

Self-Diffusion of a Molecule in Porous Vycor Glass

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We have measured the self-diffusion coefficient (D_S) of a dye molecule (azobenzene) in solution in porous Vycor glass by the technique of forced Rayleigh scattering. We find that the value of D_S for motion in the pore space is about 2 orders of magnitude less than that for free diffusion in bulk solution. By derivatizing the active surface sites we have separated the roles of the chemical and physical features of the pore space on diffusion. We believe this to be the first measurement of self-diffusion in solution in porous Vycor, which has been proposed to have a fractal pore structure.

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The transport properties of molecules in solution in porous media are of great technological importance, especially with regard to catalysis and tertiary oil recovery. Recent studies on the structure of several rocks have shown the possibility that pore spaces are fractals.¹ However, superimposed on this geometry there is also chemical heterogeneity.^{2,3} In this Letter we study molecular diffusion in a porous medium trying to distinguish between the geometrical and the chemical contributions. We present here what we believe to be the first measurements of the self-diffusion coefficient (D_S) of a probe molecule in solution in a porous silica.

The porous silica we studied was Vycor glass which is made by phase separation of boron in borosilicate glass. The phase-separated boron forms a connected path which produces the pore space when removed by acid leaching.⁴ Recent small-angle x-ray-scattering (SAXS) measurements have shown that the structure of this pore space is reminiscent of spinodal decomposition, with a broad peak in the structure factor corresponding to a length of about 300 Å.⁵ Energy-transfer measurements which probe small length scales (≤ 100 Å) suggest that the pore structure of Vycor glass is fractal with a fractal dimension (\bar{d}) of 1.74 ± 0.05 .⁶ On length scales over which the pore space is fractal one expects to observe anomalous diffusion which is given by the fractal and spectral (\bar{d}) dimensions.⁷⁻¹⁰

The Vycor was 7930 glass from Corning. Two types of disks were used: a 6-mm-thick and 25-mm-diam disk with a scalloped surface and a 1-mm-thick and 25-mm-diam disk with a flat but not polished surface. We first measured the pore size distribution using a 500-point nitrogen desorption technique.¹¹ The result is shown in Fig. 1. The distribution is sharply peaked at 30 Å radius, with essentially all the features falling between 20 and 55 Å radius.

The self-diffusion coefficient was measured by forced Rayleigh scattering (FRS).¹² Forced Rayleigh scattering is an effective tool for measuring the self-diffusion coefficient. In this case, azobenzene was used as the probe molecule. Interference fringes were created with the 488-nm argon-ion laser line ("writing

wavelength") and the scattering wavelength was 632.8 nm from He-Ne ("reading wavelength"). The Vycor glass was index matched at the writing wavelength by use of alcohol-toluene mixtures which gave an index of 1.4684. The two solutions which proved most useful were 4.3-M methanol in toluene and 3.3-M 1-propanol in toluene. The concentration of azobenzene was always 8 mM and the measurements were made at $\sim 20^\circ\text{C}$.

There are two major properties of porous materials which affect the measurements of self-diffusion. They are related to the extent to which pores are dead ended and tortuous (geometry) and to the degree that the diffusing molecules are adsorbed on surface sites (chemistry). Separating the contributions of physical and chemical traps to the diffusion of azobenzene in Vycor was a problem which we had to address. Our initial approach was to block the surface adsorption sites by adsorbing alcohol molecules. The order in which the alcohol, toluene, and azobenzene are added to the Vycor determined the degree of spatial homogeneity which could be achieved in distributing azobenzene in the Vycor. Our prescription was to imbibe in methanol over three days, then remove the excess methanol by evaporation and reexpose the Vycor to an alcohol-toluene mixture. After about two weeks the

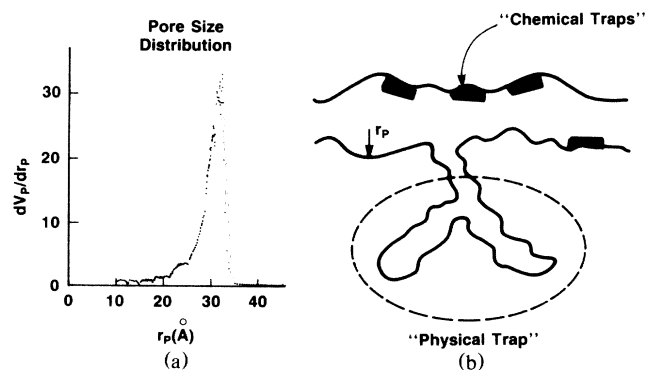


FIG. 1. (a) The pore-size distribution of porous Vycor glass. (b) A schematic representation of the chemical and physical nature of the porous glass.

