PII S0730-725X(98)00050-2

● *Contributed Paper*

DIFFUSION PROCESSES IN CONFINED MATERIALS

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The diffusion coefficient for cyclohexane confined within pores of diameter 40 to 500 Å has been measured as a function of temperature between 296 and 180 K, and is compared to values obtained for the bulk material. A substantial liquid-like signal is observed in the region of the depressed freezing points and a diffusion coefficient is measurable in all samples to well below these temperatures. The diffusion data appear to be continuous over the freezing region. These observations suggest persisting molten layers at interfaces which exchange with crystals forming within the silica pores. The diffusion coefficient of the molecules in the surface layer is three orders of magnitude larger than in the plastic phase of bulk cyclohexane. © 1998 Elsevier Science Inc.

Keywords: **Porous silica; Confined cyclohexane; NMR diffusion measurements.**

INTRODUCTION

Nuclear magnetic resonance (NMR) has become an increasingly important method for characterising porous materials and for studying the phase behaviour and dynamics of compounds confined within the porous media[1]. The freezing point of confined molecules varies inversely with the mean pore diameter[2]. By using organic molecules forming plastic crystals as adsorbates damage to the pore structures caused by ice formation can be avoided. Furthermore, the high reorientational and translational mobility of plastic crystals, as compared to rigid crystals, allows direct determination of self-diffusion coefficients using NMR.

The system chosen in the present study is cyclohexane confined within silica gel pores of nominal diameter 40 to 500 Å. The plastic phase of cyclohexane extends from the melting point at 280 K to the plastic-brittle phase transition point at 187 K.[3] The freezing-point depression is particularly large for this compound being, e.g., 67 K in 40-Å pores. The diffusion measurements were performed with the pulsed-field gradient (PFG) stimulated-echo technique. A feature of the PFG technique is that it measures diffusion directly and, therefore, the properties of translational motions. There is evidence from relaxation studies[4] that enhanced diffusion takes place in a liquid-like surface layer making diffusion measurements even more feasible than in the bulk.

EXPERIMENTAL METHODS

Sample preparation

The four test samples were prepared in 5-mm outer diameter (o.d.) NMR tubes, each filled to a height of approximately 10 mm with dried porous silica of 40, 60, 200 and 500 Å nominal pore diameter. Cyclohexane was added to the silica in order to slightly overfill the pores, with the excess going to fill the intergranular space. The NMR tubes were immediately sealed under vacuum to remove any dissolved oxygen and prevent evaporation and contamination.

NMR Measurement Procedures

The ^1H measurements were carried out at 9.4 T on a Bruker DMX 400 spectrometer at 400.13 MHz. The self-diffusion measurements were performed with a Z-shielded 5-mm probehead producing 25 GA^{-1}. The field gradients were generated by the Bruker BAFPA 40 gradient unit ($G \leq 10$ T m^{-1}). By applying gradient pre-emphasis with three-exponential correction terms the eddy current time after a gradient pulse was less than 300 μs. The strengths of the gradient pulses were calibrated indirectly by matching the measured self-diffusion con-
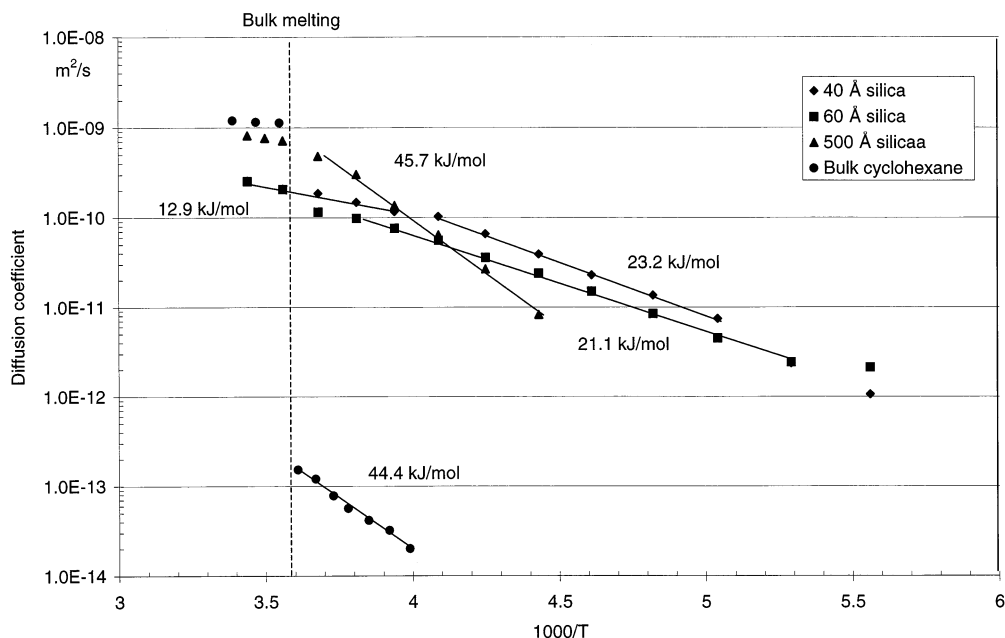
Fig. 1. Self-diffusion coefficients of cyclohexane in bulk and confined within silica pores of nominal diameter 40 to 500 Å vs. reciprocal temperature.

