Fluid transport in partially filled porous sol-gel silica glass

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Measurements of low-frequency ac electrical conductivity of a porous glass filled with different amounts of a saline solution are compared with the self-diffusion coefficient of water measured in the same sample, reported previously [F. D'Orazio *et al.*, Phys. Rev. Lett. **63**, 43 (1989)]. The two transport parameters are consistently related through the Einstein relation under saturation conditions. A more complex picture is revealed for the unsaturated sample, since the presence of a vapor phase enhances the self-diffusion coefficient. Conductivity experiments allow an independent assessment of the contribution to self-diffusion from the liquid phase. However, a comparison between the two experiments indicates that the role of the vapor phase is not well understood.

I. INTRODUCTION

The study of molecular-transport properties in porous materials is presently attracting considerable interest as a means to characterize pore spaces, and to understand fundamental processes such as sample formation, catalytic reactions, chromatography, hydrocarbon recovery, and superfluidity in restricted geometry.[1] The experimental work includes measurements of electrical conductivity, fluid diffusivity, acoustic velocity and attenuation, permeability, liquid self-diffusion, and, more recently, thermal-wave spectroscopy.[2] This has been joined by a theoretical attempt to represent the geometry of actual porous media with random or regular model structures (including fractals) that are able to reproduce, via numerical simulation, the experimental results.[3,4]

Particular effort has been directed toward defining a small set of parameters strictly linked to physical properties that characterize the porous material: porosity, specific surface area, specific pore volume, pore size, effective pore-size parameter Λ,[5] and formation factor. The obvious implication of this approach is that one hopes to evoke a general description of phenomena in porous media tied to only a few results, measured or simulated, that reflect these characteristic pore parameters. In practical cases, however, this proposition has encountered some difficulties. Examples are the power law between conductivity and porosity,[6] and the relation between permeability and NMR longitudinal relaxation,[7] which have been demonstrated only phenomenologically; the relation between permeability and conductivity,[8] which appears correct under the assumption of a wide distribution of pore sizes; the comparison between permeability and viscous wave-attenuation measurements,[9] which is a clear illustration that different properties may be a consequence of distinct structural aspects of the same pore geometry. Nevertheless, it seems appropriate to consider conductivity and self-diffusion processes as being strictly linked,[10] since they are related through the Einstein relation described below in Eq. (1). Therefore, results from experiments, or numerical simulations, of these two processes are expected to be consistent with each other in this case.

In this paper we compare the results from experiments of low-frequency ac electrical conductivity of potassium-chloride aqueous solution filling a porous glass sample in various amounts with results of water self-diffusion measurements.[11] The study of these physical properties as a function of fluid filling constitutes a useful way to understand the restricted dynamics of molecules and ions. We ascertain that the two transport processes do not reflect the geometry in the same way, since contributions from the vapor phase to molecular motion are only effective in the self-diffusion mechanism. Although our two-phase transport model fits the experimental data of self-diffusion measurements satisfactorily, there is difficulty in attempting to reconcile this interpretation with the prediction of the Einstein relation. This is most apparent close to saturation where the direct contribution to diffusion from the vapor phase is supposedly negligible. It is a fundamental question as to whether this discrepancy should be ascribed to some new physical effect of a two-phase mixture or is purely of geometric origin.

II. SAMPLE

The sample under investigation is a porous glass gelled from a mixture of colloidal silica and potassium silicate with a proportion of 10:90 by weight, respectively.[12] The porosity ϕ, defined as the ratio between the open pore volume and the total volume of the sample, is 0.85, and the pore diameter d is 240 nm, as determined by the mercury porosimetry technique. The investigation of the pore structure using nitrogen-desorption techniques suggests that, in addition to the more macroscopic geometrical features disclosed by mercury porosimetry, some

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small portion of the void space ($\sim 10\%$) is constituted by mesopores, with an average pore size of 3.6 nm. More details on the preparation, treatment, and characterization of the sample have been described previously.[12,13] The sample was leached of surface alkali-metal ions before the experiments were performed.

