

Electrical Transport in a Disordered Medium: NMR Measurement of Diffusivity and Electrical Mobility of Ionic Charge Carriers

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Electrical transport in porous media plays an important role in many fields of pure and applied science. The basic microscopic processes of the charge transport have attracted considerable theoretical interest for a long time. However, on a microscopic level there was up to now no experimental access to this problem. In the present paper we demonstrate, by using a suited porous system, that two combined NMR methods can offer such a first experimental access. We apply common PFG NMR methods and the special electrophoretic NMR (ENMR) technique for the measurement of self-diffusion coefficient D^+ and electric mobility u^+ of a cation ($(C_4H_9)_4^+$) in a disordered gel-like medium (Sephadex LH-20) filled with electrolyte solution. We find a, qualitatively expected, observation time-dependence of D^+ , but for the first time such a time-dependence is also observed for u^+ , which means the detection of the phenomenon of “anomalous field assisted diffusion” or “anomalous mobility.” For the measurement of the short-time behavior of the mobility a new pulse sequence is presented. The time-dependent mobilities were measured at three different external electrical fields E . From the long-time behavior of D^+ , u^+ , and D_{H_2O} three independent values for the tortuosity T of the porous system could be derived. We find equality of the tortuosities $T(D^+)$ and $T(u^+)$, which represents a first experimental proof of the validity of the Einstein relation ($D^+ \sim u^+$) in a disordered medium. Finally, we discuss advantages of the possible use of “anomalous field assisted diffusion” over the commonly used “anomalous diffusion” in morphology studies by dynamic imaging in porous media. © 1998 Academic Press

Key Words: electrical transport; pores; electric mobility; ENMR; dynamic imaging.

INTRODUCTION

Porous media are of high importance in many different areas of research ranging from applied physics and chemistry over geology, materials science to life sciences. Thus, there is a strong interest in transport and diffusion phenomena in three-dimensional fluid-filled porous media (1, 2). Moreover, the transport of electric current through a pore space filled with electrolyte solutions is of particular interest due to its importance in many electrochemical processes in different fields and

since electrical conductivity measurements are often applied to routine studies in the characterization of porous media (3, 4).

In the last years a rapidly increasing number of publications showed that NMR techniques proved to be very useful in the study of transport properties and the morphology of porous media (5, 6). One of the most interesting NMR tools in this respect is the measurement of the observation time-dependence of self-diffusion coefficients $D(t)$ of solvent molecules in saturated porous systems by applying pulsed magnetic field gradient (PFG) techniques (7). These measurements, for example, deliver at long times t , when the diffusing molecules of the liquid have walked a long distance compared with a typical correlation length, a steady-state diffusion coefficient D_{eff} . This quantity D_{eff} is connected with the geometrical restrictions of transport in the porous medium and has been i.a. related to the tortuosity T of the porous system by $T = D_0/D_{\text{eff}}$, where D_0 is the self-diffusion coefficient in the bulk liquid (8).

If the pore space is filled with electrolyte solution as it is, e.g., with sedimentary rocks filled with brine, the ions carry the electric current in those systems and thus the ionic transport properties are of high importance. For this reason we thought that the study of the time-dependence of ionic self-diffusion coefficient in a porous medium would be worthwhile. However, there is a further fascinating aspect, leading to the main aim of the present paper, namely to make an attempt to observe directly by NMR ions migrating along an electric field within a porous medium. The basis of this attempt is the fact that since 1982 we have successfully developed PFG techniques for the measurement of ionic mobilities in multi-component systems in our laboratory (9–11) and applied them to normal (non-confined) electrolyte solutions. This technique, today called “electrophoretic NMR” (ENMR) (12), should also offer very promising and tempting new possibilities for basic investigations of charge transport in disordered material on a microscopic level. For this reason we have recently begun with a systematic study of the applicability of ENMR to porous systems and in this paper we present our first results. In particular we will investigate if there is also an observation time-depen-

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dence of the ionic mobility u^\pm in porous material and the comparison between the effective diffusion and effective mobility might give first experimental hints if the Einstein relation, $D^\pm \sim u^\pm$, is also valid in confined electrolyte solutions. The validity of this relation is assumed in many theoretical considerations and as basis of experimental methods for the investigation of porous systems (4), but could up to now not be directly checked by an experiment.

