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● *Invited Lecture*

SELF-DIFFUSION IN FLUIDS IN POROUS GLASS: CONFINEMENT BY PORES AND LIQUID ADSORPTION LAYERS

R. KIMMICH,* S. STAPF,* A.I. MAKLAKOV,† V.D. SKIRDA,† AND E.V. KHOZINA†

*Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany, and †Kazan State University, Department of Physics, Kazan 420008, Russia/Tatarstan

Diffusion coefficients of 10 different polar and nonpolar liquids filled in porous glasses with mean pore diameters of 4 or 30 nm were determined with the aid of the NMR field-gradient technique. In the time scale of these experiments (0.3 to 500 ms) diffusion coefficients were found to be time independent. Within the experimental error, no influence of the polarity of the adsorbate can be stated. The diffusion coefficients of all investigated fluids in glass with 4 and 30 nm pores were reduced by factors of 0.17 and 0.63, respectively, relative to the bulk values. This relatively weak reduction can be explained by considering the known porosities of the adsorbents. The second objective of this study was to examine the diffusion behaviour below the melting point of adsorbates in porous glass. Fluids confined in pores do not freeze at the bulk freezing temperatures. In this respect, two phases must be distinguished. A maximal two monolayer thick film adsorbed on the inner surfaces does not crystallize at all, whereas the "free" fraction of the fluid in the pores freezes at reduced temperatures according to the Gibbs–Thompson relation. The nonfrozen surface layers form a network in which self-diffusion can be investigated. Experiments have been carried out with cyclohexane. A reduction factor of 0.06 was found relative to the extrapolated values of the entirely unfrozen fluid in porous glass with a mean pore diameter of 30 nm. It is, thus, demonstrated that molecules in adsorption layers virtually retain their translational degrees of freedom along the surfaces. The lowering of the diffusivity is mainly due to the geometric restriction rather than to the interaction with the surface.

Keywords: **Self-diffusion; Field-gradient NMR diffusometry; Confined liquids; Porous glass; Surface layers.**

INTRODUCTION

The translational diffusion of liquids confined in the pore space of porous glass and other porous media in principle may be slowed down either by the interaction with the pore walls ("adsorption effect"), and/or by the restriction of the diffusion pathways to the pore network ("geometry effect"). The objectives of this study are to experimentally distinguish these two potential sources of translational hindrance, to characterize the influence of the adsorbate polarity, and to quantify the diffusivity in nonfrozen surface layers remaining after crystallizing the "free liquid" in the pores.

It is well known that liquids confined to pores show thermodynamic properties other than in bulk. Two phases, namely "free liquid" and "adsorbed liquid," can be distinguished owing to their different phase transition behaviour. The "adsorbed liquid" is supposed to form a layer on the pore walls with a thickness in the order of the adsorbate molecule diameter.

Based on the Gibbs–Thomson relation[1] one expects a depression of the melting temperature of the "free liquid" proportional to the surface-to-volume ratio of the pores,

$$\Delta T_m \propto \frac{A_p}{V_p} . \qquad (1)$$

This recently prompted Overloop et al.[2] and Strange et al.[3] to suggest a NMR line width technique for the

Address correspondence to R. Kimmich, Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany.