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Communication: Slow proton-charge diffusion in nanoconfined water

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We investigate proton-charge mobility in nanoscopic water droplets with tuneable size. We find that the diffusion of confined proton charges causes a dielectric relaxation process with a maximum-loss frequency determined by the diffusion constant. In volumes less than ~5 nm in diameter, proton-charge diffusion slows down significantly with decreasing size; for diameters <1 nm, the diffusion constant is about 100 times smaller than in bulk water. The low mobility probably results from the more rigid hydrogen-bond network of nanoconfined water, since proton-charge mobility in water relies on collective hydrogen-bond rearrangements. Published by AIP Publishing.

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water from that of reverse micelles prepared with an aqueous HCl solution. In Figures 2(a) and 2(b) we compare this proton response with that of protons in bulk water. Whereas the proton response in bulk water is purely imaginary and given by $ik/\omega$ (with $\omega$ the frequency and $k$ the DC conductivity), the protons confined in the nanodroplets exhibit the signature of a dielectric relaxation process, which occurs for all investigated droplet sizes (Fig. 3). This dielectric relaxation arises because the migration of proton charges in response to the applied electric field comes to a halt as they reach the wall of the nanodroplet; the amount of dissipated energy is maximal when the applied electric field changes sign at the moment this halting occurs (an interfacial polarization effect). The maximum-loss frequency of the relaxation process is thus determined by the size of the nanodroplet and the proton-charge diffusion constant. The amplitude of the dielectric response associated with the proton diffusion increases with the confinement size because in larger nanodroplets a larger polarization has been built up at the moment the proton charges reach the confines. The diffusion of the counter ions should cause a similar relaxation at much lower frequencies (due to the much lower diffusion constant).

To confirm that the observed relaxation process is caused by the confinement of the protons, we measure the dielectric response of protons confined in long interconnected tubular reverse micelles, prepared with the same surfactant and $[\text{H}_2\text{O}]/[\text{surfactant}]$ ratio, but using $n$-hexane instead of cyclohexane as the apolar phase. Using hexane as the apolar phase results in less efficient solvation of the hydrophobic surfactant tails, so that the interfacial surfactant layer becomes less curved toward water, causing the spherical reverse micelles to transform into interconnected tubular structures. In these interconnected tubular reverse micelles, the proton charges do not come to a halt, and thus no relaxation process is observed (Fig. 2(c)). The absence of the relaxation process in tubular micelles (which have the same surfactant and $w_0$ as the spherical micelles) also excludes the possibility that the relaxation process is due to surface water. The observed dielectric response of the confined proton charges can be well described by a Cole-Cole relaxation process:

$$\Delta\varepsilon_H^i(\omega) = \frac{\Delta\varepsilon_H^0}{1 - (i\omega\tau_R)^{1-\alpha}},$$

where $\omega$ is the angular frequency, and $\Delta\varepsilon_H^0$, $\tau_R$, and $\alpha$ are the size-dependent amplitude, relaxation time, and broadening parameter, respectively. From least-squares fits, we determine the relaxation times for all investigated droplet sizes, see Figure 3. The relaxation time (the inverse of the maximum-loss frequency) is determined by the size of the nanodroplet and the diffusion constant. Their relation can be derived from the field-induced time-dependent spatial distribution of diffusing ions confined in a spherical volume, for which we obtain an analytic expression (see supplementary material). As an example, we
FIG. 3. Imaginary (a) and real (b) parts of the dielectric difference spectra \( \Delta \varepsilon_H^+ = \varepsilon_{HCl(aq)} - \varepsilon_{H_2O} \) showing the response of protons confined in spherical reverse micelles with different water-pool diameters. Upon increasing the reverse-micelle size, both the intensity and the center frequency increase. The black dots represent the water-background corrected response of 1M HCl solution (vertically scaled for better comparison). The curves are least-squares fits of Eq. (1) to the data.

show in Figure 4, the calculated time dependent proton distribution upon switching on a DC electric field at \( t = 0 \) (using a proton diffusion constant equal to the bulk value). The resulting time-dependent polarization can be Fourier transformed to obtain the dielectric response function.\(^{41}\) From this analysis (see supplementary material), we find that the diffusing ions exhibit a Debye-type dielectric response with a relaxation time

\[
\tau_R = \frac{(d/2)^2}{4.33D},
\]