MATERIALS AND METHODS

As the porous medium, where we want to perform the first demonstration of the applicability of our new NMR approach for the study of electrical transport in disorder media, we have chosen a well-known material in gel permeation chromatography (gel filtration), namely Sephadex LH-20 (Pharmacia Biotech, Uppsala, Sweden), using water (D_2O) as the pore-filling solvent. Sephadex is a spherical bead-formed dextran gel. According to the supplier the wet particle size range is 30 to 160 μm . Hydroxypropyl groups are attached by ether linkages to glucose units of the dextran chain. Within the beads the dextran chains are cross-linked to give a three-dimensional polysaccharide network. From size-exclusion data for Sephadex LH-20 an apparent pore size diameter within the beads of about 30 nm can be estimated. Consequently, there is inside the beads an inner volume with small apparent mesopores, determined by the density of the chain-network, and there is an outer volume, enclosed by the beads, with macropores in the range of 10 to 80 μm , determined by the size and kind of packing of the gel spheres. Thus, Sephadex represents a disordered system with a broad pore size distribution, as well in the 10-nm range as in the 10- μm range, similar as many natural and technical porous systems.

The aqueous Sephadex medium presented us with advantages for our experiments. We made the experience that in this system the NMR linewidths are not as strongly broadened by magnetic susceptibility effects as in many other heterogeneous systems. This fact favors the observation of the NMR signal of the ions of interest. Also for the reason of detection efficiency we applied ^1H ENMR and thus we used a hydrogen containing ion, namely the tetrabutylammonium cation in an aqueous 0.07 molal (C_4H_9) $_4\text{NCl}$ solution as the conducting pore fluid.

The PFG self-diffusion and mobility measurement have been performed with a homemade 300-MHz probe containing the magnetic field gradient coils and the electrophoresis cell as described elsewhere (10, 11, 13). The latter was directly cooled by a hydrogen-free liquid, namely Galden D20 (Ausimont, Milan). The experiments were carried out at a temperature of 25°C.

In porous media, due to geometrical restrictions “anomalous diffusion” occurs, resulting in an observation time-dependent self-diffusion coefficient $D(t)$ (see, e.g., (6, 7, 14, 15)). This time-dependence has been measured in the common way by the variation of the gradient pulse distance Δ in PFG stimulated

echo experiments (PFGSTE) (see Fig. 1). For the elimination of possible background gradient influences (see, e.g., (16, 17)) we reduced the pulse distance of the first two $\pi/2$ -pulses of the PFGSTE sequence to the shortest possible values, which were then in the range of 1 to 3 ms. For the measurement of the short-time behavior we applied the “13-interval pulse sequence” introduced by Cotts *et al.* (16).

The ionic drift velocity measurements in the presence of an external electric field E by ENMR are also based on PFGSTE experiments (9, 10, 12). Here in addition, electric field pulses are part of the pulse sequence in the experiment. Both, the electric field E and the magnetic field gradient g are applied in the z -direction. In contrast to the incoherent motions by diffusion, which produce a damping of the spin-echo, the coherent drift motions produce a phase shift $\Delta\varphi$ of the spin-echo signal. This phase shift is given by (10, 12)

$$\Delta\varphi = \gamma g v \delta \Delta, \quad [1]$$

where g is the strength of the magnetic field gradient, δ is the duration of the gradient pulses, and v is the velocity of the spin carrying species. In our experiments we measured in this way the ionic drift velocity v^+ in the z -direction and by determining the electric field E , acting over the sample volume inside the NMR receiver coil, we could determine the ionic mobility u^+ from

$$u^+ = v^+/E. \quad [2]$$

In the present work we performed the first *time-dependent* ENMR electric mobility measurements. When measuring the drift velocity at long times ($t > 50$ ms) we simply applied an electric field pulse of duration Δ' between the second and the third $\pi/2$ -pulse of the PFGSTE sequence (see Fig. 1a). Thus the effective time for the mobility measurement is Δ' and we measured $\Delta\varphi$ as a function of δ with constant g , Δ , and Δ' . From the slope of $\Delta\varphi(\delta)$ the drift velocity v^+ for a given $t = \Delta'$ was then determined according to Eq. [1]. From different experiments with different Δ' values the time-dependence of v^+ and thus $u^+(t)$ was obtained.

