

## Dynamics of Water in Zeolite NaY(Br) Investigated by NMR

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### 1. Introduction

Zeolites are widely used in industry as molecular sieves, selective adsorbents, catalysts and ion exchangers (e.g. [1] and references therein). Therefore there is a great interest in studying the dynamics of guest molecules in such systems. Although vigorous research has been performed in the field, a complete understanding of the complex behaviour of guest molecules is still missing. We investigated water confined in a zeolite as we are also interested in the properties of different phases of bulk water and experiments in confinement may reveal more information on the matter.

The zeolite NaY(Br) (Si:Al=2.43) was chosen because of its simple internal geometry and available complementary studies [2]. Its unit cell consists of eight  $\beta$ -cages and eight supercages. The  $\beta$ -cages are blocked by Br ion so that water can penetrate only in the supercages. The sample was filled with 18 molecules of water per supercage. Half of the water molecules were deuterated in order to perform  $^2\text{H}$  NMR in addition to proton NMR.

### 2. Results

The spin-lattice relaxation functions  $M(t)$  for  $^2\text{H}_2\text{O}$  in NaY(Br) were measured for different temperatures in a range from about 400K down to 200K. No phase transition was observed neither at the boiling nor melting point of bulk water.  $M(t)$  is exponential from high temperatures till around 230K. Below 193K the relaxation function has a multi-step shape. Moreover, the equilibrium magnetization is not reached even at  $10^4\text{s}$  after a saturation sequence is applied. We conclude that the dynamics of water molecules changes drastically in between these temperatures. Because of this finding we divide the studied interval in temperature range I (TR-I) from 400K to 230K and temperature range II (TR-II), from 193K to 120K and discuss the experimental findings for each one separately.

In TR-I the spin-lattice relaxation time  $T_1$  displays a minimum value of  $T_{1\text{min}}=2.9\text{ms}$ . Using the BPP theory, assuming a Debye spectral density [3] and using an isotropy parameter  $\delta=2\pi$  173kHz one obtains a theoretical value for  $T_{1\text{min}}$  that is a factor of about two smaller than the experimental one. There are two ways of interpreting this result: the molecular motion is anisotropic [4] or it displays a broad distribution of correlation times [5]. For the time being a clear-cut option cannot be made. Such a behaviour in  $T_1$  can be observed for molecules in confining media where dynamics in dimension dominates [6]. Nevertheless the geometry of NaY(Br) zeolite is not anisotropic and therefore we tentatively conclude that the large  $T_{1\text{min}}$  value is a result of a broad distribution of correlation times. Assuming a Cole Davidson spectral density [5] we obtained a  $\beta_{\text{CD}}=0.23$  (comparatively bulk ortho-terphenyl  $\beta_{\text{CD}}=0.519$  [5], bulk toluene  $\beta_{\text{CD}}=0.32$  [7]).

Additionally we obtained the temperature dependence of the mean correlation time  $\tau_{CD}$  corresponding to such a spectral density.

The diffusion coefficient  $D$  for  $Q=0.67 \times 10^{-3} \text{ \AA}^{-1}$  was measured by field-gradient NMR. The temperature dependence of  $1/D$  and  $\tau_{CD}$  is similar and one can easily scale them. This proves that rotation and translation motion are coupled, at least in TR-I, for temperatures where  $1/D$  and  $\tau_{CD}$  are available. Using the Einstein equation for diffusion a mean jump length  $\sqrt{\langle r^2 \rangle} = 1.5 \text{ \AA}$  is obtained.

Concerning TR-II we recorded  $^2\text{H}$  NMR spectra and stimulated echoes selecting the magnetization corresponding to the fast step in the  $^2\text{H}$  spin-lattice relaxation curve. "Two-phase" spectra are obtained demonstrating a broad distribution of correlation times  $G[\ln(\tau)]$  [8]. The stimulated echo decays  $F^{\text{cos}}$  are non-exponential, extending more than 3 decades in time, being another indication of a broad  $G[\ln(\tau)]$ . The final state of  $F^{\text{cos}}$  for an evolution time of about  $30 \mu\text{s}$  is within the experimental errors 0.25. This leads to the conclusion that the  $^2\text{H}$ -O bonds of the measured group of water molecules perform jumps between 4 sites similar to the molecules in hexagonal ice [9]. The latter finding leads us to speculate that in the TR-II a part of the water molecule freeze in an ice-like structure.

### 3. Conclusion

We studied the dynamics of water molecule in zeolite NaY(Br) in a large temperature range. The water does not display a phase transition at  $0^\circ$  or  $100^\circ\text{C}$ . It appears that a "phase separation" occurs around 200K with the molecules that have the fastest  $^2\text{H}$  spin-lattice relaxation displaying an ice-like motion. Above this temperature, the translation and rotation motion of molecules is coupled exhibiting the same temperature dependence.

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### References

- [1] H. Pfeifer, Physics Reports (Phys. Lett. C), 26 (1976), 293.
- [2] B. Boddenberg, G.U. Rakhmatkariev, S. Hufnagel, Z. Salimov, Phys. Chem. Chem. Phys., 4 (2002), 4172.
- [3] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.
- [4] J. Tabony and J. P. Korb, Mol. Phys., 56 (1985), 1281.
- [5] W. Schnauss, F. Fujara and H. Sillescu, J. Chem. Phys., 97 (1992), 1378.
- [6] M. Wilkening, W. Kuchler and P. Heitjans, Phys. Rev. Lett., 97 (2006), 065901.
- [7] E. Rossler and H. Sillescu, Chem. Phys. Lett., 112 (1984), 94.
- [8] R. Böhmer, G. Diezemann, G. Hinze and E. Rössler, Prog. NMR Spectrosc., 39 (2001), 191.
- [9] B. Geil, T.M. Kirshgen and F. Fujara, Phys. Rev. B, 72 (2005), 014304.