$\chi^2_{\text{new}} \text{ is less then } \chi^2_{\text{old}}$$

The agreement between experimental and the current configuration is improved by the move, thus the move is accepted and another move is made, if $\chi^2_{\text{new}}$ is increased, it is not rejected outright but accepted with the conditional probability

$$\exp\left(-\frac{(\chi^2_{\text{new}} - \chi^2_{\text{old}})}{2}\right)$$

The process is then repeated until $\chi^2$ fluctuates around an equilibrium value. When satisfactory agreement between experimental and calculated data sets is obtained, the resulting configuration should be a three-dimensional structure compatible with the experimental data and the detailed structural information such as the number of coordination, the nearest neighbors positions and bond angle distribution functions can be calculated from atomic networks.

Four available experimental partial distribution functions $G_{XX}^{Exp}(r), G_{XH}^{Exp}(r), G_{HH}^{Exp}(r), G_{Cl\alpha}^{Exp}(r)$ obtained by the neutrons scattering technique from the isotopic substitution are used [2, 4, 5, 6, 8]. Where the subscript $X$ defines all atom species except the hydrogen one, while $Cl\alpha$ represents the correlation between Cl and all the other species.

$$G_{XX}(r) = 0.685g_{OO}(r) + 0.37g_{OCl}(r) - 0.085g_{OLi}(r) + 0.05g_{ClCl}(r) - 0.023g_{CLCl}(r) + 0.026g_{LiLi}(r)$$

$$G_{XH}(r) = 0.828g_{OH}(r) + 0.224g_{HCl}(r) - 0.051g_{HLi}(r)$$

$$G_{HH}(r) = g_{HH}(r)$$

$$G_{Cl\alpha}(r) = 0.28g_{OCl}(r) + 0.624g_{HCl}(r) + 0.104g_{ClCl}(r) - 0.025g_{CLCl}(r)$$
The initial configuration is a cubic box of 2880 atoms with periodic boundary conditions, where the oxygen atoms forms initially a face-centered cubic lattice and the chlorine and lithium atoms are placed in the interstices. The new configurations are obtained by random choices and moves of atoms under geometric constraints and they are accepted or rejected according the same conditions of MMC algorithm. Simulation parameters are summarized in Tables 1 and 2.

| Table 1. | Closest approach distances $S_{ij}(\text{Å})$ between atom pairs in Å . $S_{ij}^0(\text{Å})$ are used for initially setting up a disordered hard sphere fluid before introducing the experimental curves in the RMC simulation. |
|----------|---------------------------------------------------------------|
|          | OO   | OH   | OCl  | OLi  | HH   | HCl  | HLi  | ClCl  | ClLi  | LiLi  |
| $S_{ij}(\text{Å})$ | 2    | 0.92 | 2.1  | 1.75 | 0.9  | 1.85 | 2.1  | 3.75  | 2.9   | 3.2   |
| $S_{ij}^0(\text{Å})$ | 3    | 0.94 | 2.8  | 2.0  | 1.55 | 2.25 | 2.7  | 4.9   | 4.8   | 3.2   |

| Table 2. | Number of atoms of each species, the total number of atoms $N$, the total atomic density $\rho$, the simulation box length $L$ and the temperature of the LiCl6H2O system for three thermodynamic states; liquid, supercooled liquid and glass. |
|----------|---------------------------------------------------------------|
|          | $N_O$ | $N_H$ | $N_{Cl}$ | $N_{Li}$ | $N$ | $\rho$ | $L$ | $T$ |
| Liquid   | 0.09394 | 31.297 | 300 |
| Supercooled | 864 | 1728 | 144 | 144 | 2880 | 0.09575 | 31.0993 | 162 |
| Glassy   | 0.09599 | 31.0734 | 120 |

3. RESULTS AND DISCUSSION

3.1. Partial correlation functions $H(r)$

The Partial Correlation Functions (PCF), $H(r)$ equivalent to the Partial Distribution Functions $G(r)$ given by $H(r) = G(r) - 1$, are shown in figures 1. The experimental PCFs and also those computed by RMC for the supercooled liquid state, the difference $\Delta H$ between them is also drawn to permit an easy comparison. A good agreement and a clear concordance are highlighted between all of the computed and the experimental results. Consequently, the generated 3-dimensional configurations are compatible with the experimental data and thus allow displaying all of the pair distribution functions.

3.2. Pair distribution functions

The effect of LiCl on the structure of a solution will be discussed as usually in terms of the water-water correlations.

3.2.1. Water-water

Main intermolecular correlations of the $H_2O$ molecule are observed in the Fig.2. In the pair distribution function $g_{OO}(r)$ (Fig.2.a) a describing water-water correlations. The pair correlation functions between two atoms of the $H_2O$ molecule three thermodynamic states are compared to those of the pure water. The principal peak of $g_{OO}(r)$ is not affected by ions and has kept the
same position. The peak of the second coordination (Fig.2.a) shows an interesting behavior. In the glassy state this pick oscillates in phase and practically with the same intensity of the pure water showing a significant order, while no structure is visible in the liquid. We can also estimate that the coordination numbers of water and the glassy solution are practically the same. The supercooled state possesses an intermediate structure between liquid and the glassy state. It suggests that the lattice hydrogen bond beginning to reorganize at the supercooled state when the temperature decrease, the solution passes from a state where no meaningful order is observed, to another state more ordered via the metastable supercooled state. This suggests that this structure is broken when the temperature increases.

For the other functions, the first intramolecular peak of both $g_{OH}(r)$ (Fig.2.b) and that of $g_{HH}(r)$ (Fig.2.c) are identical in OH the three thermodynamic states, suggesting that the internal structure of the water molecule didn’t change in any case.

Hence, neither the state changes nor the presence of ions affect the well know structure of the water molecule. However, a small shift has been observed for the first and the second coordination of $g_{OH}(r)$ (situated at $r = 2\text{Å}$ and $r = 3.36\text{Å}$ respectively) in the solution with respect to the pure water, probably due to the presence of ions. For the same reason the peak of the first and the second coordination in $g_{HH}(r)$ (located at $1.56\text{Å}$ and $2.49\text{Å}$ respectively) are raised in the pure water case. Otherwise, for the third coordination (situated at $3.9\text{Å}$), the peak of the

**Figure 1.** Experimental and computed Partial Correlation Functions $H_{ij}(r)$ for the supercooled liquid state, $\Delta H_{ij}$ is the difference between them.
solution is more intense. This is synonym of the greater role of the ions in the raising of the long-range order.

Figure 2. Pair distribution functions water-water: $g_{OO}(r)$ (a), $g_{OH}(r)$ (b) and $g_{HH}(r)$ (c) at Glassy, Liquid and Supercooled Liquid state contrasted to the pure water at room temperature.

4. CONCLUSIONS
In this paper, we have investigated the structure of the chloride lithium aqueous solution $LiCl6H2O$ at the supercooled liquid state by the Reverse Monte Carlo simulation on the basis of available neutron diffraction data. The main peaks of some PCFs for the supercooled state are more intense instead to be between the liquid and the glassy states. We suggest through the inspection of the linear combination of these functions, that the causes of this behavior are the water-water discussed in the framework of this work and the chlorine-water correlations in the restructuring of the hydrogen bonds and the hydration shells from the liquid to the glassy state.

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