For short-time electric mobility measurements we developed and tested a new ENMR pulse sequence as shown in Fig. 1b. This pulse sequence is based on the fact that in ENMR PFG experiments the ionic motion under observation can be controlled by the experimentalist by switching on and off the electric field E or by varying the field strength of E and thus the electric current I (10, 12). We point out the fact that the diffusive translational motion in time-dependent diffusion measurements cannot at all be switched on and off and its variation is only possible by a temperature change or by change in mass and size of the diffusing particles (7). Thus, the possibility of switching on and off the drift motion offers an easy access to short-time velocity measurements by simply

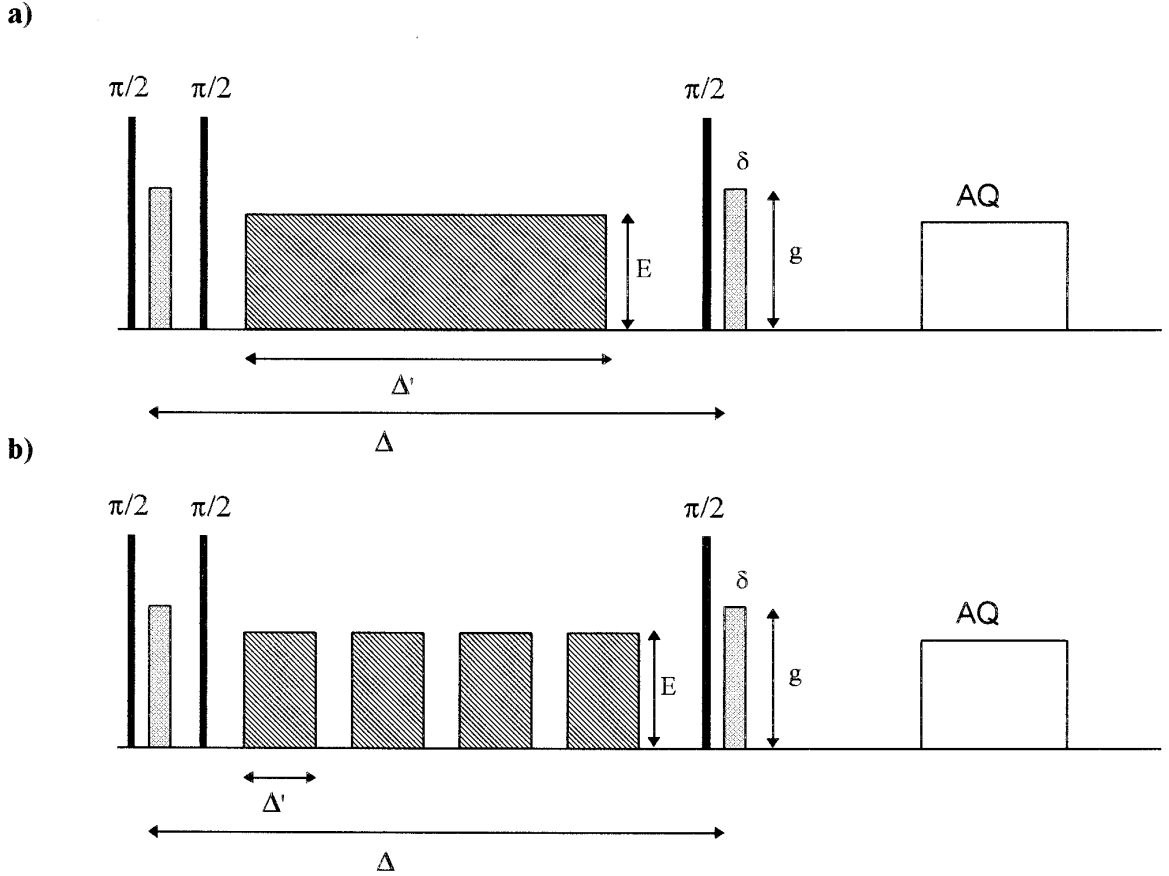


FIG. 1. (a) ENMR pulsed field gradient stimulated echo experiment (PFGSTE) with three $\pi/2$ RF pulses, two magnetic field pulses of strength g and duration δ , and an electric field pulse with strength E and duration Δ' . AQ represents the signal acquisition time. (b) The new ENMR pulse sequence for short-time mobility measurements with n (here four) short electric field pulses each with strength E and duration Δ' . All other details as in Fig. 1a.

applying short electric field pulses (small Δ' values) while keeping Δ constant. As shown in Fig. 1b we use in our pulse sequence for short time velocity measurements a series of n electric field pulses.