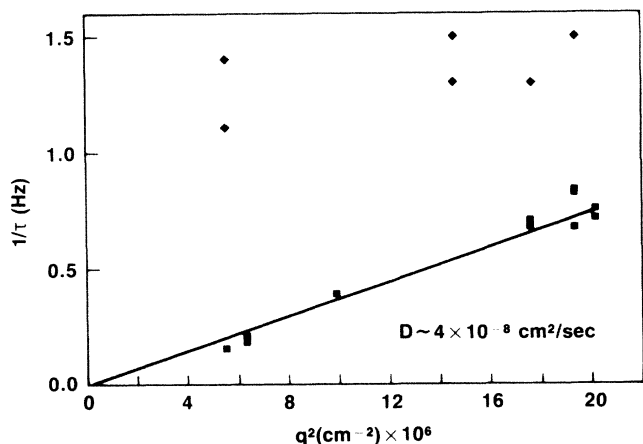


FIG. 2. FRS data for azobenzene in underivatized Vycor with methanol-toluene as solvent. Squares are experimental data points. The solid line is a fit through the origin which gives $D_S = 4.2 \times 10^{-8} \text{ cm}^2/\text{sec}$. The diamonds are data from nonexponential decays.

sample was nearly index matched. The excess alcohol and toluene was removed and replaced with a solution of alcohol and toluene with azobenzene. After an additional week there was enough FRS signal to conduct the diffusion measurement.

D_S is determined from the decay rates of the Bragg scattering from fringes of several spacings.¹² For an exponential decay with rate τ^{-1} , we have

$$D_S q^2 = 1/\tau - 1/\tau_r, \quad (1)$$

where q is the wave vector of the fringes [$2\pi/(\text{fringe period})$] and $1/\tau_r$ is the thermal relaxation rate of *cis*-azobenzene to *trans*-azobenzene. The result for azobenzene in 4.3-M methanol in toluene is shown in Fig. 2. Note the collection of points at $1/\tau \cong 1 \text{ Hz}$. Relaxations of about this rate were found independent of fringe spacing, showing it to be an intrinsic relaxation of the dye molecules adsorbed to the pore surface rather than arising from diffusion. The decay of the Bragg scattering was also decidedly nonexponential for these cases. By movement of the sample, q -dependent decays could be found, which are also shown in Fig. 2. These signals displayed a good exponential decay which obeys Eq. (1). If we identify the q -independent, nonexponential signals as those coming from azobenzene chemisorbed to the surface and the rest as coming from free dye diffusing within the pore space, we obtain $D_S = (4.2 \pm 0.3) \times 10^{-8} \text{ cm}^2/\text{sec}$.

Although we were able to measure D_S for these samples, the extent of spatial inhomogeneity indicated that the methanol did not effectively block all the active sites of the Vycor glass. To achieve a more complete chemical passivation of the surface sites we derivatized the silanol groups by reacting them with 1-propanol. This esterification reaction was carried out

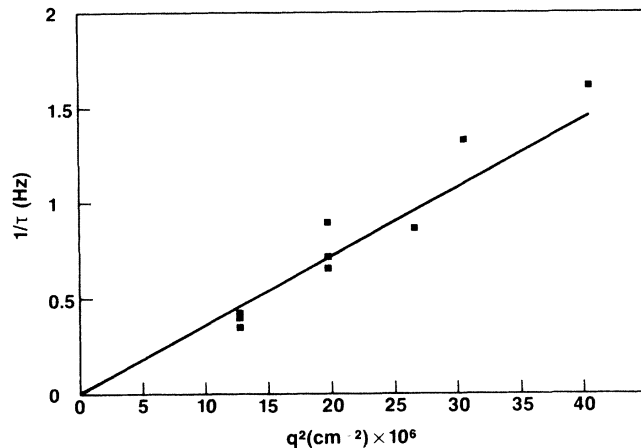
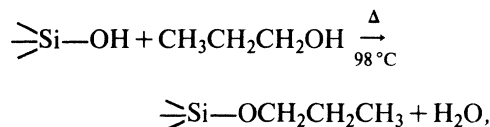


FIG. 3. FRS data for diffusion of azobenzene in derivatized Vycor with 1-propanol-toluene as solvent. Squares are experimental data and the solid line is a least-squares fit with $D_S = 2.4 \times 10^{-8} \text{ cm}^2/\text{sec}$ and $\tau_r^{-1} = 0.22 \text{ Hz}$.