III. THEORY: ELECTRICAL CONDUCTIVITY AND SELF-DIFFUSION

The electrical conductivity of a medium containing charged particles, such as an ionic solution, is related to self-diffusion under conditions of thermodynamic equilibrium through the Einstein relation

$$\frac{\mu_i}{D_i} = \frac{q_i}{k_B T} , \tag{1}$$

where μ_i, D_i, and q_i are, respectively, the mobility, the self-diffusion coefficient, and the charge of the ions, k_B is the Boltzmann constant, and T is the temperature. The conductivity depends on the mobility according to

$$\sigma = \sum_i q_i n_i \mu_i , \tag{2}$$

where n_i is the number of ions per unit volume, and the sum is over all ion species present in the system. Not all space is available for transport of ions contained in a solution filling a porous medium. In this respect we need to take into account two factors. First, only a fraction ϕ of the entire volume of the sample is accessible to an external fluid. Also, it may occur that the sample is not completely filled with solution (unsaturated conditions). Therefore, the density of carriers in the pure aqueous solution differs from that in the porous medium by a factor $\phi V/V_0$, where V is the volume of solution actually present in the sample and V_0 is the total available open-pore volume. In the following the quantity V/V_0 will be referred to as the *filling factor*. It is assumed that the hindrance to ionic diffusion and conductivity comes exclusively from geometrical features of the liquid-glass system so that, in particular, diffusion is reduced in the same way for all ion species as well as for the solvent molecules. Then the relation between the ionic conductivity and the self-diffusion coefficient may be expressed as

$$\frac{\sigma}{\sigma_0} = \frac{D_l}{D_l^0} \phi \frac{V}{V_0} , \tag{3}$$

where σ is the conductivity of the solution-sample system, σ_0 is the conductivity of the pure solution at the same ionic concentration, D_l is the liquid-phase contribution to the self-diffusion coefficient of solvent molecules in the pore structure, and D_l^0 is the corresponding value for the pure solution. The validity of Eq. (3) is strictly linked to the assumption stated above that the ratio between the transport parameters inside and outside the pore geometry is the same for all ions or molecules considered. This is true provided that there is no alteration in the ion-ion, ion-water, or water-water interactions inside the pores. In particular, contributions from interfacial conduction[5] and particle-size effects[14] are neglected. This is expected for the glass sample we have used, due to its large pore size and open geometry. In addition to that, the homogeneity of the water-glass system is also a fundamental requisite for Eq. (3) to be valid. In particular, in order to make a direct comparison between the two results, the characteristic length scales in the conductivity and self-diffusion experiments should both be larger than the minimum-length scale over which the liquid-sample system can be considered to be homogeneous.

If the conditions just mentioned are met, Eq. (3) gives an exact relation between the two transport properties. However, no information about the quantities σ/σ_0 or D_l/D_l^0 is given except the notion that they are expected to be less than unity, due to the increased tortuosity of the transport path. It has been noted that the electrical conductivity of a variety of samples can be described phenomenologically by[6]

$$\frac{\sigma}{\sigma_0} = \phi^{p'} \left(\frac{V}{V_0} \right)^p . \tag{4}$$

The exponents p and p', which are empirical values, have no rigorous theoretical explanation and usually range between 1.5 and 2 depending on the nature of the porous sample under examination. Earlier experimental observations have revealed that $p \geq p'$, meaning that drying the sample is more effective in increasing the tortuosity than decreasing its porosity.[6] The equation above is commonly known as Archie's law. This phenomengological result, when compared with the theoretical relation given in Eq. (3), provides the following expression for the self-diffusion coefficient:

$$\frac{D_l}{D_l^0} = \phi^{m'} \left(\frac{V}{V_0} \right)^m , \tag{5}$$

where $m = p - 1$ and $m' = p' - 1$.