There are three outstanding advantages of this sequence for time-dependent mobility measurements. First, it is technically much easier to generate short electric field pulses in the electrophoresis cell than to create magnetic field gradient pulses separated by a short distance. Second, when investigating the short-time behavior the necessary small Δ' values result in only small signal phase shifts $\Delta\varphi$, which are often difficult to measure. However, in the given sequence (Fig. 1b) an accumulative effect produces a total phase shift of $n \cdot \Delta\varphi = n \cdot (\gamma g v \delta \Delta')$, which can be detected much easier. The third advantage comes from the fact that during the application of the magnetic field gradient pulses the drift motion is switched off, avoiding the otherwise necessary corrections for the finite gradient pulse duration δ .

We would like to mention here that we have checked experimentally the efficiency of this new ENMR pulse sequence. In the non-confined electrolyte solution, we therefore measured with one long current pulse of duration Δ'_1 , finding exactly the

same phase shift $\Delta\varphi_1$ as with n short current pulses, having together the same duration $n \cdot \Delta'_s = \Delta'_1$, that is, $n \cdot \Delta\varphi_s = \Delta\varphi_1$. In a confined electrolyte solution, we measured in the short-time range with a series of n short current pulses of duration Δ'_s n times the phase shift of one current pulse with Δ'_s . But keeping the equality $n \cdot \Delta'_s = \Delta'_1$ we then found

$$g v \delta n \Delta'_s = n \Delta\varphi_s > \Delta\varphi_1 = \gamma g v \delta \Delta'_1.$$

This inequality is a consequence of an observation time-dependent drift velocity (see below).

Finally we emphasize that our sequence with multiple electric field pulses (Fig. 1b) is also generally suited for the study of transient effects connected with switching-on of currents in complex systems as, e.g., in electrolyte solutions containing charged long-chain molecules.

RESULTS AND DISCUSSION

A. Time-Dependent Self-Diffusion Coefficients

In Fig. 2 we show our results for the time-dependent self-diffusion coefficients $D^+(t)$ of the tetrabutylammonium cation

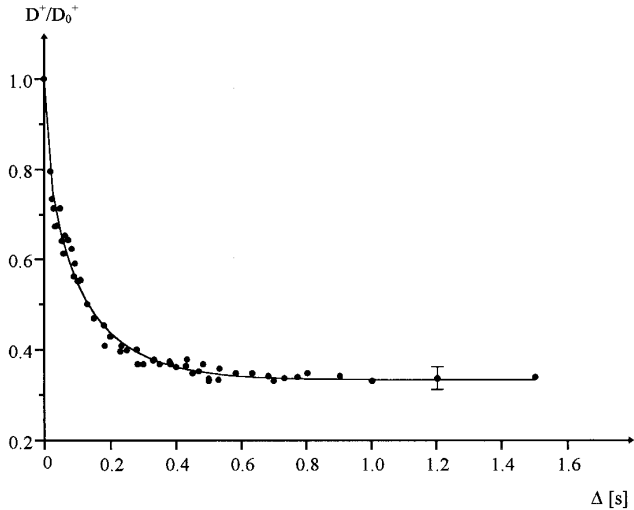


FIG. 2. The observation time Δ dependence of the relative ionic self-diffusion coefficient D^+/D_0^+ of the $(\text{C}_4\text{H}_9)_4^+$ cation in aqueous solution confined in the porous medium Sephadex LH-20 at 25°C. $D_0^+ = 0.49 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

in D_2O as pore fluid of Sephadex LH-20. $D^+(t)$ is given relative to $D_0^+ = (0.49 \pm 0.04) \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, the ionic self-diffusion coefficient in the bulk electrolyte solution. We recognize the typical time dependence as it has been found for pure liquids in many previous investigations (see, e.g., Refs. (6–8, 18)). In the literature several theoretical approaches for the behavior of $D(t)/D_0$ as a function of time can be found (15, 18–20), where the short-time behavior is, e.g., given by (20)

$$D(t)/D_0 = 1 - A_0(D_0 t)^{1/2} + B_0 D_0 t + O(D_0 t)^{3/2} \quad [3]$$

and where A_0 and B_0 are connected with S/V_p , the surface to volume ratio of the space occupied by the fluid.