stant of dried glycerine with the reported value (1.73×10^{-12} m^2 s^{-1} at 298 K). [5] The 90° transmitter pulses were carefully calibrated (*ca.* 6 μs) for all samples and temperatures. The sample temperature was regulated and stabilised to within ± 0.5 K by means of a B-VT 2000 Bruker temperature-control unit. All measurements were taken by increasing the temperature after having cooled the samples down to low temperature initially to prevent the complication of supercooling or hysteresis.

The diffusion coefficients were measured using the stimulated spin-echo sequence:

$$[T - 90° - \delta - t_r - 90° - \delta_s - \tau - 90° - \delta - t_r$$
$$- echo],$$

where $T \geq 5T_1$, δ is the length of the gradient pulse (1 ms), t_r is the ring-down time, δ_s is the gradient spoiler time and the gradient pulse spacing $\Delta = \delta + t_r + \delta_s + \tau$ (usually 10 ms). The signal height of the Fourier transformed echo may be written $A = const \times \exp[-\gamma^2 G^2 D\delta^2 (\Delta - \delta/3)]$ where G is the strength of the gradient pulses. The *const* term contains a factor $\exp(-2\tau_1/T_2)$ where $\tau_1 = \delta + t_r$ ($\geq$1.3 ms for the present measurements) which severely attenuates the measured echo for short spin-spin relaxation times T_2. A few diffusion measurements were also made using the 13-sequence program of Sørland et al.[6] which eliminates the effect of internal gradients. The diffusion coefficients

obtained using the two different pulse sequences agreed within experimental error confirming that the effect of internal gradients is negligible in the present systems.

RESULTS AND DISCUSSION

The translational jump frequency of plastic cyclohexane decreases from *ca.* 10^7 s^{-1} at the melting point to 10^3 s^{-1} at 190 K[7]. Fast exchange between molecules at the surface and the interior of the pore ($\sim$100 Å) will, therefore, take place in the high-temperature region resulting in weighted average NMR parameters:

$$O = p_a O_a + p_c P_c, \tag{1}$$

where p_a and p_c are the relative fractions of the adsorbed and crystalline phases, respectively. The observable parameter O may represent the relaxation rates $1/T_{1,2}$ or the diffusion coefficient D.

T_2 measurements of confined cyclohexane using the Carr–Purcell–Meiboom–Gill technique revealed two distinct components below *ca.* 200, 215 and 260 K for the 40, 60 and 200 Å pores, respectively. For the latter system, the component with the longer T_2 contributed ca. 60% at 260 K and 4% at 150 K.[4] A similar observation was made by Stapf et al.[8] for cyclohexane confined in 40-Å porous glasses. A two-component region was not seen for the 500-Å silica from the relaxation measure-

