diffusion-fundamentals

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

Diffusion of Cyclohexane and Cyclopentane Confined in Mesoporous MCM-41

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1. Introduction

A feature of the pulsed field gradient (PFG) NMR technique is that it measures diffusion over distances of the order of a few micrometers [1]. If crystallites of sufficient size can be obtained (>10 μm), intracrystalline self-diffusion can be observed without complications from boundary or inter-particle effects. This work presents the diffusion properties of cyclohexane and cyclopentane confined in a MCM-41 solid.

2. Experimental

The crystalline MCM-41 sample with pore diameter 3.2 nm was prepared according to a method of Karlsson et al. [2]. The diffusivity (*D*) was measured on a Bruker Avance DMX 400 spectrometer using the 13-interval pulse sequence due to Sørland et al. [3], which minimizes the effect of internal field gradients. The length of the gradient pulses (δ) and the spacing between the RF pulses (τ) were always fixed to 0.5 and 1.1 ms, respectively. The value of the z-storage time was 4 and 8 ms for cyclopentane and cyclohexane, respectively. The natural logarithm of the echo attenuation $\ln(I/I_0)$ was plotted vs. the square of the field gradient strength g^2, and *D* was extracted from the initial part of the curve.

3. Results and discussion

The diffusivity *D* of bulk and confined cyclohexane and cyclopentane versus inverse temperature, are shown in Fig. 1. To minimize the effect of T_2 relaxation, τ should be shorter than T_2 for the confined samples, a requirement that is fulfilled for essentially the whole temperature region.

At all temperatures, the natural logarithm of the initial part of the spin-echo attenuation of confined cyclohexane showed a g^2 dependence corresponding to a Gaussian distribution. The same behaviour was observed for the cyclopentane systems below 270 K. At higher temperatures, however, the attenuation curves were non-exponential at low field gradient strengths owing to the contribution of a fast-diffusing component. At 270 K, the confined cyclopentane molecules may travel a root-mean-square distance of ca. 5 μm, i.e., a distance approaching the size of the crystallites (≥10 μm). Inevitably, some molecules may escape into the intercrystalline space and constitute the fast-diffusing component. This component was eliminated by removing the first 1 - 3 data points from the attenuation curves.

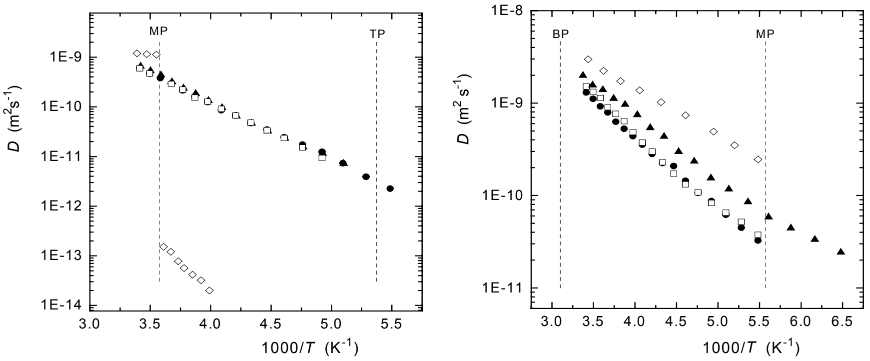

Fig. 1: Temperature dependence of the diffusivity *D* of cyclohexane (left) and cyclopentane (right) confined in MCM-41; 60% filling (▲), 80% filling (□), 104% filling (●), bulk compound (◇).

Within the liquid region, the reduced diffusion rate of the non-polar cyclohexane and cyclopentane is mainly attributed to geometrical restrictions rather than to interactions with the pore surface [4]. The diffusivity of cyclopentane is only moderately reduced when using higher pore fillings than 80%, while the diffusivity of cyclohexane is practically independent of pore filling. The diffusivity curves of cyclohexane are continuous and linear throughout the whole temperature region indicating that essentially no solidification is taking place inside the pores.

4. Conclusion

The diffusion behaviour of confined cyclohexane and cyclopentane is similar although the two compounds exhibited different bulk phases at corresponding temperatures. In both systems, a high diffusion rate is observed for all filling grades over a wide temperature range.

References

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