diffusion-fundamentals

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

The working range of static field gradient NMR illustrated by measurements of the intracrystalline diffusion of water in NaA-zeolites

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1. Introduction

Measuring diffusion in zeolites is a long-lasting challenge. For more than 70 years many efforts have been made to determine the diffusion coefficient of host molecules in the porous framework of zeolites [1]. Actually the different techniques, which were applied, observed different processes and provided dissenting diffusion coefficients. Precisely, there are methods observing diffusion on a macroscopic or a microscopic scale, under equilibrium or non-equilibrium conditions. We are interested in the molecular dynamics of water inside a crystallite, i.e. the intracrystalline *self-diffusion* coefficient. Common zeolites, as used in our experiments, have crystallite radii of about 0.5 μm, therefore we need a high spatial resolution to determine the diffusion coefficient of the molecules inside the crystallites. Static field gradient NMR can provide such a high resolution under certain conditions. In our contribution we discuss the potential and limitations of this method.

2. The working range of SFG-NMR

Field gradient NMR uses stimulated echo experiments with three-pulse sequences "(pulse) – τ – (pulse) – t – (pulse) – τ – (echo)" to measure the echo height $S_{echo}(\tau,t)$. During the first time interval τ the spins are dephasing, during the second interval τ they are rephasing. In an inhomogeneous magnetic field, the dominant dephasing mechanism arises from a spacially varying Larmor frequency $\omega [\mathbf{r}(t)] = \gamma \mathbf{B} [\mathbf{r}(t)] = \gamma \mathbf{g} \mathbf{r}(t)$, where γ is the gyromagnetic ratio, **g** is the magnetic field-gradient, and **r**(t) is the time dependent spin position. For the limit $t \gg \tau$ one can introduce the "generalized scattering vector" $\mathbf{Q} = \gamma \tau \mathbf{g}$ [2], so that one obtains for isotropic free diffusion not affected by any boundary conditions, considering T_2-relaxation in the de- and rephasing periods and T_1-relaxation in the storage period, the measured echo height $S_{echo}(\tau,t)$ is given by

$$S_{echo}(\tau,t) = \exp[-Q^2 D\, t] \exp[-2\tau/T_2] \exp[-t/T_1] \qquad (1)$$

with *D* being the self diffusion coefficient. Figure 1 shows the trajectories of two particles performing free diffusion represented in a log(t) vs. log(Q) plot by arrows of slope -2. According to eq. 1 the competing relaxation induced cofactors and the given maximum gradient strength lead to

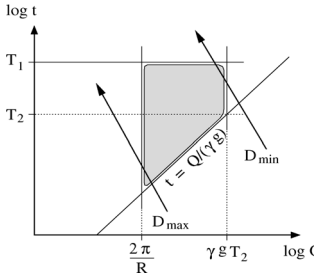

Fig. 1 Schematic representation of the working range (shaded area) of FG-NMR in confined geometries.

an upper bound $t_{max} \approx T_1$ of accessible storage times and an upper bound $Q_{max} \approx \tau_{max} \gamma g_{max}$, where $\tau_{max} \approx T_2$ has been used. The lower bound t_{min} is, roughly speaking, determined by the condition of applicability of eq. 1, that is $t_{min} \approx \tau_{max}$. This limit implies $t_{min} \approx T_2$ at $Q_{max,}$ whereas smaller Q-values permit correspondingly smaller t_{min}. The essential limitation in our context is given by the crystallite size R within which the diffusion can be considered to be free. From this follows the lower bound $Q_{min} \approx 2 \pi R^{-1}$.

3. The intracrystalline diffusion of water in NaA-zeolites

The experiments have been carried out in a specially designed static magnetic field gradient at the ^{1}H frequency of 99.55 MHz at gradient values of 58, 135 and 185 T/m. The stimulated echo height S_{echo} was recorded as a function of the diffusion time t at fixed dephasing times τ. The results (Fig. 2) show an extremely strong Q-dependence of D_{app}, turning over toward a Q-independent plateau value. The transition takes place roughly at a Q-value of 10^{-3} Å^{-1}, which is consistent with the crystallite size. At smaller Q-values the increasingly high apparent diffusion coefficients coincide with deviations of the experimental $S_{echo}(t)$ from a behaviour predicted by eq. 1, maybe due to partly intercrystalline diffusion or to surface relaxation effects. However, at larger Q-values the Q-independent plateau value of D is indeed the intracrystalline diffusion coefficient.

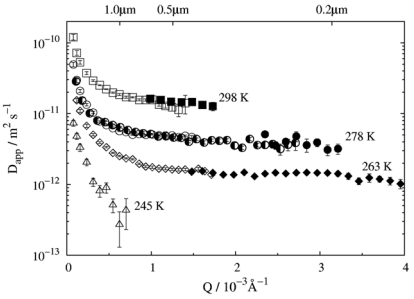

Fig. 2Q-dependence of the apparent diffusion coefficient D_{app} of H_2O in polycrystalline NaA-zeolites as obtained by fits of eq. 1 to experimental echo decay curves in a magnetic field gradient (open symbols: 58 T/m; half-filled: 135 T/m, filled: 185 T/m).

4. Conclusion

From NMR stimulated echo experiments in very high static magnetic field gradients it has been possible to obtain intracrystalline diffusion coefficients for water diffusion in µm-size NaA-zeolites. Based on the experimental results, we are going to show in our poster contribution further considerations on the effective working range of SFG-NMR.

Acknowledgement

Aleksander Gutsze, who passed away at 28th april 2004, had proposed this work. We thank Włodzimierz Masierak for the sample preparation [3].

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