If the medium is interconnected, for long times and with $\sqrt{Dt} \gg \xi$, where ξ is the correlation length of the porous medium, the diffusion coefficient approaches a constant value

$$D_{\text{eff}} = D(t \rightarrow \infty) = \frac{1}{T} \cdot D_0 \quad [4a]$$

as mentioned above. We have to point out that in the system under investigation in the present work, the experimental accessible observation times are limited to comparatively short values and therefore a completely time-dependent D_{eff} should not be observed. On the other hand, as can be seen from Fig. 2, $D(t)/D_0$ reaches already after about one second an almost constant value. As shown by other authors (8, 15, 18, 21), T can be obtained from a fit to the theoretical approach for the long-time behavior of $D(t)/D_0$,

$$D(t)/D_0 = 1/T + \beta_1/t - \beta_2/t^{3/2}, \quad [4b]$$

where β_1 and β_2 are constants (21).

The tortuosity, T , obtained from a fit of the ionic self-diffusion coefficients in Fig. 2 to Eq. [4b], is $T(D^+) = 2.87 \pm 0.15$. Unfortunately, this value cannot be compared with reference data, since in the literature no tortuosities could be found for the Sephadex-water system.

To our knowledge the given tortuosity value is the very first which has been derived via an ionic diffusion coefficient. Therefore we asked the question if there is an agreement with the tortuosity derived via the commonly used solvent (water) diffusion coefficient in the same system. Under the assumption that only geometric restrictions are influencing the value of the steady-state diffusion coefficients D_{eff} , we should obtain in the same system equal tortuosities from the diffusion coefficients of different particles of similar size. Thus we performed analogous time-dependent diffusion measurements on the solvent molecules (H_2O) in Sephadex LH 20 yielding a tortuosity $T(D_{\text{H}_2\text{O}}) = 1.89 \pm 0.04$, which is markedly lower than the above given $T(D^+)$. Thus we have to conclude that at the salt concentration of 0.07 molal at least the ratio D_0^+/D^+ is influenced by non-geometric effects, which are most probably ion-wall or ion-network interactions. If one assumes that $T(D_{\text{H}_2\text{O}})$ is the pure geometrical tortuosity, the ratio $T(D_{\text{H}_2\text{O}})/T(D^+) = p_{\text{free}}$ might yield information about the time of adherence of ions at the pore wall or at the chains of the network. In a simple two-site model, where one site corresponds to a bound ion and the other site to a free ion, $p_{\text{free}} = 1 - t_b/t$ would represent the probability of the ion to be in the free state (t_b/t is the fraction of time for an ion in the bound state). In the present case we obtain $p_{\text{free}} = 1.89/2.87 = 0.66$ for the tetrabutylammonium cation at the given salt concentration. (We expect that with increasing salt concentration p_{free} will also increase and finally approach the value of 1 at high salt concentrations. This expected behavior shall be checked in a further work from our laboratory by measurements at higher salt concentrations.)

B. Time-Dependent Ionic Mobility Measurements

In Fig. 3 we present the first results of ionic mobilities u^+ measured in a disordered system by ENMR. The mobilities of the tetrabutylammonium ion have been measured at three different external electric fields ($E = 960, 1770, \text{ and } 4000 \text{ Vm}^{-1}$). We recognize that we observe qualitatively the same observation time-dependence as we found for the ionic self-diffusion. Thus we detect here for the first time the phenomenon of “anomalous field assisted diffusion” or “anomalous mobility” in a porous medium. This finding is not surprising since we know that “anomalous diffusion” and thus also “anomalous mobility” is caused by confining geometries which are probed by the displacement of the particle under observation. Thus, the mean square displacement $\langle z^2(t) \rangle$ and the mean displacement $\langle z(t) \rangle$, respectively, play a

