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Slow proton-charge diffusion in nanoconfined water

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I. EXPERIMENTAL

A. Sample preparation

The sample composition is determined the molar water surfactant ratio

\[ w_0 = \frac{[\text{H}_2\text{O}]}{[\text{surfactant}]} \]

and the surfactant mass fraction

\[ c_s = \frac{m_{\text{surfactant}}}{m_{\text{oil}} + m_{\text{surfactant}}} \tag{1} \]

where \( m_{\text{surfactant}} \) and \( m_{\text{oil}} \) are the masses of surfactant and oil, respectively. Reverse micellar samples were prepared by first dissolving the required amount of Igepal CO-520 (pentaoxyethylene nonylphenylether, average molar mass 441) in the oil phase; cyclohexane (>99.9% HPLC grade) for spherical reverse micelles and \( n \)-hexane (>99.9% HPLC grade) for tubular reverse micelles. Subsequently the required amount of water (Milli-Q 18.2 MΩ·cm) or electrolyte solution [1M aqueous HCl (Fluka 1 M HCl (1N)), LiCl, NaCl or KCl] was added. To prepare the 1M salt solutions LiCl (BioXtra, >99.0%), NaCl (TraceSELECT, >99.999%) and KCl (BioXtra, >99.0%) were dissolved in the aqueous phase prior to the reverse-micelle preparation. All samples were shaken and sonicated. For the spherical reverse micelles we prepared samples with \( w_0 = 0, 3, 5, 8 \) at \( c_s = 0.33 \), and with \( w_0 = 10, 15 \) at \( c_s = 0.28 \). A larger \( c_s \) (and hence larger micelle concentration) was used for the smaller reverse micelles in order to obtain a sufficiently strong dielectric response. Tubular reverse micelles where prepared using \( w_0 = 5 \) and \( c_s = 0.37 \). For the samples with the largest micelles, full equilibration took several hours, whereas the smallest reverse micelles equilibrated within minutes. After equilibration, all samples were optically clear and stable.

B. Small-angle x-ray scattering

SAXS measurements were performed at the high brilliance laboratory Gallium Anode Low Angle X-ray Instrument GALAXI at the Jülich research center (Germany) equipped with a BRUKER AXS MetalJet x-ray source. The reverse micellar samples were filled in quartz capillaries with an inner diameter of 1.5 mm and measured at room temperature (T=298 K). The data were recorded with a 1 M Pilatus detector (DECTRIS) at a sample to detector distance of 1.7 m and a wavelength of 0.134 nm covering a range of momentum transfer of \( 0.06 \leq q \leq 4 \text{nm}^{-1} \) (\( q = 4\pi\text{sin}(\theta)/\lambda \) is the modulus of the scattering vector, \( 2\theta \) is the scattering angle and \( \lambda \) is the wavelength). The collected
data were radially averaged and normalized to the intensity of the transmitted beam. Solvent scattering was subtracted prior to data analysis. All samples were made at the same surfactant in oil concentrations $c_s$ as used for the dielectric experiments. The SAXS data for spherical reverse micelles were fitted by a model function based on Vrij’s analytical solution for a multi-component system of hard spheres.\textsuperscript{1–3} Additions of salts, e.g. 1M HCl or LiCl, does not lead to significant changes in the structure of the reverse micelles. In order to analyze the tubular reverse micellar system it was necessary to measure a full concentration series at $w_0 = 5$ ($c_s = 0.14 — 0.56$). In this way structural information could be retrieved at low $c_s$ for isolated long cylindrical reverse micelles analyzed using the Kholodenko model for long semi-flexible worm-like micelles.\textsuperscript{4} For the interconnected cylindrical networks at high $c_s$ the Teubner-Strey Model was employed to fit the microemulsion peak occurring that is typical for bicontinuous microemulsion or sponge phases.\textsuperscript{5} The data for the full series published earlier\textsuperscript{6} Here, we show for $c_s = 0.37$ that employing 1M HCL or LiCl as aqueous phase does not introduce structural changes.

