

Correlating PFG NMR and IR Diffusion Measurements in Porous Glasses

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1. Introduction

Molecular diffusion is among the famous topics of current research on nanoporous materials [1]. Diffusion of molecules in porous media can be measured by a large variety of experimental methods. However, diffusivities measured with different techniques for the same system vary in several zeolitic systems over more than two orders of magnitude [2]. In many cases the origin of this discrepancy still remains unclear, even after 30 years of zeolite research. Hence, demonstrating agreement between results measured by different techniques on identical material assumes an important step in the concerted efforts to solve the existing, formidable puzzle about molecular transport in zeolites and other nanoporous materials.

With the rise of a new class of nanoporous glasses now ideal conditions are provided to solve this challenging task. In the present work we show the perfect agreement of diffusivities yielded by two prominent representatives of experimental techniques, namely pulsed field gradient (PFG) NMR and IR Microscopy (IRM).

2. Experimental

A new and innovative material, the porous glass, is among the top systems of interest in the current research. This novel material shows the following interesting properties: controlled pore size down to 1 nm, narrow pore size distribution, high mechanical and chemical stability and flexible geometrical shape [3]. In this study, we considered two specimens of porous glasses with pore sizes of 1.3 nm and 2 nm, respectively.

The loading dependence of transport and self-diffusivity and the adsorption isotherm were measured at 298 K for cyclohexane and n-hexane with PFG NMR and IRM.

3. Results and discussion

The PFG NMR spin echo attenuation curves decay with monoexponential behavior as function of the square of the gradient intensity. Implicating a homogenous diffusivity this finding proves the uniformity of the pore space for n-hexane and cyclohexane.

The protocol of sample activation, e.g. influencing the amount of residual pore water, has been found to influence the adsorption and transport properties considerably. This

statement is illustrated in Fig. 1, showing the influence of activation on two isotherms measured by NMR. Good agreement between different measurements and between results from both techniques could be obtained only by following one and the same protocol of sample activation, and was, hence, found to be of crucial importance for such a study.

The diffusivity we measured in both samples as function of the concentration of the adsorbent. As a typical feature the results exhibit nice agreement at low loadings while they seem to diverge at higher loadings (Fig. 2).

At low loadings, these results show, for the first time, a perfect agreement of diffusivity yielded by PFG NMR and IRM ($D_{\text{self}} \approx D_T$). As expected, at high loadings however, the transport diffusivities determined by IR is higher than the NMR self-diffusivities in both samples, finally exceeding them by more than two orders of magnitude. This difference at high loadings might be referred to the influence of the liquid phase which obviously dominates the diffusivity at high loadings.

Based on the excellent agreement between the results obtained by PFG NMR and IRM we want to highlight this system of porous glass as a most promising candidate for showing the consistency of results from all common techniques employed for diffusion measurements in porous materials.

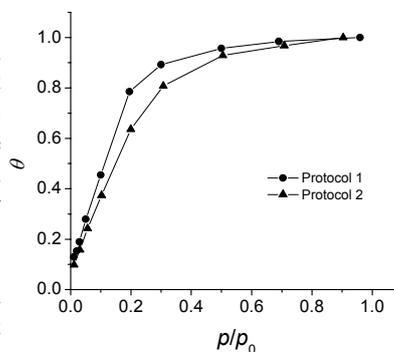


Fig 1. NMR isotherm of n-hexane in 1.3 nm porous glass sample.

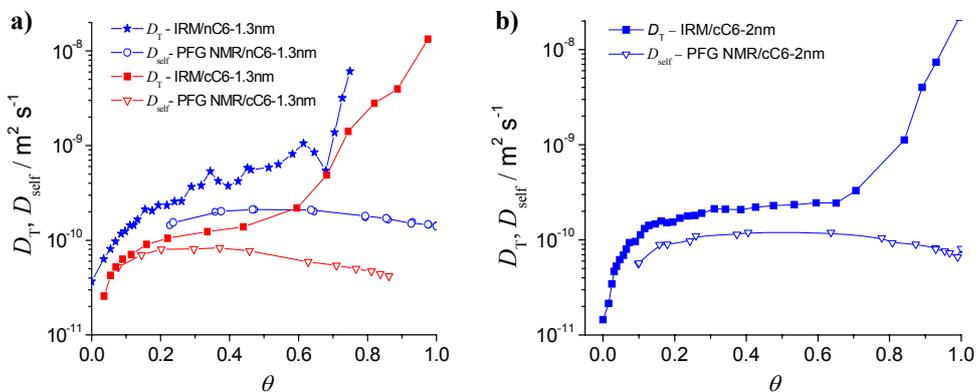


Fig. 2. Diffusion as function of sorbate loading: **a)** n-hexane and cyclohexane in 1.3 nm porous glass, **b)** cyclohexane in 2 nm porous glass.

References

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