IV. EXPERIMENT

A. Self-diffusion

Recently, we reported NMR measurements on deionized water in porous silica glasses.[11,13] NMR longitudinal and transverse relaxation experiments revealed single exponential recovery of the proton nuclear magnetization of the water and a linear dependence between the two relaxation times and the amount of water filling the sample. This confirms that, at each step of drying, the liquid-glass system is homogeneous over length scales corresponding to the root-mean-square displacement $x_{\rm rms}$ of a proton due to molecular diffusion during the time of the experiment t, typically between 1 and 100 μs. A pulsed magnetic-field-gradient (PFG) technique[15] was used to investigate the transport properties of the system with varying water content. A first result showed by PFG measurements is that the mean-square displacement was proportional to time in the range $1-10$ μs. This suggests that classical diffusion takes place. Therefore, the length

scale probed by both experiments is defined as $x_{rms}=(6Dt)^{1/2}$. Typically the self-diffusion coefficient D is of the order of 10^{-5} cm^2/s for water, so x_{rms} is expected to be of the order of 10 μm for both relaxation and self-diffusion experiments. Therefore, we can assert that inhomogeneity of the sample is confined to smaller scales, namely comparable to the pore size.

The results of PFG measurements at room temperature are shown in Fig. 1 (from Ref. 11, sample 10:90), where the self-diffusion coefficient is plotted as a function of the filling factor V/V_0. As the amount of water in the sample was reduced, the self-diffusion coefficient exceeded, up to more than three times, the value for bulk water D_l^0. This was attributed to the presence of vapor as a dominant medium for molecular transport at low water content. The solid line in Fig. 1 represents our theoretical prediction involving two-phase (vapor-liquid) diffusion having no adjustable parameters.[11] In the range of V/V_0 covered by our experiments, the number of molecules in the vapor phase is much smaller than the number of molecules in the liquid phase. Therefore, the self- diffusion coefficient can be analytically expressed as[11]

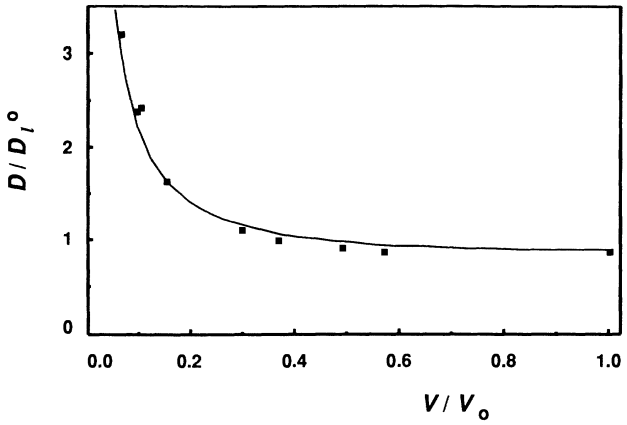

FIG. 1. Measured self-diffusion coefficient D of water in porous sol-gel glass (squares) as a function of the filling factor V/V_0, obtained with the PFG-NMR technique at room temperature (from Ref. 11). The increase of the measured values up to more than three times larger than the self-diffusion of bulk water D_l^0, as the water filling is reduced, is interpreted in terms of a multiphase transport involving vapor as well as liquid water, and fitted (solid line) using Eq. (6).

$$D=\phi^{m'}\left[\left[\frac{V}{V_0}\right]^{m_l}D_l^0+\frac{(V_0/V)(1-V/V_0)^{m_v+1}\rho_v/\rho_l}{(D_v^0)^{-1}[\frac{1}{3}d(1-V/V_0)^{1/2}(8k_BT/\pi M)^{1/2}]^{-1}}\right], \tag{6}$$

where the subscripts l and v refer to the liquid and vapor phases, respectively, ρ is the mass density, D^0 is the bulk self-diffusion coefficient, d is the pore diameter, ϕ is the porosity of the sample, k_B is the Boltzmann constant, T is the temperature, and M is the mass of a water molecule. The exponents m and m' reflect Archie's law as expressed in Eq. (5). The exponent m may differ for the liquid and vapor contributions since the geometry of the two phases may depend on the fact that the liquid is wetting.

