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Water dynamics of LiCl solutions confined in nanopores

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Abstract

The self-diffusion of water in aqueous solutions of lithium chloride in bulk solutions and in these solutions confined to porous glass monoliths with bimodal pore structure has been studied by PFG NMR. The concentration dependent data for the bulk solutions are analyzed by the description of Sevrugin et al. [1], which yields information about the water dynamics within the ion's hydration shell. For an application to confined diffusion, this description is extended by introducing a tortuosity factor. Whereas in the larger macropores no influence on the water dynamics within the hydration shell is detected, in the smaller mesopores, a significant increase of the mobility of the hydrating water molecules is observed.

Keywords

PFG NMR, self-diffusion coefficient, nanoporous glasses, tortuosity, hydration dynamics

Introduction

Based on a fast exchange of molecules within and around an ion's solvation shell, Sevrugin et al. proposed a general description of the concentration dependent self-diffusion coefficient of the solute molecules within an electrolytic solution [1]:

$$D(c) = D_0 \ \exp\left(h \frac{M_w}{M_s} Kc\right). \qquad (1)$$

Here D_0 denotes the self-diffusion coefficient of the pure solvent molecules, h the solvation number, M_w and M_s the molar masses of the solvent and the dissolved salt, respectively, and c the gravimetric concentration of the solution. The parameter K is given by

$$K \equiv \frac{\tau_0}{\tau_1} - \frac{{l_0}^2}{{l_1}^2}, \qquad (2)$$

where τ_0 and τ_1 represent the averages of the characteristic correlation times and l_0 and l_1 the characteristic correlation lengths of the elementary diffusion jumps of the pure solvent molecules and the molecules "trapped" in the ion's solvation shell, respectively [1].

For aqueous electrolytes, this description is valid as far as the water molecules exist in two separate states, namely, located within and beyond the hydration shell. Thus, by assuming a hydration number of $h_{\mathrm{Li}^+} = 4$ for Li^+ [2] and of $h_{\mathrm{Cl}^-} = 6$ [3] for Cl^-, in an aqueous solution of lithium chloride ($LiCl_{(aq)}$), this description is feasible for concentrations smaller than about 0.25 g/g.

The presence of a confinement is further influencing the dynamics within the fluid. Additionally to the sheer presence of the solid matrix (volume exclusion and tortuosity effect), also the nature of the inner surface and thus, the interaction between the pore fluid and the surface determines the dynamic behavior. The tortuosity factor τ represents the increase of the transport pathway in the porous host system and can be determined, e. g., by NMR self-diffusion studies via [4]

$$\tau = \frac{D_0}{D_\mathrm{p}} \tag{3}$$

Here D_p and D_0 denote the self-diffusion coefficients of the solution confined to the pore space and in the bulk, respectively.

Combining the Eqs. (1) and (3) yields a prediction for the concentration dependence of the solvent self-diffusion coefficient in electrolyte solutions confined to a porous network:

$$D_\mathrm{p}(c) = \frac{1}{\tau} D_0 \, \exp\left(h \frac{M_w}{M_s} Kc\right) \tag{4}$$

It is the purpose of this paper to investigate the water dynamics within the ion's hydration shell by application of Eq. (4). Especially, we are interested in the dynamics of the liquid electrolytes in nanoporous systems. Therefore, we investigated water self-diffusion in $LiCl_{(aq)}$ confined to nanoporous glasses by nondestructive ^{1}H pulsed field gradient (PFG) NMR.

Methods and Materials

The PFG NMR self-diffusion measurements were carried out by means of the home-build NMR spectrometer FEGRIS NT operating at a proton resonance frequency of 125 MHz [5]. In PFG NMR, the spin echo signal attenuation Ψ is observed as a function of the so-called b-value. It obeys the relation

$$\Psi(b) = \sum_n q_n \exp(-bD_n) \tag{5}$$

with q_n denoting the amount of molecules having the self-diffusion coefficient D_n. The NMR signal was generated by using the primary spin echo pulse sequence [6], where for rectangular shaped gradients $b = \gamma^2 \delta^2 G^2 (\Delta - \delta/3)$, with γ denoting the gyromagnetic ratio. In the experiments, the magnetic field gradient width δ was fixed to 500 µs, the observation time Δ was 10 ms and the magnetic field gradient amplitude G was incremented up to 37 $\mathrm{T\,m^{-1}}$. All measurements were performed at a temperature of (298±1) K.