in neat 1-propanol at its boiling point for 24 h. The reaction that took place was¹³



which yields a more hydrophobic surface that is less active towards adsorption of azobenzene. With this derivatized Vycor the procedure for preparing samples was the same, except that no pretreatment with methanol was used. The important result obtained is that it was *spatially homogeneous* as measured by FRS. These samples showed *no* nonexponential, q -independent signals. The q -dependent relaxation was the same over the entire sample clearly suggesting that the diffusion of azobenzene was not restricted by chemisorption to the pore surface. The results for the azobenzene in 1-propanol-toluene solution in 1-propanol-derivatized Vycor are shown in Fig. 3, $D_S = (2.4 \pm 0.4) \times 10^{-8} \text{ cm}^2/\text{sec}$. The value of D_S for methanol-toluene in the derivatized Vycor, Fig. 4, is $(3.6 \pm 0.6) \times 10^{-8} \text{ cm}^2/\text{sec}$. The methanol-toluene value suggests that the derivatization had no effect on the diffusion coefficient, since D_S before and after derivatization are essentially the same. It should also be noted that the difference between D_S in the two solvent systems is completely explained by the differences in the viscosities of the solvents. We also measured the free bulk diffusion D_0 in the two solvents by the same FRS method and found the values to be $(2.4 \pm 0.5) \times 10^{-6} \text{ cm}^2/\text{sec}$ and $(1.4 \pm 0.3) \times 10^{-6} \text{ cm}^2/\text{sec}$ in methanol-toluene and 1-propanol-toluene, respectively. D_S is 2 orders of magnitude lower than for free bulk diffusion.

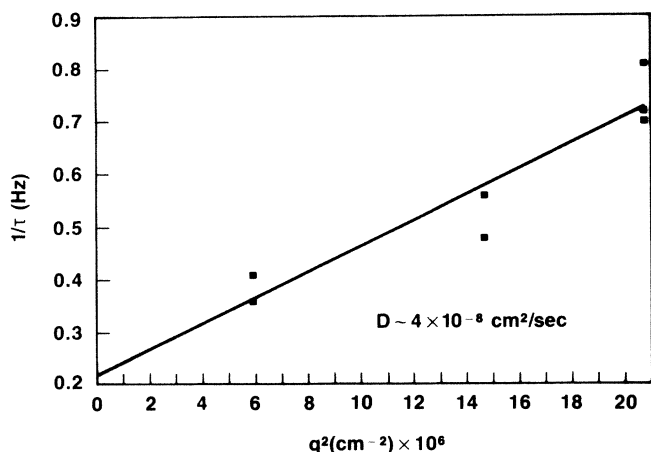


FIG. 4. FRS data for azobenzene in derivatized Vycor with methanol-toluene as the solvent; $D_S = 3.6 \times 10^{-8}$ cm²/sec.

Similar behavior has been observed by Karger *et al.*,¹⁴ who used NMR to study self-diffusion in porous glasses. However, it is not clear from the work whether the experiments measured self-diffusion in a liquid-saturated pore or surface diffusion. But their results are strongly affected by the chemically active surface sites, an important issue which we have eliminated from our results.

We now present two possible models to interpret the slow dynamics observed by the FRS in porous Vycor. We first follow the parallel-pore model¹⁴ proposed to describe a monodispersed pore-size distribution in porous catalysts. In this case the diffusion is related to D_0 in a phenomenological way through the porosity Φ and the tortuosity factor δ ¹⁵:

$$D_S = D_0(\Phi/\delta). \quad (2)$$

In order to determine the tortuosity factor we also measured the porosity of the Vycor by two techniques: nitrogen adsorption and spontaneous liquid imbibition. The nitrogen-adsorption method yielded a porosity Φ of 0.40 ± 0.04 for pores above 10 Å radius and indicated a micropore porosity of 0.14 ± 0.05 for pores with a radius between 5 and 10 Å. The second technique was based on the spontaneous imbibition of a liquid, where the volume of solution imbibed was compared to the volume of the Vycor disk. This kind of measurement is prone to interference by the surface sites and by the relationship between the size of the imbibing molecules and the pore structure.¹⁶ Therefore, porosity measurements were made with use of a solution of the same composition as that used for index matching of the pore space for the light-scattering experiments. The porosity measured by imbibition was 0.28 ± 0.03 for both 4.3-M methanol in toluene and 3.3-M 1-propanol in toluene. This apparent difference in the porosity between the two techniques may in fact be

due to the difference in the molecular yardsticks used to probe the pore space.