For the sample under consideration, the exponents m', m_l, and m_v were calculated as follows. The value $m'=0.70$ was determined by averaging the results of PFG self-diffusion measurements[11] performed on a set of five water-saturated silica-glass samples having the same porosity but different pore sizes. These samples were prepared using a procedure similar to that described in Sec. II but a different relative ratio of colloidal silica to potassium silicate. At the early stages of drying ($0.4<V/V_0<1$), D was found to be nearly independent of the water content. In this interval the entire second term in large square brackets in Eq. (6) is negligible. This suggests that $m_l=0$, a result that we have previously attributed to a picture in which wetting maintains the connectivity of the liquid phase even under unsaturated conditions.[11] However, the results of conductivity experiments which we present next in Sec. IV B are in conflict with this interpretation. By performing a fitting of the experimental data shown in Fig. 1, using m_v as a free parameter, we were able to determine only that it was of the order of unity. Therefore, without further justification m_v was chosen to be equal to m'.

The derivation of Eq. (6) is based on the assumption that a parallel molecular transport process takes place between the liquid and vapor phases and that the interaction between water molecules is not affected by the porous medium. However, the effectiveness of vapor diffusion is reduced by the presence of the Knudsen effect.[16] On the time scale of the experiment, coupling between the two phases is also assumed: each molecule spends a fraction of time in each phase, in proportion to the relative number of molecules in the two phases, a condition indicated as *fast exchange*.

B. Electrical conductivity

The ac conductivity experiment was performed using a four-lead method in order to eliminate the effect of the contact resistance on the measured values. A schematic of the circuit is shown in Fig. 2. The voltage was supplied by a power source providing sinusoidal output with an amplitude up to 5 V and a wide range of frequency. The sample dimensions were 1.03 cm$\times$0.46 cm and the four leads were attached by twisting thin copper wires around the sample at four different locations transverse to the larger dimension. The distance between the two current leads was 0.74 cm and the distance between the two voltage leads (centered with respect to the current leads) was 0.40 cm. The experiment was conducted by first saturating the sample with a 0.01-M concentration of KCl aqueous solution and then letting the water evaporate slowly enough to assure homogeneity in the distribution of the solution in the sample itself at each stage.

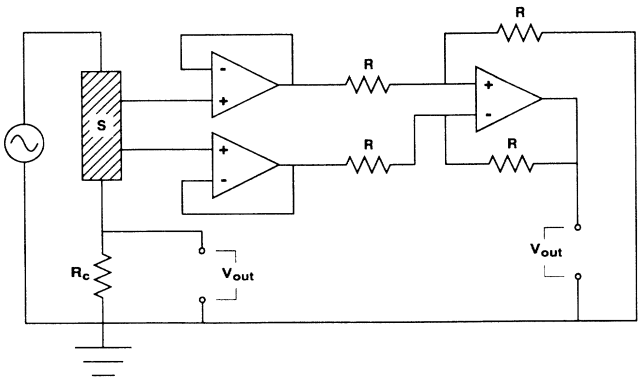

FIG. 2. Schematic of the electronic circuit used for ac conductivity measurements of the sample (S). The value of the resistance (R) was 300 kΩ; the value of the resistance (R_c) was chosen to optimize the signal-to-noise ratio of both output signals (V_{out}) and ranged between 0.3 and 12 kΩ.

During this process the sample was placed on a microbalance and its weight was recorded simultaneously with the resistance measurements. The four leads were connected to the ac circuit using fine copper wires (25 μm in diameter) in order to guarantee an accurate weight reading. The volume V of water was subsequently determined by subtracting the dry weight of the sample from the values collected during drying. The drying procedure is identical to the preparation of unsaturated samples in the self-diffusion measurements. Therefore, we infer that the way the liquid is distributed inside the sample in the two experiments is similar for the same filling conditions.

