

Enhanced Self-Diffusion of Water in Restricted Geometry

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(Received 10 March 1989)

Self-diffusion of water contained in a porous glass is observed to be strongly enhanced if the pore space is only partially filled. This can be explained by a novel mechanism involving indirect molecular exchange between the liquid and the vapor phase. A theoretical model fits the pulsed-field-gradient NMR diffusion measurements with no adjustable parameters. NMR relaxation measurements were performed to provide a characterization of the homogeneity of the samples.

PACS numbers: 66.10.Cb, 05.40.+j, 47.55.Mh, 76.60.Es

Relaxation and transport phenomena of fluids in confined structures are presently attracting wide interest¹ from a number of points of view. Understanding the modifications from bulk liquid behavior introduced by the porous medium provides a tool for their characterization, significant to various technologies such as heterogeneous catalysis and oil recovery from natural reservoirs. However, there may also be cases in which the liquid contained in the porous medium exhibits a completely new phenomenon that cannot be described as a modification of bulk properties. In this paper we report such a discovery in porous glass partially filled with water. We have observed that the self-diffusion of the liquid is markedly enhanced by an indirect process involving exchange with the vapor phase. Crucial to this process is that the liquid should wet the solid surface creating two interpenetrating porous systems, that of the liquid and that of the vapor, each with a different geometry.

Nuclear magnetic resonance (NMR) experiments were performed on water imbibed into porous silica glasses. These include longitudinal and transverse relaxation, as well as measurements of the self-diffusion coefficient at various temperatures. Most importantly, experiments were performed for different filling fractions of water in the pore space of the glass samples, as is shown in the accompanying figures. The samples under study were chosen among a set of five porous silica glasses, gelled from mixtures of colloidal silica and potassium silicate,² which we identify in the following by their colloidal silica-to-potassium-silicate mixture ratio (for example, 10:90). Each sample was leached² in order to remove surface alkali ions, and sealed after impregnation with deionized water, in an NMR tube with a Teflon rod filling the dead volume of the tube in order to prevent water loss from the sample itself. These samples are characterized by very high porosity (85%) and by progressively increasing pore sizes as the fraction of colloidal silica is reduced.² The pore-size distributions are relatively narrow, and the peak position ranges between

470 Å (for sample 30:70) and 2400 Å (for sample 10:90), as determined by the mercury porosimetry technique.² We have previously reported NMR relaxation measurements performed on saturated samples.³

Before we describe the results of diffusion measurements it is appropriate to discuss our characterization of the water-glass system under study. Longitudinal and transverse relaxation measurements were conducted with different water coverage using, respectively, the inversion recovery sequence⁴ and the Carr-Purcell-Meiboom-Gill sequence.⁵ In the latter, the time between radio-frequency pulses was short enough (typically 500 μs) that attenuation of the magnetization signal due to diffusion in magnetic field inhomogeneities was negligible. All proton NMR experiments were performed at 25 MHz. Longitudinal and transverse relaxation curves were obtained for different water contents in samples 10:90 ($d=2400$ Å) and 20:80 ($d=950$ Å) at room temperature. The volume-to-surface ratios for these samples are 826 and 469 Å, respectively.³ In all cases, as discussed in Ref. 3, the nuclear magnetization was observed to be a precise exponential decay in time, with characteristic relaxation times defined as T_1 and T_2 for longitudinal and transverse experiments, respectively. In Fig. 1 the values of T_1 and T_2 , for sample 10:90, are plotted as a function of pore saturation; a similar behavior is observed for sample 20:80. Both data sets are well fitted by straight lines crossing the origin of coordinates. In all cases, the water content was determined by weight.

From these relaxation experiments several important conclusions can be derived. First of all, the observed exponential relaxation of the nuclear magnetization is evidence of fast exchange among molecules contained in the pore space. Second, the linear dependence in Fig. 1 indicates that the sample is highly homogeneous at all coverages down to eight molecular layers and is in accurate agreement with the theory for fast exchange^{6,7} given by

$$\frac{1}{T} = \frac{1}{T_b} + \frac{S}{V} \frac{\lambda}{T_s}, \quad (1)$$

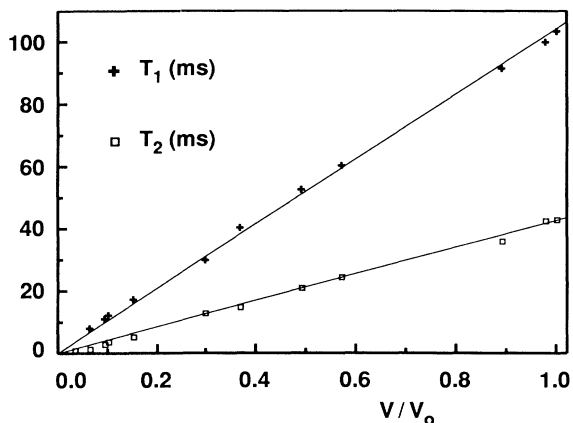


FIG. 1. Longitudinal (T_1) and transverse (T_2) relaxation times for water as a function of filling ratio for sample 10:90. The linear fits, consistent with Eq. (1), confirm the fast exchange theory and demonstrate homogeneity of the sample.