where \( d \) is the diameter of the water sphere and \( D \) the diffusion constant. Using Eq. (2) and the observed water-pool diameters and relaxation times, we determine the proton diffusion constant \( D_{H^+} \) in the nanodroplets. It should be noted that the experimentally observed proton spectra are Cole-Cole (broadened Debye) modes, whereas the theory predicts a normal Debye response (\( \alpha = 0 \)). This broadening of the Debye mode is caused by the polydispersity of the reverse-micelle size (~10%) and by the inhomogeneity of the water structure inside the reverse micelles that gives rise to a distribution of diffusion constants, an effect that has been characterized recently using molecular dynamics simulations of water confined in surfactant phases.\(^{42}\) The \( D_{H^+} \) obtained from our data is averaged over the micelle size distribution and over potential spatial inhomogeneities of the diffusion constant. We find that for small sizes (up to about 3 nm diameter), the amplitude of the dielectric response grows approximately quadratically with the nanopool size as predicted by our theoretical analysis (see supplementary material). For larger sizes, the amplitude grows less than quadratically, probably due to local-field effects\(^{36}\) (the water volume fraction in the samples with large nanopool size is much larger, see supplementary material). An important advantage of our experiment is that the diffusing proton charges are observed directly and in a non-perturbative manner (the strength of the applied oscillating electric field is negligible compared to the local electric fields of molecular partial charges), and no probe molecules are required. In the remainder, we focus on the effective diffusion constant obtained by analyzing our data using Eqs. (1) and (2). A more detailed quantitative interpretation of our experiments would require state-of-the-art ab initio molecular-dynamics simulations, and we hope our results will stimulate work in this direction.

We find that the proton-charge diffusion constant depends strongly on the size of the nanoscopic water volume (see Fig. 5, where we have also indicated the bulk diffusion constant). For the smallest investigated water-pool diameter (1.2 nm), the diffusion constant is about 100 times smaller than in bulk water. For large droplet sizes, the proton-charge diffusion constant

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However, while the diffusion constant decreases by a factor and the diffusion constant of the proton. We indeed find reorientation rate decreases in a similar manner with decreas-

In view of the above-discussed relation between proton-
charge diffusion and water dynamics, it is interesting to inv-
vestigate whether a correlation exists between the average charge diffusion and water dynamics, it is interesting to

The precise confinement volume below which such collective dynamics, and thus proton-charge diffusion, slows down may be system dependent, and may be slightly larger in sys-
tems in which (unlike reverse micelles) more than one water molecule contributes to the observed uniform slowing down of the proton-charge diffusion. However, it cannot be the main cause since even for the smallest nanopools (where proton-charge diffusion virtually comes to a standstill), the fraction of surface water is comparatively small. For instance, we found previously that in the $d = 2.1$ nm nanopools the surface-water fraction is slightly below 50%, whereas the proton-charge diffusion is about 20 times slower than in bulk water (Figure 5). It therefore seems that a slowing down of collective water dynamics upon nanoconfinement is the main cause of the slow proton-charge diffusion in nanoconfined water. The precise confinement volume below which such collective dynamics, and thus proton-charge diffusion, slows down may be system dependent, and may be slightly larger in systems in which (unlike reverse micelles) more than one water monolayer is immobilized by surface binding.

In the core of the nanodroplet, we would observe different relaxation modes, corre-
sponding to proton diffusion in the interfacial layers and proton diffusion in the core of the nanodroplet. Instead, we observe for each nanodroplet size a single relaxation mode, of which the frequency of the maximum response gradually changes with the size of the nanodroplet. Hence, the decreased proton diffusion constant appears to be a quite uniform property of the water nanodroplet. This uniform behavior presents an interesting contrast to the reorientation and hydrogen-bond dynamics of water molecules in water nanodroplets: previous work has shown evidence that in reverse micelles only a single layer of water molecules is immobilized by binding to the surfactant head groups, and that the slowing down of the hydrogen-bond dynamics is caused mostly by surface-induced restructuring of the water hydrogen-bond network. However, proton-charge diffusion is known to involve the concerted motion of many water molecules, and hence is intimately connected with the hydrogen-bond dynamics of a large volume of water molecules. In nanoconfined water, this concerted motion will probably also involve water molecules in the interfacial layers. The slowing down of these interfacial water molecules contributes to the observed uniform slowing down of the proton-charge diffusion. However, it cannot be the main cause since even for the smallest nanopools (where proton-charge diffusion virtually comes to a standstill), the fraction of surface water is comparatively small. For instance, we found previously that in the $d = 2.1$ nm nanopools the surface-water fraction is slightly below 50%, whereas the proton-charge diffusion is about 20 times slower than in bulk water (Figure 5). It therefore seems that a slowing down of collective water dynamics upon nanoconfinement is the main cause of the slow proton-charge diffusion in nanoconfined water. The precise confinement volume below which such collective dynamics, and thus proton-charge diffusion, slows down may be system dependent, and may be slightly larger in systems in which (unlike reverse micelles) more than one water monolayer is immobilized by surface binding.

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49 We tentatively assign the weak feature around 0.1 GHz in the alkali solutions to the diffusion of the alkali ions.