The resistance of the sample was calculated by comparing the voltage drop across a standard precision resistor R_c in series with the sample with the drop across the voltage leads. The relative phase of the two signals was also measured by detecting the two signals with the two channels of an oscilloscope (Tektronix 2235) set in the X-Y mode, in order to check for the presence of capacitance effects between the leads and in the sample. During the experiment, as the sample resistance increased due to drying, the standard resistor R_c was varied accordingly among a set covering a wide range of values in order to have a comparable signal-to-noise ratio in both channels, and, therefore, to minimize the error in the value of the sample resistance. The impedance of the sample could be calculated by separating resistive and capacitive effects.

It has to be noted that for the purpose of making direct comparison between self-diffusion and conductivity measurements, the resistive component is the only relevant impedance. Therefore, it is preferable to work in a situation in which no phase difference between current and voltage is observed. However, this situation cannot be achieved in dc measurements, since a spatial buildup of charge may occur in that case, with a consequent drastic drop in the electric current. It is convenient to perform ac measurements in the limit of low frequencies. In principle, capacitive impedance may have contributions coming from the geometry of the pores and a frequency dependence study may lead to other interesting information.[17] However, one has to be able to separate such effects from spurious contributions due to contacts between the sample and the electrical wires and to the geometrical dimensions of the sample. Moreover, contributions from the capacitance of the electronic elements of the circuit may also be apparent. In our work, no appreciable frequency dependence and no dephasing of the two output signals were observed between 10 and 2000 Hz, indicating that capacitive effects were negligible. Investigations at a higher frequency were disregarded because of the nonideal frequency response of the electronic components, tested by replacing the sample by standard precision resistors of known impedance. The conductivity was finally derived from the calculated resistance and the known geometry of the sample.

Since the change in liquid filling was achieved by drying the sample, it is clear that the saline concentration was increasing as the water evaporated during the course of the experiment; this was taken into account in the interpretation of the transport properties of the ions. In Fig. 3 we report the results in the form of the ratio σ/σ_0 as a function of the relative water content V/V_0. The experiment was performed at room temperature (24 °C). The derivation of the concentration at each water content is straightforward once we assume that the salt ions are uniformly distributed inside the sample during evaporation. The conductivity of the initial solution was checked experimentally and compared to the value given in the literature adjusted for the temperature of the experiment;[18] the agreement was better than 1%. Subsequent values of the bulk conductivity at different ion concentrations were simply derived from the literature.[18]

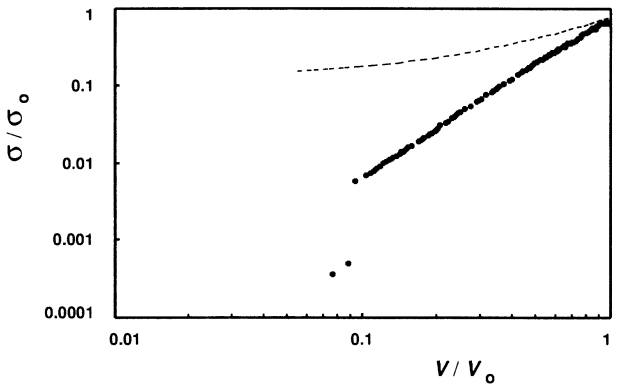

FIG. 3. The conductivity σ of KCl aqueous solution in porous sol-gel glass, normalized to the bulk conductivity σ_0 of the same solution, is plotted as a function of the filling factor. The data can be fitted to a power law, with the exponent 2.05, as expected from Archie's law. The dashed line is the plot of the quantity $(D/D_l^0)\phi V/V_0$, where D is the fitting curve of Fig. 1, as obtained from Eq. (6). According to the Einstein relation, the plotted function should be equal to σ/σ_0, as indicated by Eq. (3). The departure of the dashed line from the experimental results is evidence of the contribution of the vapor phase to self-diffusion, which is effective at all water contents, arbitrarily close to conditions of saturation.