where the rate $1/T$ refers to either longitudinal or transverse experiments, $1/T_b$ is the corresponding rate for the bulk liquid ($< 0.4 \text{ s}^{-1}$) which is sufficiently small to be neglected, $1/T_s$ is the enhancement of the relaxation rate of fluid molecules within a single molecular distance λ from the liquid-solid interface, S is the total area of this interface, and V is the volume occupied by the water. Under heterogeneous conditions, due for example to a distribution of pore sizes or, more relevantly for the present purpose, to a nonuniform spreading of the water in the sample, Eq. (1) would give different values for distinct regions since the ratio S/V should be replaced by a local surface-to-volume ratio s/v . In that case, multiple exponential decay would result for the magnetization. This is not what we observed. Our conclusion is that the system is homogeneous for all water coverages; therefore, not only the pore space itself, but also the way the fluid is distributed in it under partial filling conditions, is homogeneous throughout the sample. It should be noted that this inference of homogeneity applies only over a length scale larger than a molecular diffusion length. The root-mean-square displacement of a fluid molecule during the time t of an NMR experiment is given by $(6Dt)^{1/2}$, where D is the diffusion coefficient of the fluid in the porous structure. From a typical value of D larger than $10^{-5} \text{ cm}^2/\text{s}$ (more precise values may be found in the latter discussion) and experimental times t larger than 1 ms we estimate that the system constituted by fluid and porous solid is homogeneous on length scales larger than a few micrometers.

From the values of the total surface area, determined by a Brunauer-Emmett-Teller analysis of nitrogen adsorption isotherms at liquid-nitrogen temperature, and of the total open-pore volume V_0 , we can relate the slopes of the fitting lines in Fig. 1 with the surface interaction parameter λ/T_s in Eq. (1), obtaining $\lambda/T_{1s} = 6.7 \times 10^{-5}$

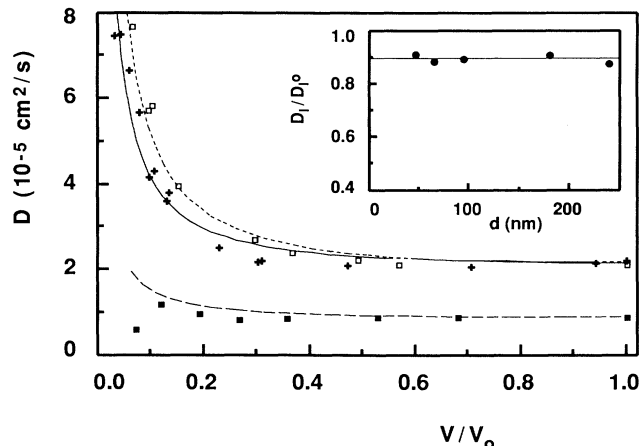


FIG. 2. Diffusion coefficients of water in porous sol-gel glasses as a function of filling fraction. Measured values at 26.6°C (\square , 10:90, $d=2400 \text{ \AA}$; $+$, 20:80, $d=950 \text{ \AA}$) increase monotonically as the coverage is reduced below 30% of the saturation, reaching values more than 3 times larger than that of bulk water. The fitting curves (dotted, 10:90; solid, 20:80) are derived from Eq. (3) and consider the contribution of the vapor phase to molecular transport. The value of m' in Eq. (3) is obtained from the diffusion coefficient for five water-saturated glass samples with different pore sizes d but with the same porosity, as indicated in the inset. At 2.2°C the contribution to diffusion (\blacksquare) from the vapor phase in 10:90 is strongly suppressed. The dashed line represents the corresponding fit.

cm/s and $\lambda/T_{2s} = 1.6 \times 10^{-4} \text{ cm/s}$. These values are somewhat different from our previous measurements³ on saturated samples taken from different parts of the same sample batch. In experiments on leached borosilicate glasses we found that the surface layer thickness λ was 2.8 \AA ; then surface relaxation times may be calculated: $T_{1s} = 0.42 \text{ ms}$ and $T_{2s} = 0.17 \text{ ms}$.

