diffusion-fundamentals

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

From "fast" to "slow" liquid-vapor exchange in partially filled porous media. A field-gradient NMR diffusometry study

I. Ardelean, G. Farrher, C. Mattea, R. Kimmich

* Technical University from Cluj-Napoca, Physics Department, 400020 Cluj-Napoca, Romania; E-mail: ioan.ardelean@phys.utcluj.ro

**Universität Ulm, Sektion Kernresonanzspektroskopie, 89079 Ulm, Germany

1. Introduction

If a macroscopic sample contains a two-phase system formed by a liquid in thermal equilibrium with its vapor, the acquired NMR signals normally are entirely dominated by the magnetization of the liquid phase. The reason is that the density of the vapor phase at room temperature is three orders of magnitude less than that of the same species in the liquid phase. Consequently the contribution to the signal from the vapor phase can be neglected. However, in some cases, diffusion measurements of liquids partially filling porous media indicated self-diffusion enhanced relative to the bulk phase [1-4] (see Fig.1) for low filling factors. The reason for such observations is the molecular exchange process between the two phases: liquid and saturated vapor. Molecular exchange means that the solvent molecules are intermittently subject to diffusion features in either phase. Translational displacements in the vapor phase are much faster than in the liquid phase and contribute to the enhancement of the effective diffusion coefficient.

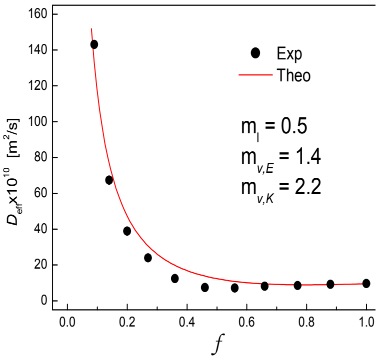

Fig.1. The enhancement of the effective diffusion coefficient due to the vapor phase in Vitrapor#5 partially filled with cyclohexane. The theoretical curve has been calculated on the basis of the general liquid-vapor exchange model

2. Results

In our report, the contribution of the vapor phase to molecular diffusion in silica glasses with nanometer (Vycor: pore diameter 4 nm) and micrometer (Vitrapor#5: pore diameter 1 µm; Vitrapor#4: pore diameter 10 µm; Vitrapor#C: pore diameter 50 µm) pores partially filled with cyclohexane (non-polar) or water (polar) was investigated with the aid of field-gradient NMR diffusometry. For the same liquid species and for the same diffusion time a transition from "fast" to "slow" exchange was observed by increasing the pore dimension. It can be concluded that the pore size plays a crucial role for the relevance of molecular exchange limits relative to the experimental diffusion/exchange time.

The experimental results can be well described in the frame of a general two-phase liquid-vapor exchange model [4]. The model is based on a two-region approximation as suggested for gas diffusion in zeolites [5]. In the case of vapor/liquid phase systems we always have the conditions

$$p_{\mathrm{v}} << p_l; \;\; D_{\mathrm{v}} >> D_l; \;\; T_{1,\mathrm{v}} >> T_{1,l}, \qquad (1)$$

where: p_l, p_{v} is the fraction of molecules; D_l, D_v are the effective diffusivities and $T_{1,l}$, $T_{1,\mathrm{v}}$ the longitudinal relaxation times in the liquid and vapor phase respectively. Based on the above conditions the model predicts a dependence of the stimulated echo amplitude versus the wave number k given by

$$\frac{A_{STE}(k,\Delta)}{A_{STE}(k,0)} = \exp\left[-k^2\left(D_l + \frac{p_{\mathrm{v}} D_{\mathrm{v}}}{k^2 \tau_l p_{\mathrm{v}} D_{\mathrm{v}} + 1}\right)\Delta\right], \qquad (2)$$

where Δ represents the diffusion interval. The relaxation term has been discarded in the above expression because in experiments with constant intervals but variable gradient strength it does not affect the echo attenuation curve apart from a constant reduction factor. Note that the attenuation of the stimulated echo versus the square of the wave number is not exponential. It depends on the mean residence time τ_l of molecules in the liquid phase.

3. Conclusions

The vapor phase effect on diffusion as a function of the filling degree was clearly demonstrated. Due to the molecular exchange, the values of the effective diffusion coefficient in the case of cyclohexane in VitraPor#5 (1 μm pores), exceed the bulk value by a factor of up to ten for low filling factors (see Fig.1). Moreover, for diffusion in the vapor phase, two mechanisms can be distinguished, namely ordinary (“Einstein”) and Knudsen diffusion with (possibly different) tortuosity effects for a given pore space structure. Finally, the mean residence time of the solvent molecules in the liquid phase can be evaluated from fits of the theory to the experimental echo attenuation data.

References

[1] J. Kärger, H. Pfeifer, E. Riedel, H.J. Winkler, J. Coll. Interface Sci. 1973; 44; 187-188

[2] F.D’Orazio, S.Bhattacharja, P.Halperin, and R.Gerhardt, Phys.Rev.Lett. 63, 43(1989).

[3] R. Kimmich, S. Stapf, P. Callaghan, and A. Coy, Magn. Res. Imag. 12, 339(1994).

[4] I. Ardelean, G. Farrher, C. Mattea, and R. Kimmich, J.Chem.Phys 120, 9809(2004).

[5] J. Kärger and D. M. Ruthven, *Diffusion in zeolites and other microporous solids*, John Wiley & Sons, 1992