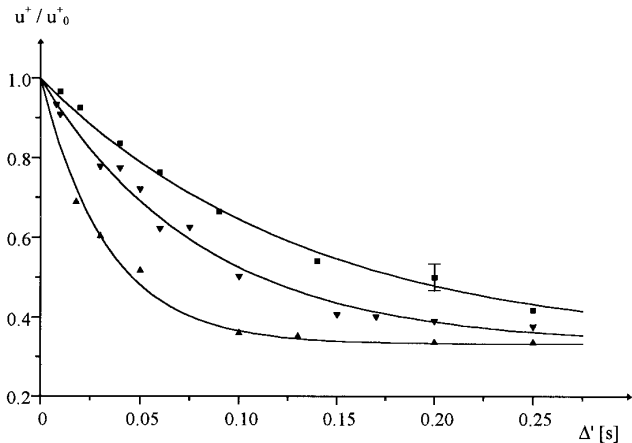


FIG. 3. Observation time Δ' dependence of the relative ionic mobility u^+/u_0^+ of $(C_4H_9)_4^+$ in aqueous solution confined in the porous medium Sephadex LH-20. $T = 25^\circ\text{C}$. The measurements were performed at three different external electric fields $E = 960 \text{ Vm}^{-1}$ (■); 1770 Vm^{-1} (▼); 4000 Vm^{-1} (▲). The data are given relative to $u_0^+ = 1.22 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, the ionic mobility in the non-confined bulk solution.

central role. In the case of diffusion, with a given D , $\langle z^2(t) \rangle$ is only a function of time, namely,

$$\langle z^2(t) \rangle \propto 2 D t^\kappa \quad [5]$$

($\kappa = 1$ for normal diffusion and $\kappa < 1$ for anomalous diffusion). On the other hand the mean displacement of the migrating ion in the electric field is determined by the product of the drift velocity v in the direction of the magnetic field gradient and the time t :

$$\langle z(t) \rangle = vt = uEt. \quad [6]$$

Thus we expect that in this case the mean displacement $\langle z(t) \rangle$ finally depends on the product Et .

We can check the validity of this expectation by plotting the mobility data in Fig. 3 versus Et , as it is shown in Fig. 4, displaying an impressive agreement of the experimental data obtained at different electric fields and in accordance with the theoretical expectation. Thus, the result that all experimental data points fall on one curve in Fig. 4 proves that in the porous medium under investigation the displacement of the ion along the macroscopic electric field direction z is a linear function of E as in the non-confined electrolyte solution. The fact that the drift velocity in the disordered system varies in proportion to E already indicates that the Einstein relation is not violated. At first glance we recognize from Fig. 4 that u^+/u_0^+ approaches at high $E\Delta'$ -values a limiting value which is almost exactly the same as that for D^+/D_0^+ in Fig. 2.

In an analogous way as in the case of self-diffusion we can derive from the data in Fig. 4 the tortuosity, here as $T(u^+) = u_0^+/u_{\text{eff}}^+$, where u_0^+ and u_{eff}^+ are cationic mobilities in the bulk

and in the porous system for $Et \rightarrow \infty$, respectively. The evaluation of the results in Fig. 4 delivers $T(u^+) = 2.82 \pm 0.25$, which means, within the experimental error limits, a perfect agreement of $T(D^+)$ and $T(u^+)$. From our finding $D_0^+/D_{\text{eff}}^+ = u_0^+/u_{\text{eff}}^+$ and from the validity of $D_0^+ \sim u_0^+$ in the bulk solution, it follows that $D_{\text{eff}}^+ \sim u_{\text{eff}}^+$ is valid in our gel-like porous medium. This means that we could, to our knowledge for the first time, experimentally prove that in a disordered system the Einstein relation is still valid as it is, e.g., assumed in many theoretical approaches and in computer simulations of electrical transport in porous systems (4, 22).

CONCLUSIONS

In conclusion we have demonstrated that in a porous medium, saturated with electrolyte solution, the diffusivity and the electric mobility of ionic charge carries can be studied by PFG NMR and ENMR, respectively. Consequently, ENMR in principle offers a novel experimental access to microscopic investigations of charge transport and electrical conductivity in porous media as, e.g., in salt-water-saturated rocks (23) or in other disordered continuum systems as ceramics or catalytic beads. It allows the experimental check of theoretical models and their inherent assumptions (22, 24, 25). Furthermore our results indicate that those ENMR techniques might also be suited for the investigation of ion transport in different kinds of membranes. In particular, we found that there is an analogous, typical observation time-dependence for diffusion and electric mobility of the ion, which obviously will allow the use of the drift velocity (electric mobility) for probing the microgeometry of porous media by a kind of “dynamic imaging” experiment (7).