Self-diffusion measurements of water were performed using the NMR pulsed-field-gradient (PFG) technique as described by Stejskal and Tanner.⁸ Values of the diffusion coefficient measured at room temperature for samples 10:90 and 20:80 are reported in Fig. 2 for different water contents. Small deviations from an average temperature (26.6°C) in each experiment were accounted for by introducing corrections for the temperature dependence of the quantities involved in the context of the interpretative model explained later; however, these deviations are very small ($< 10\%$) and do not affect the physical interpretation. For both samples the self-diffusion coefficients are approximately constant for water filling more than 30% of the pore volume. For smaller water filling fractions, the diffusion coefficient increases monotonically above the bulk value ($2.4 \times 10^{-5} \text{ cm}^2/\text{s}$ at 26.6°C) as the coverage is decreased. To our knowledge, this peculiar result has never been observed before. Two possible explanations have occurred to us: enhanced self-diffusion at the liquid-solid interface and

contributions to self-diffusion from the vapor phase. The first hypothesis appears unlikely since we should rather expect hindered diffusion for the polar water molecules, as manifested by the small surface relaxation times calculated from T_1 and T_2 experiments. This effect is clearly seen in similar experiments we have made on porous glasses with smaller porosity and higher specific surface area.⁹ Consequently, we interpret the anomalous coverage dependence of the diffusion coefficient in terms of a two-phase process. In an unsaturated sample, the liquid phase is confined in a layer adsorbed on the surface; the thickness of this layer depends on the degree of impregnation. The remainder of the pore volume is clearly occupied by air saturated by a vapor phase which can be thought of as an independent porous system, with reduced porosity. Fast molecular exchange between the two phases during typical experimental times ensures that the measured self-diffusion of the water molecules through the sample consists of a parallel process in which contributions from the two phases simply sum together:

$$D_m = \frac{V\rho_l}{V\rho_l + (V_0 - V)\rho_v} D_l + \frac{(V_0 - V)\rho_v}{V\rho_l + (V_0 - V)\rho_v} D_v, \quad (2)$$

where ρ represents the mass density and the subscripts l and v refer to the liquid and the vapor phases, respectively.

We need to emphasize that, in principle, both D_l and D_v are reduced, due to the tortuosity of the diffusion path, with respect to the corresponding bulk values D_l^0 and D_v^0 which would be obtained for infinitely large phase domains. The way of describing the tortuosity for a multiphase system is not a trivial problem; in particular, the different geometries characterizing the two phases suggest that their tortuosities depend differently on coverage. The crudest approach is to allow separate models for each phase. Following Archie's law,¹⁰ the diffusion coefficient of the liquid phase is reduced by a factor $\alpha = \phi^{m'}$, where ϕ is the porosity of the sample and

m' has to be determined experimentally. In this notation the conductivity of an electrolytic solution would be reduced by the factor $\phi^{m'+1}$.¹¹ Our measurements in the region where $V/V_0 > 0.3$ indicate that the reduction α is coverage independent, a result we attribute to the wetting of the liquid on the surface. This can be explained if we consider that the main contribution to the tortuosity of the diffusion path comes from the interconnection of adjacent "pores." The essential phenomenological interpretation of Archie's law is that such interconnection can be described by a power law of the porosity ϕ . However, if the filling fluid wets the surface of the sample, no reduction in the connectivity is expected when the filling factor is reduced. Our observations are consistent with the study performed by Kärger *et al.*¹² in which no essential change in the diffusion coefficient of several liquids in porous glasses was observed down to a filling factor of 0.24. However, substantial deviation from this constant value may be possible at very low coverage. On the other hand, the different geometry of the vapor phase suggests that its diffusion coefficient be proportional to ϵ^m , where an effective vapor porosity $\epsilon = \phi(1 - V/V_0)$ is defined, and the coefficient m may differ from m' . In fact, as stated before, the nonwetting vapor domains are confined to the center of the pores and constitute a new porous system with reduced effective porosity. If we also take into account the Knudsen effect¹³ at the vapor-liquid interface, the expression for diffusion in the gas phase may be written as follows:

$$D_v = \phi^m (1 - V/V_0)^m / (1/D_v^0 + 1/D_K).$$

The Knudsen term D_K is well approximated by the quantity $(2a/3)(8k_B T/\pi M)^{1/2}$, where k_B is the Boltzmann constant, T is the absolute temperature, M is the mass of the molecules, and a is the size of the vapor-phase domains. The last quantity is clearly related to the saturation of the sample, and also depends on the shape of the pores. For a cylindrical geometry $2a = d(1 - V/V_0)^{1/2}$, where d is the pore diameter. A final expression for the diffusion coefficient is then obtained:

