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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Water in Chabazite Revisited: Self Diffusion and Rotational Relaxation

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1. Introduction

The presence of aluminium ions in zeolites leads to an anionic character of the framework, the negative charge in the crystalline lattice being neutralized by extra-framework cations. The presence of cations in the zeolite voids makes these materials hydrophilic and the interactions between water molecules and cations play an important role in the resulting functional properties.

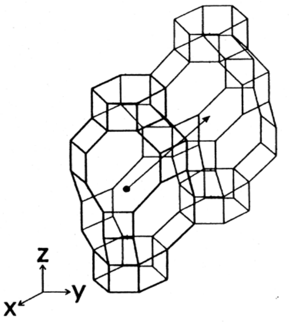

Fig. 1: Schematic view of the chabazite framework.

The behavior of BJH [1] model-water in chabazite, a zeolite containing Ca^{2+} ions, in particular ionic hydration, has been investigated by Jost *et al.* [2]. However, these simulations had to be run at temperatures much above room temperature, which limited direct comparisons with experiments. Now, more accurate calculations using the computationally more efficient SPC/E water model [3] have been carried out. We have focused this study also on the rotational auto-correlation function.

At low water contents, the water-cation interactions dominate over the interactions of other types and virtually all water molecules are attracted to calcium ions. In the fully hydrated system about one third of the molecules exist as a phase with liquid-like density. However, these molecules form only about one hydrogen bond per molecule, which is significantly less than in bulk liquid water, and are thus quasi free. We observe that the self-diffusion coefficient first increases with water concentration, reaches a maximum and then decreases. This can be explained by the number of free water molecules and the space available. It has been found that the exchange between free and coordinated water plays an important role in the diffusion process. We also investigated the influence of the procedure used to compute the electrostatic interactions (e.g. the Ewald summation) on the rotational dynamics.

2. Model

The Simulation box has a dimension of 26.4 x 22.863 x 30.2 Ǻ^3 (2 x 1 x 2 unit cells), containing 864 lattice atoms, corresponding to $Ca_2Al_4Si_8O_{24}$, per cage, for 24 cages, and different numbers of water molecules. The two cations per cavity were initially put at random places. Because the water-cation interactions strongly dominate, the lattice flexibility has been neglected. The molecular dynamics simulations are carried out using the DL_POLY program, version 2.19 [4].

3. Results and Discussion

Fig. 2 shows the concentration dependence of the water self-diffusion in chabazite at 500 K and 600 K. Using the Ewald summation instead of shifted force has an effect at high concentrations and high temperatures, and gives the same trend as in Arbuckle *et al.* [5]. With including the Ewald summation, the self-diffusion coefficient increases by about 15 % at 500 K and about 25 % at 600 K, at the highest concentration. Our simulations improved Jost *et al.* results. Simulations were now also possible at 300 K. From a simple jump model, the anisotropy coefficient (D_z/D_{xy}) was found to be equal 0.8 in [6]. Contrary to [2], the anisotropy coefficient at 300 K was now found to be 0.45, which is close to the experimental value of 0.4. The dampening of auto-correlation function increases with increasing loading. There are fairly strong hindrances to water rotations in the water-zeolite interactions that get weakened when more water is added.

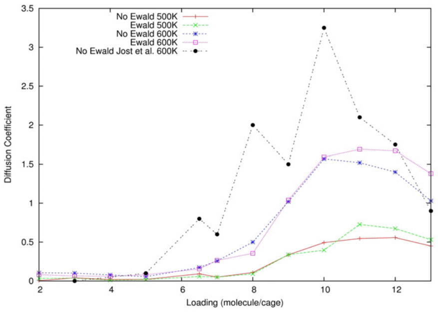

Fig. 2: The variation of the self-diffusion coefficient D, in units of 10^{-10} m^2s^{-1}, with concentration at $T = 500$ K and 600 K.

4. Conclusion

For the concentration dependence of water diffusion in chabazite, the Ewald summation is necessary for high concentration and high temperature. Jost's results at 600 K are approximately correct. We could do the simulation also at 300 K. Finally, we get much better agreement between computed and experimental anisotropy coefficients.

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