The bilogarithmic plot shown in Fig. 3 suggests that a dependence exists between the normalized conductivity and the filling factor which can be expressed as

$$\frac{\sigma}{\sigma_0} = A \left[\frac{V}{V_0} \right]^p , \tag{7}$$

in agreement with Eq. (4). The best fit to the data is obtained with an exponent $p=2.05$ and a coefficient $A=0.79$. The main source of error for these two values may be attributed to the uncertainty in the measurement of the dry weight and the saturated weight, leading to error in the values of V and V_0 and, therefore, indirectly in the calculated value of σ_0. In both cases, we estimate the relative error to be a few percent. The value of A obtained corresponds to an exponent $p'=1.5$ in Eq. (4). The difference between the two exponents p and p' simply means that the volume accessible to ions in the unsaturated sample is described by a different geometrical structure than in the saturated case: the first situation cannot be viewed as a saturated sample with a reduced effective porosity. The values of p and p' obtained are both consistent with general observations for porous media,[6] as discussed in Sec. III.

The data at low coverage became inaccurate when the internal resistance of the operational amplifiers used was comparable to the total imedance of the sample. This situation arose at low filling when the resistance due to the contacts between sample and electrical wires increased. Just below the value $V/V_0=0.17$, the total current was observed to decrease rapidly as the water content decreased slowly. However, no corresponding change in the trend of the actual measured resistance of the sample was observed down to $V/V_0=0.09$. At this point the resistance of the contacts became so high that reliable measurements were no longer possible. Consequently, the two data points at the lowest water content shown in Fig. 3 cannot be considered to be reliable.

V. DISCUSSION

A first comparison between self-diffusion and electrical conductivity experiments can be made applying Eq. (3) to the experiments under saturation conditions, that is, for $V/V_0=1$. We observe good agreement between the value of $\sigma/\sigma_0 \equiv A=0.79$ and the value $\phi D_l/D_l^0=0.77$ deduced from Ref. 11. Using Eqs. (4) and (5) for $V/V_0=1$, and averaging the results, we find $p'=1.6\pm0.1$. However, when measurements performed under unsaturated conditions are considered, the agreement between the two experiments fails. In fact, in Sec. IV A we inferred an exponent $m_l=0$. This result, when compared with Eq. (5), corresponds to $p=1$ in Eq. (4), in direct contrast with the results of the conductivity experiment where a value of 2.05 was found. We conclude that the self-diffusion coefficient of the solute ions in the conductivity experiments and the self-diffusion coefficient of the water molecules are subject to the same geometrical constraints only for the case of a saturated sample. This disagreement is graphically represented in Fig. 3 where the quantity $(D/D_l^0)(\phi V/V_0)$ is plotted as a dashed line and compared with the measured conductivity, as suggested by Eq. (3). Let us analyze the possible causes of this discrepancy for the unsaturated case.

One possibility is that the length scales probed by the two experiments are different, being essentially the entire distance between the two voltage leads in the conductivity measurements, and a diffusion length of the order of 10 μm in the self-diffusion measurements. In order for these different length scales to cause a different dependence on water filling, we should hypothesize that water molecules are distributed in the sample heterogeneously over length scales intermediate to those of the two experiments. In this case the overall conductivity would result from an average over different parts of the sample, with more weight from regions with smaller water content. However, this is in contrast with our observations of NMR relaxation and self-diffusion measurements from which we inferred homogeneity in the geometrical and transport properties of water over length scales larger than 10 μm, as discussed in Sec. IV A.

Another possibility is that only the solute ions are inhomogeneously distributed but the only reason for this to happen would be an effect of surface charges. Therefore, one should expect less sensitivity to this effect close to saturation when surface charges can be neglected with respect to bulk charges. In principle, this line of argument should exclude all possible contributions from interactions at the surface since, in that case, they should be more and more effective at lower coverages, but negligible at higher.

