

Characterization of the Diffusivity of Alkanes Using Lateral Diffusion in Nanoporous Thin Film Glass



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Abstract:

The mobility of molecules when highly confined in nanometer-sized regions is a topic of significant interest in emerging areas of nanoscience. These include creating heterojunction solar cells by filling nanoporous media with organic molecules, to the operation of molecular sieves, the diffusion of process environments into nanoporous films in device technologies, and the separation and sensing of biomolecules. The diffusivity of nano-confined molecules has been characterized dominantly using nuclear magnetic resonance (NMR) and small-angle neutron scattering (SANS) techniques. However, the usage of these techniques has been limited by their complex implementation and data analysis. We present a novel technique to characterize the diffusivity with straightforward optical measurements of the motion of the liquid diffusion front in a nanoporous thin film glass. Using this technique, the diffusion of alkanes under nanoconfinement was tested at varied temperatures and the scaling in terms of molecular weight is similar. Increasing molecular weight resulted in decreasing diffusivity. Also increasing temperature resulted in increased diffusivity.

Introduction:

The mobility of molecules in the highly confined interconnected nanoporous regions presents interesting fundamental and technological questions. Nanoporous films are being actively developed for use as size-selective molecular nanofilters, biosensors, biological scaffolds, optical waveguides, and ultra-low dielectric constant layers in electronic devices [1-4]. The pores in nanoporous materials containing more than ~ 20 vol.% porosity are nearly always interconnected and the films are frequently exposed to molecular species in process or service environments. The fixed pathways in the interconnected nanoporous films provide ideal nanoscale environments to explore mobility of confined molecules and the results have implications for a number of technologies where nanoporous materials are in contact with molecules. We show that alkane behavior in nanoporous glass is very different than in bulk alkane fluid.

Experimental Details:

A 200 nm transparent layer of silicon nitride was deposited on top of methyl silsesquioxane (MSSQ) glass film (average pore size: 2.1 nm) using plasma enhanced vapor deposition (PECVD). Samples of with approximate dimensions 10 × 10 mm were cleaved and affixed on aluminum sample mounts using adhesive dots. Next, approximately 18 ml of alkane was poured into a Petri® dish and the dish was placed onto a hot plate and warmed for approximately 30 minutes and then the temperature was measured using a glass thermometer. Now ready to begin the experiment, simultaneously a sample was immersed in the alkane and a timer was started. In the capped

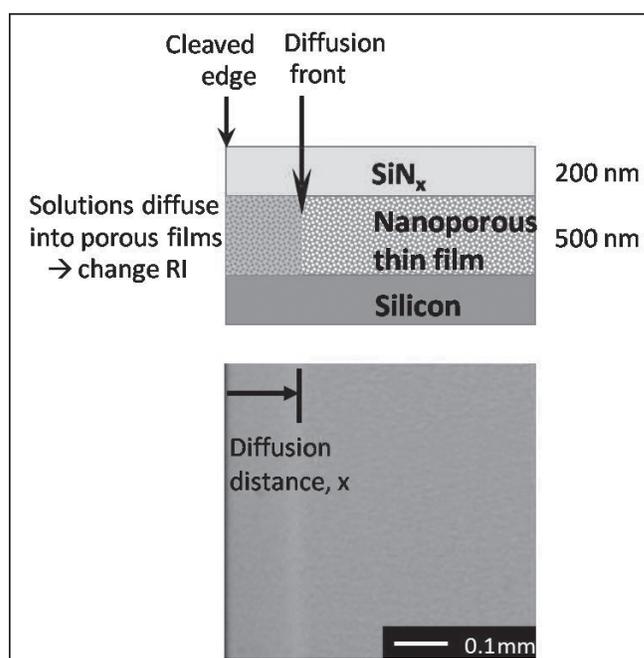


Figure 1: Diffusion front in silicon nitride capped MSSQ film.

MSSQ film, a one-dimensional diffusion front could be measured. As the fluid penetrated into the film, the refractive index of the film changed and left a visible trail as can be seen in Figure 1. The hot plate was moved underneath an optical microscope with a CCD camera and onto a height adjustable platform. The height was adjusted to bring the image into

focus and pictures were taken at roughly even intervals throughout the duration of the test.