A sodium borosilicate initial glass with the composition 70 wt.-% SiO_2, 23 wt.-% B_2O_3 and 7 wt.-% Na_2O was used for the generation of the porous glass monoliths. The general preparation procedure was described previously [7-9]. The selected preparation conditions resulted in porous glass monoliths with a spatially separated, bimodal pore system of mesopores (diameter: 6 nm) in the center of the monolith and macropores (diameter: 100 nm) in the outer shell of the monolith, whereas the surface properties of all pores are mainly determined by hydrophilic silanol groups.

The $LiCl_{(aq)}$ solutions were prepared by weight by dissolving anhydrous lithium chloride (ACS grade, Sigma-Aldrich®) in distilled water. The investigated concentrations range from pure water up to 0.25 g of lithium chloride dissolved per g of water. Filling the accessible pores of the monoliths with the solutions occurred by capillary action under applying a reduced pressure, where the lower part of the monoliths was immersed into the solution. For the PFG NMR measurements, the bulk solutions as well as the solutions soaked into the porous glass monoliths were inserted in NMR glassware tubes, which were sealed immediately after preparation by melting in order to prevent an evaporation of the solvent.

Results and Discussion

Figure 1 (a) shows ^{1}H PFG NMR spin echo attenuation curves for water in $\mathrm{LiCl_{(aq)}}$ at $c = 0.249\ \mathrm{g/g}$ in bulk and soaked into the porous glass monoliths. The observed signal attenuations were approximated best by Eq. (5) via mono-exponential decay ($n = 1$) for the bulk data and bi-exponential decay ($n = 2$) for the porous glass monoliths. The bi-exponential decay is caused by the two, spatially separated pore size regimes of the glass monoliths. The lower values of the self-diffusion coefficient were assigned to the small (6 nm) pores since, compared to the large (100 nm) pores, their diffusion resistance is expected to be higher. Thus, the two extracted self-diffusion coefficients represent the overall mobility of the water in the two separated fractions of pore sizes.

