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Diffusion of Water in LTA Zeolites: a Molecular Dynamics Computer Simulation Study

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1. Introduction

The microscopic behaviour of water in hydrated zeolites Linde A type is of interest because it is involved in ion exchange and in some molecular sieving mechanisms. Experimental data on water diffusivity in zeolites A Na and NaCa A have been reported for different temperatures and loadings, but different results were obtained when they were investigated with different experimental techniques [1,2]. These differences were interpreted by Paoli *et al.* [2] by recalling that the typical length scale involved in PFG NMR experiments is of the order of the μm, whereas in QENS techniques the scale is that of nanometers. In order to cast some more light on the reasons of these difference, besides the general interest in the details of the diffusion mechanism, we attempted a detailed microscopic study of the diffusion mechanism of water using molecular dynamics (MD) simulation technique [3]. In a previous paper [4] we showed that MD is able to reproduce satisfactorily most structural and vibrational properties of water adsorbed in zeolite Na A at different loading and temperatures. A modified interaction potential, yielding a better reproduction of experimental hydration energy and water diffusivity across a number of different zeolites, was proposed. The results of MD simulations were close to the known experimental structural data and the variation of simulated vibrational with temperature and size of nanoclusters were in good agreement with experiment. The simulated water nanoclusters in zeolite A Na were found to be too small to crystallize and at low temperature behaved as amorphous ice, in agreement with recent experimental results for similar water nanoclusters in reverse micelles [5].

2. Simulations and results

Extended MD simulations lasting several nanoseconds, were performed for zeolites Na A and Na Ca A at the same loadings as reported in Ref. [2] and for ranges of temperature slightly higher than the ones chosen in Ref. [2], because the values of the computed diffusivities were close to the lowest limit reachable by the method. At least three temperatures per each loading and each zeolite were selected. The starting structures were taken from the available experimental data and the diffusion coefficients were evaluated by means of the Einstein formula. In addition, direct inspection of some trajectories was used to study the microscopic diffusion mechanism. Overall, the computed diffusivities and the related activation energies result to be intermediate between those obtained from PFG NMR and QENS experiments, although it would be expected a better reproduction of QENS data. This is probably due to the cation(s)-water interactions that in the model are slightly too strong, but this drawback should not influence the diffusion mechanism. The inspection of the trajectories shows that at low loadings (5 molecules/cage) the diffusion of the water molecules, which are for most time coordinated to the cations, occurs by sudden jumps from the coordination shell of a cation to that of the adjacent one, and these jumps are assisted by other water molecules through the formation of transient hydrogen bonds. At higher loadings (15 molecules/cage) the diffusivity is increased by the presence of more water molecules, but the diffusion mechanism does not change substantially. At loadings close to the saturation (25 molecules/cage) the diffusion coefficients become smaller because of the scarcer availability of free sites sufficiently close to the molecules to allow them to jump.

3. Conclusion

Molecular dynamics simulation of the diffusion of water in zeolites Na A and CaNa A yield diffusion coefficients and activation energies of the correct order of magnitude, intermediate between those obtained from PFG NMR and QENS experiments. The diffusion mechanism involves coordinated jumps of the water molecules favoured by the formation of transient hydrogen bonds.

References

[1] J. Kärger, D.M. Ruthven, Diffusion in Zeolites and Other Microporous Solids, Wiley, New York, 1992

[2] H. Paoli, A. Méthivier, H. Jobic, C. Krause, H. Pfeifer, F. Stallmach, J. Kärger, Microp. and Mesop. Mater. 55 (2002) 147-158.

[3] P. Demontis, G. B. Suffritti, Chem. Rev. 97 (1997) 2485-2478.

[4] P. Demontis, J. Gulín Gonzáles, H. Jobic, M. Masia, R. Sale, G.B. Suffritti, ACS Nano, 2 (2008) 1603-1614.

[5] A.M. Dokter, C. Petersen, S. H. Bakker, J. Chem. Phys. 128 (2008) 044509.