C. GHz dielectric relaxation spectroscopy

We performed dielectric relaxation spectroscopic (DRS) measurements of reverse micelles in the frequency range between 100 MHz to 30 GHz with a vector network analyzer (VNA, Rhode-Schwartz model ZVA67). With this system we perform reflectometry measurements using two different home-built sample cells, thus directly obtaining the complex scattering parameters as a function of frequency.

At low frequencies (100 MHz to 2 GHz) we used a cell based on the design of Göttman et al.\textsuperscript{7} In this cell the outer coaxial electrode extends several cm from the cable/cell plane, thereby enclosing the liquid sample in the form of a cylindrical column, whereas the inner electrode sticks into the sample as a pin over a distance of 1.8 mm. In the frequency range of 1 to 30 GHz a coaxial cut-off disc cell was used where both coaxial electrodes are terminated at the sample interface. This cell was based on the design of Blackham et al.\textsuperscript{8,9} A phase-stable coaxial cable (Rhode-Schwartz, ZV-Z96) was connected to the measurement port of the VNA and was calibrated using the accompanying calibration kit (ZV-Z218) employing matched, open and short standards. Further calibration upon connection of the respective sample cells was performed by measuring the scattering parameters for air and pure water (Milli-Q, 18.2 MΩ cm). For the low-frequency pin-cell a 4M NaCl solution was further used to shortcut the cell, while conductive silver paint
(Pelco, Ted Pella Inc.) was used for short-cutting the cut-off disc cell. A three-term error model\textsuperscript{10} was applied to each frequency point, moving the calibration plane from the end of the coaxial cable to the probe/sample interface. From the corrected parameters the complex permittivities of the liquid samples could be directly calculated.\textsuperscript{7,8} All DRS experiments were carried out at $22 \pm 5$°C.

II. MODEL FOR THE DIELECTRIC RESPONSE OF IONS DIFFUSING IN A SPHERE

The dielectric response of the reverse micelles containing electrolytes can be calculated by solving the driven-diffusion equation for charges in a sphere.

A. Time-dependent distribution

The protons are confined in a sphere with radius $R$. First we calculate the response if at $t = 0$ we switch on a DC electric field with strength $E_0$ in the positive $z$-direction. The driven diffusion equation describing the time-dependent analytical number density of charge carriers $n(r,t)$ is

$$\frac{\partial n}{\partial t} = D \nabla^2 n - v \frac{\partial n}{\partial z},$$

(2)

with $D$ the proton diffusion constant and $v$ the drift velocity, which is given by $v = E_0 e D / kT$ with $e$ the proton charge, $k$ the Boltzmann constant, and $T$ the temperature.\textsuperscript{11} Using spherical coordinates, the initial distribution is $n(r,\theta,t=0) = n_0$, and the boundary condition is that at $r = R$ the total flow in the outward radial direction should be zero at all times:

$$(\vec{J}_{\text{diffusion}} + \vec{J}_{\text{drift}}) \cdot \vec{e}_r = -D \frac{\partial n}{\partial r} + nv\cos\theta = 0.$$  

(3)

Note that the flow caused by the field-induced drift (second term) is directed in the $z$-direction, so its component in the outward radial direction is $nv\cos\theta$. The steady-state solution of (2) is a Boltzmann distribution

$$n(r,\theta,\infty) \propto e^{\frac{vz}{D}} = e^{vr\cos\theta/D},$$

(4)

as can be verified by substitution. For physically relevant confinement lengths $R$, we have $vR/D \ll 1$ (typically on the order of $10^{-5}$), so (4) differs only slightly from a uniform distribution, and can be very well approximated by a first-order expansion:

$$n(r,\theta,\infty) \approx n_0 + n_0 vr \cos\theta/D.$$  

(5)
Since the change in the distribution due to the electric field is so small, eq. 2 can be solved in a perturbative manner. Defining the instantaneous deviation $f$ from the steady-state distribution through