$$D_m = \frac{1}{1 + (V_0/V - 1)\rho_v/\rho_l} \left[\phi^{m'} D_l^0 + \frac{\phi^m (V_0/V) (1 - V/V_0)^{m+1} \rho_v/\rho_l}{(D_v^0)^{-1} + [\frac{1}{3} d (1 - V/V_0)^{1/2} (8k_B T/\pi M)^{1/2}]^{-1}} \right]; \quad (3)$$

this has been used to fit the experimental data shown in Fig. 2. The value $m' = 0.70$, corresponding to $\alpha = 0.89$, was obtained from the self-diffusion coefficient of the five water-saturated samples, i.e., $V = V_0$ in Eq. (3), at room temperature, as shown in the inset of Fig. 2. This result is similar to the value $\alpha = 0.92$ we derived from conductivity measurements on sample 10:90 saturated with a KCl aqueous solution. To determine the value of the other coefficient m , one could, in principle, keep it as a free parameter, and then derive it by a best-fit procedure. However, we found that the fitting was not very sensitive to the value of m . The only indication from our attempt was that m was of the order of unity. Conse-

quently, we choose the value $m = m' = 0.70$. This ensures that the tortuosity for a single diffusing phase (vapor or liquid) be the same. Therefore, Eq. (3) becomes a relation with *no adjustable parameters* in the context of this model.

To proceed in the fitting of the experimental data we took into account the temperature dependence of the quantities D_v^0 and ρ_v .¹⁴ It is interesting to note that, even if $\rho_v \ll \rho_l$ ($\rho_l = 4.0 \times 10^4 \rho_v$ at 26.6 °C), the other inequality $D_v^0 \gg D_l^0$ ($D_v^0 = 1.0 \times 10^4 D_l^0$ at 26.6 °C) implies that the contribution of vapor transport dominates as water content decreases. The results of the fit are

presented in Fig. 2, for samples 10:90 and 20:80. The two upper lines represent the theoretical curve calculated from Eq. (3) at $T = 26.6^\circ\text{C}$. Since the two samples have the same porosity, the only difference between the corresponding fitting curves is due to the pore size which appears in the Knudsen term. Consequently, the theoretical curve for sample 20:80, which has a smaller pore size, is below that for sample 10:90 at small water filling factors. From the plots in Fig. 2, it is clear that Eq. (3) gives an excellent prediction of the experimental values of self-diffusion coefficients in unsaturated porous sol-gel glass. We ascertain thereby an important two-phase transport phenomenon in which the vapor contribution becomes dominant as the liquid filling factor is reduced. Note that in the range of water content covered by our experiments the prefactor to the square bracket in Eq. (3) is practically unity.

In our interpretation leading to Eq. (3), we have taken the diffusion contribution of the liquid phase to be coverage independent, as indicated by the experimental data for $V/V_0 > 0.3$. However, for lower coverage, the exact behavior of the liquid phase is hidden by the increasing contribution from the vapor phase. To investigate this point more extensively, we repeated PFG experiments for sample 10:90 as a function of coverage at a much lower temperature. Under these conditions, the contribution from the vapor phase would be expected to be reduced since its density is strongly temperature dependent. The results of our experiments at 2.2°C are also shown in Fig. 2, together with the theoretical fit (lower curve) calculated from Eq. (3) at the same temperature. Again, the agreement with the experimental data is good. The value of m' in this case was recalculated in order to constrain the fitting curve to the experimental value at full sample saturation. The experiments at 2.2°C show a drop in the diffusion coefficient at the very lowest water content, a result not explained by our model. We speculate that a combined reduction of vapor pressure and of diffusivity of the liquid phase may occur in thin water films when the freezing temperature is approached.

In conclusion, we have demonstrated that anomalously high self-diffusion coefficients for water in unsaturated porous materials may be explained by a simple model which considers fast interphase exchange between vapor and liquid. In particular, we have identified a key role played by wettability of the liquid water on the solid surface. This assures connectivity of the liquid phase down

to very low filling factors and confines the vapor phase in domains whose collection constitutes by itself a well-defined porous structure of reduced porosity. It would be interesting to compare the results reported in the present Letter with analogous experiments on structures with smaller pore sizes, in order to determine the importance of other parameters, such as surface chemical conditions, surface homogeneity, and relative size of the fluid molecules with respect to pore structure, and how they may influence multiphase transport in porous media.

This work was supported by the Department of Energy, Grant No. DE-FG02-86ER45251. Nitrogen adsorption-desorption characterization equipment was obtained from the Department of Energy, Grant No. DE-FG05-86ER75295.

¹See, for example, "Molecular Dynamics in Restricted Geometries," edited by J. Klafter and J. M. Drake (Wiley, New York, to be published).

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