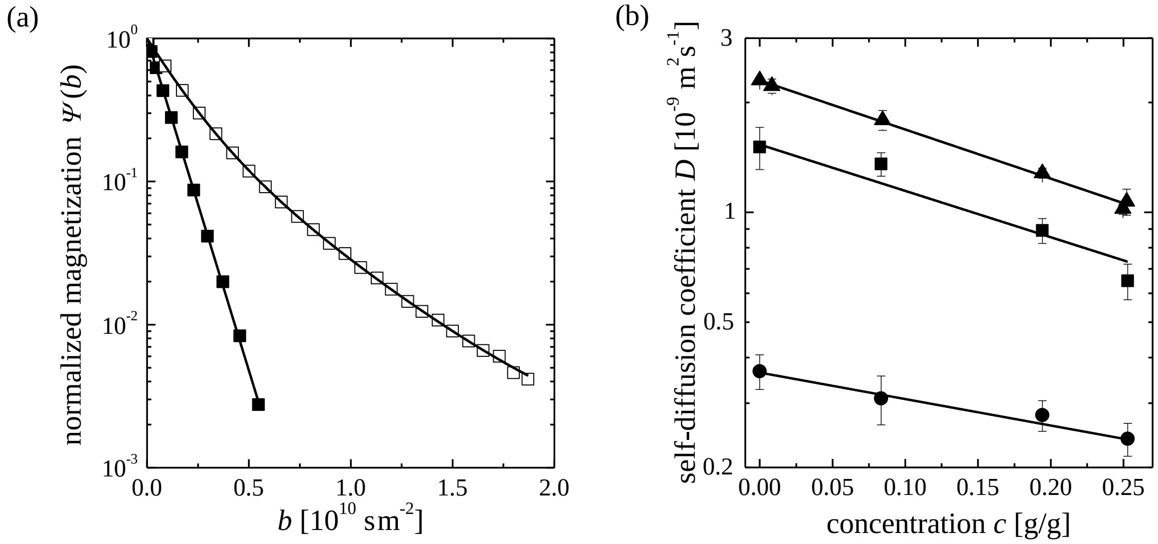

Figure 1. (a): Example for observed PFG NMR spin echo attenuations. Experimental data are shown for the bulk $\mathrm{LiCl_{(aq)}}$ solution (filled squares) at $c = 0.249\ \mathrm{g/g}$ and the same solution confined to the porous glass (open squares). The solid lines were obtained by fitting with Eq. (5). (b): Water self-diffusion as function of concentration for the bulk solutions (triangles) and the solutions confined in the pores of the glass monoliths (squares: 100 nm, circles: 6 nm). The lines represent the concentration dependences obtained with the model (Eqs. (1) and (4)) and the parameters described in the text. For more details we refer the reader to ref. [9].

The concentration dependence of the self-diffusion coefficients is plotted in Fig. 1 (b) for the bulk and the confined solutions, respectively. The bulk data were analyzed by using Eq. (1), where $D_0 = 2.299 \cdot 10^{-9}\ \mathrm{m^2s^{-1}}$ [6], $h = h_{\mathrm{Li^+}} + h_{\mathrm{Cl^-}} = 10$ and K served as adjustable parameter. The experimental data are approximated best by $K = -0.73 \pm 0.02$. The confined solutions were analyzed by our modification, Eq. (4) with K and the tortuosity factor τ as adjustable parameters. The results are $\tau = 1.5 \pm 0.1$ and $K = -0.69 \pm 0.14$ for the 100 nm pores and $\tau = 6.3 \pm 0.2$ and $K = -0.39 \pm 0.03$ for the 6 nm pores, respectively.

In Sevrugin's description, a negative K indicates that the ratio of ${l_1}^2$ and τ_1 is smaller than the ratio of ${l_0}^2$ and τ_0. Using the Einstein relation [10] to translate these ratios into a corresponding self-diffusion coefficient, $D_i = {l_i}^2/(6\tau_i)$, one ends up with the reasonable result that the self-diffusion of the water molecules within the hydration shell is slower compared to the self-diffusion in pure water. Thus, due to the decreased water mobility in the ion's hydration shell, the overall mobility of the water and its apparent self-diffusion coefficient in $\mathrm{LiCl_{(aq)}}$ is reduced.

A comparison of the K-value determined for the bulk solutions with that obtained for the 100 nm pores yields no significant influence of the confinement. Thus, we conclude that the water mobility within the hydration shell is not significantly altered, if the solution is confined by these large pores. The reduction of the self-diffusion coefficients is only induced by the steric hindrance in the porous network, which is represented by the tortuosity factor.

The smaller magnitude of the K-value, determined for the 6 nm pores, indicates an unexpected increase of the water mobility within the hydration shell. If our modification of Sevrugin's description, Eq. (4), is applicable for such small pores, the confinement significantly enhances the hydration shell dynamics. For more details of the data interpretation, we refer the reader to ref. [9].

Our experimental finding is in agreement with recent results of molecular dynamics simulations for water confined in hydrophilic, silanol group covered pores (diameter 3 nm) of Lerbret et al. [11]. These water molecules undergo interfacial interaction with the silanol groups, which causes a significant distortion of their hydrogen bond network. We believe that in the present case such a breakdown of the hydrogen network in the 6 nm pores facilitates the exchange of the hydrating water molecules and thus leads to the observed enhancement of the water mobility within the hydration shell.

Conclusions

The description of Sevrugin et al. [1] for concentration dependent solvent self-diffusion coefficients in electrolyte solutions has been modified by introducing a tortuosity factor. A molecular level interpretation of the fit parameters was used to analyze the water self-diffusion coefficients observed by ^{1}H PFG NMR in $LiCl_{(aq)}$ solutions confined to porous glasses. The obtained tortuosity factors consider the prolonged pathway of the water molecules through the porous network and take reasonable values for well interconnected pores of 6 nm and 100 nm size. The K-values, which describe the relation between the correlation time and length of diffusion for molecules in pure water and within an ion's hydration shell, exhibit no significant difference between the bulk solutions and these solutions confined to the 100 nm pores. However, in the 6 nm pores the mobility of the water molecules "trapped" in the ion's hydration shell appears to be increased. A distortion of the hydrogen network caused by the silanol groups at the pore surface represents most likely the reason for this increased water mobility.

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