A third possibility was suggested by Guyer,[19] who used an effective-medium theory[20] and included a particular choice of pore-size distribution, capillary condensation[21] for water in the pore space, and the influence of vapor diffusion. Although this model has qualitative features in agreement with our observations, the predicted transport properties at large coverage are necessarily consistent with Eq. (3), in contrast with our experimental results.

From the above discussion it appears that there is an unsettled discrepancy between the quadratic behavior of the conductivity as a function of filling factor and the independence of the self-diffusion experiments on water content at high values of V/V_0. A valid interpretation of the observed phenomena must consider that the presence of vapor plays a role in self-diffusion of water at all water contents, arbitrarily close to the condition $V/V_0=1$.

In our original model, to account for the dramatic increase in self-diffusion at low water concentrations, we proposed a parallel transport process in two strongly interconnected pore structures, that of the liquid phase and that of the vapor. A more rigorous interpretation should include the feature that, at high water filling, a parallel process does not describe the transport accurately, because the vapor phase is not expected to be interconnected but rather to form isolated domains below the percolation threshold. According to this picture, the tortuosity of a diffusion path through the liquid phase would vary as V/V_0, but a water molecule may not see such a restriction since connectivity between physically separated liquid domains is still assured through the vapor. In other words, it is only an approximation to claim a distinction between transport in the two phases since they are

intermingled. However, details of how the two phases are coupled together are essential to the interpretation of the transport results. For example, an infinitely fast exchange of molecules between liquid and vapor would necessarily lead to a negative slope of the self-diffusion coefficient as a function of water content, even at $V/V_0=1$. Therefore, the observed independence of the self-diffusion coefficient on water filling appears to be a peculiar coincidence, even more so given that the same behavior was observed at a lower temperature[11] when the relative contribution to transport of the two phases changes markedly.

Another way of expressing the transport of fluid in the system may be by picturing a short time-scale fluctuation in size and position of the vapor and liquid domains due to a rapid evaporation-condensation process. This would only contribute to the diffusion of the solvent molecules without involving the solute ions and, therefore, without affecting the conductivity measurements.

We note here that a substantially different picture has emerged in preliminary self-diffusion measurements performed on a different porous glass, to be reported upon elsewhere.[22] In that case the sample was characterized by a lower porosity (0.35), and a much smaller characteristic pore size ($d=3.5$ nm). The self-diffusion coefficient decreases linearly with water content down to one molecular layer. This result is consistent with Eq. (6) where the Knudsen term suppresses any contribution from the vapor and then, surprisingly, $m_l=1.0$.

VI. CONCLUSIONS

Comparisons between the results of self-diffusion of water molecules and the low-frequency ac electrical conductivity of aqueous solutions in porous media help in understanding the mechanisms of transport in random geometries. The choice of the porous glass used in this work was particularly fortunate because of its homogeneity, open-pore structure ($\phi=0.85$), and large pore size (240 nm) allowing exclusion of spurious contributions to the observed results other than pure geometrical effects. Self-diffusion was measured using NMR-PFG techniques and observed to be classical over length scales of the order of 10 μm. Conductivity measurements were made on the same sample containing an aqueous solution of KCl. The study of the two transport properties at partial solvent content confirmed that the connectivity of the liquid decreases regularly as a function of the relative fraction of open-pore volume occupied by the liquid itself. However, the presence of a separate vapor phase affects the self-diffusion process. This feature appears to be present arbitrarily close to liquid saturation, causing the measured self-diffusion coefficient to be independent of the fraction of pore volume occupied by water, provided it exceeds 40%. This is in addition to its dramatic effect on diffusion as filling is reduced below that value, a result discussed earlier by D'Orazio *et al.*[11] There is no successful model for understanding the process by which the vapor phase contributes to diffusion close to saturation. The difficulty seems to be linked to the property that self-diffusion depends on the nature of molecular transfer between the two phases of the liquid-vapor system. It appears that this may be effective in enhancing water transport even under near-saturation conditions in which the vapor phase does not percolate.

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