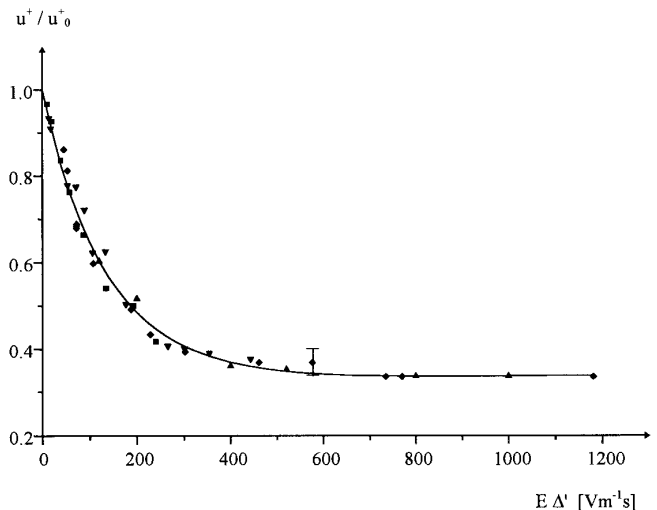


FIG. 4. Relative ionic mobilities u^+/u_0^+ , obtained from the data in Fig. 3, plotted vs the quantity $E\Delta'$, the product of observation time Δ' and the external electric field E . All other details correspond to Fig. 3. (A number of additional data points (◆) have been obtained with electric fields in the range $1000\text{--}3500 \text{ Vm}^{-1}$, however, not at those E values as given in Fig. 3.)

Moreover, we emphasize that field assisted diffusion experiments have interesting advantages. The first can be immediately recognized from inspection of Figs. 2–4. Due to the experimental difficulties with the generation of magnetic gradient pulses with short distance we have at observation times shorter than about 30 ms in Fig. 2 less or even no data points, whereas in Fig. 3 in this range and in the range of low Et values in Fig. 4 enough data points could be obtained. Thus it is easier to observe the short-time (small displacement) behavior by drift velocity measurements using short electric potential gradient pulses. This aspect is in particular of importance when the short-time behavior must be accurately analyzed and when measurements are extended to systems with smaller pore diameters, where the time-dependence occurs at markedly shorter times. There is a further interesting point with respect to the observation of the short-time behavior. Since ion migration in the electric field can be switched off during the application of the magnetic gradient pulses, problems due to finite gradient pulse widths, as in diffusion measurements (18), should not occur here.

The second advantage is given by the fact that by variation of the external electric field, the probe drift velocity can be more easily adapted to the geometry of the porous system of interest than the probe self-diffusion. Finally, we emphasize that NMR velocity measurements are in heterogeneous systems less affected by magnetic background field gradients than PFG diffusion measurements, since there enter no cross-terms between the background gradient and the applied external gradients as it is in PFG diffusion experiments (16).

We saw that the long-time behavior of D^+ and u^+ yielding the quantities D_{eff}^+ and u_{eff}^+ might also be of considerable interest. From a comparison of the tortuosities $T(D_{\text{liquid}})$ and $T(D^{\pm})$, obtained via the self-diffusion of an inert liquid and of an ion at different ion concentrations, respectively, information about adherence times of ions at the pore surface might be obtained, allowing the detection of specific interactions as ion-wall or ion-network interactions. By determination of both $T(D^{\pm})$ and $T(u^{\pm})$ the validity of the Einstein relation can experimentally be checked. We could show that in the meso- and macropores-containing system used in the present work, the Einstein relation is still valid; however, it remains whether this is also true for other systems as, e.g., microporous media. Monte Carlo simulations (26, 27) indicate that indeed deviations from Einstein's law could occur, depending on the disorder of the medium and the applied electric field strength.

Generally, we can state that ENMR in fluid-filled porous systems might also be an interesting tool if applied to micropores. For example, there is considerable interest in the mobilities of ions in aqueous solutions in narrow channels (28). Work to extend our ENMR studies to media with smaller pores or channels is currently in progress.

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