Observation of Single-File Diffusion of Xe in One-Dimensional Nanochannels by Diffusion NMR

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Introduction

Single-file diffusion (SFD) is a non-Fickian diffusion that can be expected in one-dimensional channels under conditions when the channel radius is smaller than the diameter of diffusing molecules. In this case mutual passages of sorbate molecules inside the channels are excluded. As a result, instead of the normal proportionality of the mean square displacement (MSD) to the diffusion time that is observed for Fickian Diffusion, the MSD in single-file diffusion (SFD) increases as the square root of time. In this work ^{129}Xe pulsed field gradient (PFG) NMR was used to study details of single-file diffusion of Xe atoms inside two types of nanotubes.

Experimental

The channels of the dipeptide L-Ala-L-Val (AV) and its retroanalog L-Val-L-Alan (VA) were used as sorbents. The Xe atom, with a diameter of 0.44 nm, satisfies the single-file requirement in AV and VA, where the mean channel diameters are 0.51 and 0.49 nm, respectively. Studies of Xe diffusion in AV and VA were performed by ^{129}Xe PFG NMR using a wide-bore 17.6 T Bruker BioSpin spectrometer located at AMRIS, University of Florida. Magnetic field gradients with amplitudes up to 30 T/m were generated using a diff60 diffusion probe and Great60 gradient amplifier (Bruker BioSpin).

Results and Discussion

Fig. 1 shows examples of the measured PFG NMR attenuation curves for Xe diffusion in VA at 297 K.[1] The measurements were performed for a broad range of diffusion times covering almost 3 orders of magnitude. In the presentation of this figure coincidence of the attenuation curves implies that the mean square displacement (MSD) of Xe grows as the square root of diffusion time. Hence, the results in Fig.1 clearly demonstrate that Xe diffusion in VA occurs according to the mechanism of SFD. Qualitatively similar results were also observed for Xe diffusion in AV nanotubes.[1,2] PFG NMR attenuation curves allowed obtaining single-file mobility factors of Xe. They were found to be equal to $6 \pm 0.7 \cdot 10^{-13}$ $m^2 s^{-1/2}$ and $4.4 \pm 0.2 \cdot 10^{-13}$ $m^2 s^{-1/2}$ at 297 K in AV and VA nanotubes, respectively. Xe diffusion in AV and VA nanochannels was also investigated by hyperpolarized tracer exchange (HTE) NMR under the same measurement conditions.[1] The HTE NMR data confirmed that Xe atoms diffuse according to the mechanism of SFD in AV and VA nanotubes.

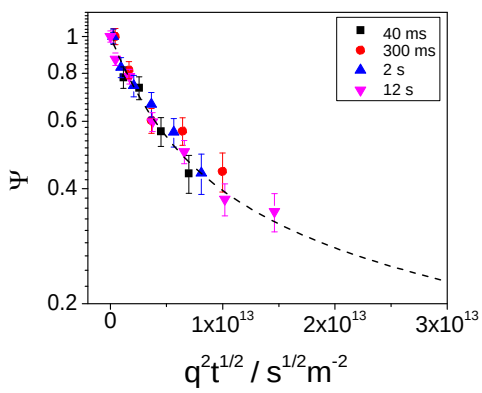

Fig. 1. ^{129}Xe PFG NMR attenuation curves measured for Xe diffusion in VA nanotubes for different diffusion times at 297 K.

Conclusions

Combined application of PFG NMR and HTE NMR yielded unequivocal experimental evidence of single-file diffusion of Xe in AV and VA nanotubes spanning three orders of magnitude variation in the diffusion time.

Acknowledgements

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References

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[2] Dvoyashkin, M.; *et al.*, Microporous and Mesoporous Materials **178**, 119-122 (2013).