For porosity $\Phi = 0.28$ and from Eq. (2) we obtain the tortuosity factor $\delta \cong 18$. This δ is much higher than the value 5.6 found previously from the diffusion of hydrogen.¹⁵ From the measurements of D_0 we calculated the hydrodynamic radius of the *cis*-azobenzene to be about 4.1 ± 0.7 Å in the propanol-toluene and 6.5 ± 1 Å in methanol-toluene. These radii are not much larger than a hydrogen-molecule radius with respect to the available pore space, since the pores have a narrow size distribution. It could be that since under steady-state flow conditions (the conditions under which the gas diffusion measurements are done) "dead-end" pores do not contribute to the measurement, so one should renormalize Φ to account for only that fraction of the pore space that contributes to the diffusion. The FRS experiment is done under conditions of macroscopic equilibrium. If one assumes that δ is the same in both experiments, then the result suggests that $\frac{2}{3}$ of the pore space is not contributing to the diffusion. If that were the case, the FRS signal would lose $\frac{1}{3}$ of its intensity in a relatively short time and the result would decay at either an extremely slow rate or at a rate of $1/\tau_r$, whichever is faster. This is not what is observed. If instead we take Φ to be the measured value then the difference in δ is understood as an additional effect of "tortuosity" since the lost time spent in dead-end pores should affect the diffusion constant in the FRS experiment. The concept of tortuosity bears a clear, intuitive meaning, which probably gives the correct trend. It is, however, not directly measurable and not well defined.^{15,17}

A second possibility is to model the geometrical disorder by a fractal, self-similar structure. Thus, we assume, based on previous suggestions,⁶ that the pore structure of porous Vycor has a fractal character on length scales $l_1 < l < l_2$, where l_1 and l_2 are the lower and upper cutoffs of the fractal range, respectively. We calculate the time τ that it takes a molecule to diffuse over lengths of the order of the fringe spacing L . It is clear that, since the range of the fringe spacing is between 1 and 100 μm, $L \gg l_2$, namely we measure diffusion over lengths larger than those expected to exhibit anomalous diffusion.⁷⁻¹⁰ On scales such that $L \gg l_2$ classical diffusion sets in and the scattering intensity should decay exponentially with time, as we experimentally observed. From a crossover argument for a random walker on a structure which is fractal for $l_1 < l < l_2$ we obtain

$$\tau = \tau_0 (l_2/l_1)^{2\bar{d}/\bar{d}} (L/l_2)^2, \quad L \gg l_2, \quad (3)$$

where τ_0 is the elementary step time of the walker and \bar{d} is the spectral dimension. Using the relationship between D_S and τ , Eq. (1) where τ_r is very large, we

rewrite Eq. (3) in terms of diffusion constants:

$$D = D_0(l_1/l_2)^{2(\bar{d}/\bar{d}-1)}, \quad (4)$$

where $l_1^2 \sim D_0\tau_0$.

Let us assume, for instance, that the fractal and spectral dimensions have the three-dimensional percolation values $\bar{d} \sim 2.5$ and $\bar{d} \sim 1.3$. Then for the ratio $D/D_0 = 1.75 \times 10^{-2}$ measured in methanol-toluene solutions we obtain through Eq. (4) the ratio $l_1/l_2 \sim 0.1$. This means that if the lower cutoff is taken as the average pore size, $l_1 \sim 30 \text{ \AA}$, the upper cutoff is $l_2 \sim 300 \text{ \AA}$. The porosity of a fractal pore geometry is given by¹

$$\Phi \approx (l_1/l_2)^{3-\bar{d}}. \quad (5)$$

For the assumed values of l_1/l_2 and \bar{d} we calculate a porosity $\Phi \sim 0.31$ which is close to the porosity measured by imbibition. As mentioned above, different molecules may probe different portions of the pore space. Even *et al.* measured $\bar{d} \sim 1.74$ which may be attributed¹⁶ to the larger molecules used in their experiment. We would like to emphasize that the values we chose to model the system are quite heuristic. One can assume other parameters \bar{d} and \bar{d} which are also consistent with the observed diffusion and porosity. More independent measurements of the various parameters and molecular size effects are needed.

In summary, although in most porous surfaces chemical heterogeneity is superimposed on the geometrical disorder, we have managed to separate these two contributions by blocking the chemical traps by derivatization. We measured the pore-size distribution of the Vycor and its porosity and related them to the self-diffusion of the azobenzene molecule through a conventional phenomenological approach which relies on the concept of a tortuosity factor and through a more detailed fractal model which involves the basic parameters \bar{d} and \bar{d} and the range of the fractal behavior.

We have demonstrated the applicability of the FRS technique as a method to study dynamics in transparent porous media. More details and results on different porous silicas with controlled pore-size distributions will be published elsewhere.

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