Results and Conclusions:

Previous work suggested that the diffusivity through the glass film would follow a square root time dependence. As you can see below the plots were quite linear when graphed in this manner and therefore were consistent with Fick's First Law: $x = \sqrt{Dt}$, where D is the diffusivity and x is the diffusion distance. In the diffusivity vs. square root time plots as in Figure 2, the diffusivity is the valued slope of the best fit line through the plot squared. In comparing the diffusivities of the same alkanes at different temperatures, we found that the diffusivity increased as temperature increased. We also observed a scaled dependency of the alkanes as a function of molecular weight where $D \sim M^{-\alpha}$.

In our results, this dependency increased as function of temperature as can be seen in Figure 3. Consequently, we found that the diffusivity dependence on molecular weight changed differently with temperature in bulk fluid than in nanoconfinement. In the bulk it has been observed that the molecular weight dependence decreases as a function of temperature. Also diffusion coefficients are lower in nanoconfinement than in bulk fluid as can be seen in Figure 3 and Figure 4.

Overall our technique allowed for the diffusion coefficient to be easily calculated using optical microscope measurements so that diffusion trends could be investigated. In addition, Fickian diffusion was observed in the MSSQ film. Moreover, diffusivity scales similarly with molecular weight in both bulk fluid and nanoconfinement. However, the diffusivity under the nanoconfinement decreased by factor of 5 compared to that in the bulk. Lastly, as temperature increases, diffusivity depends more on molecular weight in nanoconfinement, and less on molecular weight in bulk fluid.

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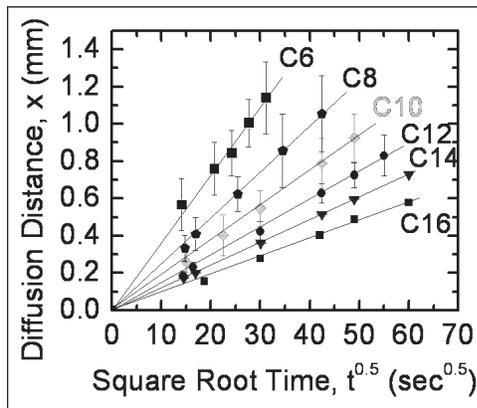


Figure 2: Fickian plot of the diffusivity of alkanes at room temperature ($22.0 \pm 1^\circ\text{C}$).

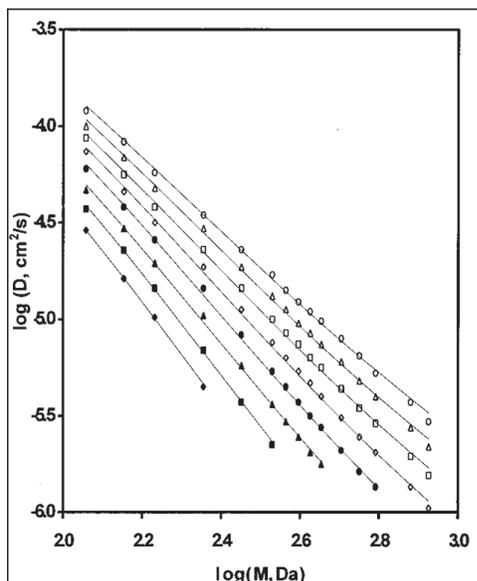


Figure 3: Power law plot of the diffusion coefficient as a function of molecular weight in MSSQ at varied temperatures.

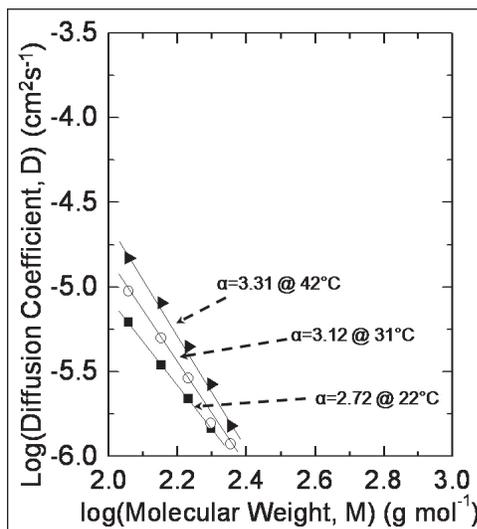


Figure 4: Power law plot of the diffusion coefficient as a function of molecular weight in bulk fluid at varied temperatures [5]. The bottommost line has $\alpha = 2.72$ at 30°C , and the topmost line has $\alpha = 1.85$ at 170°C .