ments, apparently because the proportion of molecules at the surface when compared to the interior of the pore became too small to be observed under the experimental conditions. However, line-width measurements clearly revealed a two-component region also for the 500-Å silica, which is consistent with observations made for cyclohexane in porous glasses with diameters up to 2080 Å.[7] The appearance of two components indicates slow exchange between the liquid-like or glassy component at the surface and the plastic phase in the centre of the pore. However, due to short T_2 the contribution from the crystalline component to the spin-echo signal when the diffusion coefficient is being measured is small because $\tau_1 \geq 1.3$ ms, i.e. we largely observe the diffusion of molecules in the mobile layer at the surface of the pores. In contrast, Stapf et al.[7] using a constant field gradient and very short τ_1 values (≥ 50 μs), observed a weighted average of D over the two components. On the time-scale of the experiment (10 ms), the geometrical restrictions of confined molecules will be averaged over a region that exceeds by far the mean pore diameter.

A semi-logarithmic plot of the measured self-diffusion coefficients versus reciprocal temperature is shown in Fig. 1. (The diffusion data for 200-Å silica are omitted for clarity).

The diffusion coefficient of bulk cyclohexane displays a discontinuous change of almost four orders of magnitude at the melting point. The diffusion rate of confined cyclohexane is reduced with decreasing pore size in the liquid above the bulk melting point, and our results essentially agree with those obtained by Kimmich et al.[8] In this temperature region, the observed value of D is an average of the liquid at the centre of the pores and the liquid at the surface, which are in fast exchange. A high diffusion rate of the supercooled liquid within the pores is observed over a wide temperature range-even well below the region of the depressed freezing points. Indeed, the observed D values are approximately three orders of magnitude larger than in the plastic phase of bulk cyclohexane reflecting fast diffusion of mobile molecules at the surface layer. Only a slight increase of the diffusion coefficient with reduced pore size (increased surface-to-volume ratio) is seen in Fig. 1 as expected, because the contribution of the crystallites at the interior

of the pore is small due to short T_2. The diffusion data of the confined cyclohexane appear to be continuous over the region of the depressed freezing points in all samples, unlike those previously reported[8] for Bioran (300 Å). This suggests persisting molten layers at interfaces which exchange with crystals forming within the silica pores. However, a marked increase of slope is seen at the solidification temperature. The activation energy, obtained from the linear region of the slope, increases slightly from 21.1 kJ mol^{-1} in 40-Å silica to 24.0 kJ mol^{-1} in 200-Å silica, whereas a dramatic increase to 45.7 kJ mol^{-1} is seen for the 500-Å silica. The latter activation energy is close to the directly observed value for bulk cyclohexane in the plastic phase (44.4 kJ mol^{-1}), whereas the value evaluated from T_2 measurements is somewhat smaller (41.9 kJ mol^{-1})[7].

REFERENCES

1. Barrie, P.J. NMR applications to porous solids. Ann. Rep. NMR Spectrosc. 30:37–95; 1995.
2. Jackson, C.L.; McKenna, G.B. The melting behavior of organic materials confined in porous solids. J. Chem. Phys. 93:9002–9011; 1990.
3. Sherwood, J.N. (Ed.). The Plastically Crystalline State. New York: Wiley; 1979.
4. Booth, H.F.; Strange, J.H. Organic nanocrystals: An NMR study of cyclohexane in porous silica. Mol. Phys. 93:263–269; 1998.
5. Hrovat, M.I.; Wade, C.G. NMR pulsed-gradient diffusion measurements: spin-echo stability and gradient calibration. J. Magn. Reson. 44:62–75; 1981.
6. Sørland, G.H.; Hafskjold, B.; Herstad, O. A stimulated-echo method for diffusion measurements in heterogeneous media using pulsed field gradients. J. Magn. Reson. 124: 172–176; 1997.
7. Stapf, S; Kimmich, R.; Zavada, T. Dynamics of plastic and liquid cyclohexane in bulk and in porous glasses studied by NMR methods. Appl. Magn. Reson. 12:199–212; 1997.
8. Kimmich, R.; Stapf, S.; Maklakov A.I.; Skirda V.D.; Khozina E.V. Self-diffusion in fluids in porous glass: confinement by pores and liquid adsorption layers. Magn. Reson. Imaging 14:793–797; 1996.