$$n(r, \theta, t) = n(r, \theta, \infty) + f(r, \theta, t)$$

we have $f(r, \theta, 0) = -n_0v_r \cos \theta / D$ and $f(r, \theta, \infty) = 0$. The vanishing of $f$ happens sufficiently fast that the changes in the distribution due to the drift term can be neglected. We can therefore determine the time dependence of $f$ from

$$\frac{\partial f}{\partial t} = D \nabla^2 f$$

with

$$f(r, \theta, 0) = -n_0v_r \cos \theta / D$$

and the boundary condition

$$D \frac{\partial f}{\partial r} = 0,$$

in which the drift term has again been neglected. This much simpler problem can be solved using separation of variables, and we obtain a solution of the form

$$f(r, \theta, t) = \sum_{n,i} C_{ni} j_n(a_{ni} r / R) P_n(\cos \theta) e^{-Da_{ni}^2 t / R^2}$$

where $j_n$ is a spherical Bessel function of the first kind, and where the $a_{ni}$ values follow from the boundary condition (8), $a_{ni}$ being the $i$th positive root of

$$j'_n(a) = 0.$$ 

The coefficients $C_{ni}$ are determined by the initial distribution through

$$C_{ni} = \frac{\int_0^R \int_0^\pi f(r, \theta, 0) j_n(a_{ni} r) P_n(\cos \theta) r^2 \sin \theta d\theta dr}{\int_0^R \int_0^\pi j_n(a_{ni} r)^2 P_n(\cos \theta)^2 r^2 \sin \theta d\theta dr}$$

$$= -\delta_{n1} \left( \frac{n_0vR}{D} \right) c_i$$

with

$$c_i = \frac{\int_0^1 j_1(a_{1i}x) x^3 dx}{\int_0^1 j_1(a_{1i}x)^2 x^2 dx}.$$ 

The final solution is thus

$$f(r, \theta, t) = -\frac{n_0vR \cos \theta}{D} \sum_i c_i j_1(a_{1i} r / R) e^{-Da_{1i}^2 t / R^2}.$$
The first 5 values of $a_{1i}$ and $c_i$ are listed in table S1. Figure S1 shows the concentration change $n(r, \theta, t) - n_0$ for protons dissolved in a water sphere with a diameter of 4 nm, for a series of times $t$ after switching on the electric field. It is interesting to note that the concentration changes start at the boundary.

**B. Dielectric response**

To calculate the dielectric response we determine the time-dependent induced dipole moment of the sphere, which is given by

$$ p(t) = e \int_0^R \int_0^\pi \int_0^{2\pi} [n(r, \theta, t) - n_0] zr^2 \sin \theta d\phi d\theta dr $$

$$ = \frac{4\pi n_0 e^2 E R^5}{3kT} \left( \frac{1}{2} - \sum_i p_i e^{-Da_{1i}^2 t/R^2} \right), \quad (13) $$

and where

$$ p_i = c_i \int_0^1 j_1(a_{11}x) x^3 dx. $$

The first five values of $p_i$ are listed in Table S1. Inspection of these values shows that $p(t)$ can be approximated to within 1\% by the first term of the summation:

$$ p(t) \approx \frac{4\pi n_0 e^2 E R^5}{15kT} \left( 1 - e^{-Da_{11}^2 t/R^2} \right). \quad (14) $$

The dielectric response is thus a Debye relaxation with a relaxation time

$$ \tau_R = R^2/a_{11}^2 D \approx R^2/4.33D. \quad (15) $$

For a sphere of 4 nm diameter, we have $\tau_R \approx 100$ ps (the time scale of the equilibration of the charge distribution in Fig. S1). Dividing eq. 13 by the volume $V = \frac{4}{3} \pi R^3$, we obtain the polarization

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_{1i}$</th>
<th>$c_i$</th>
<th>$p_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.081575977</td>
<td>1.96542</td>
<td>0.197851</td>
</tr>
<tr>
<td>2</td>
<td>5.940369990</td>
<td>-0.35748</td>
<td>0.001702</td>
</tr>
<tr>
<td>3</td>
<td>9.205840142</td>
<td>0.222566</td>
<td>0.000285</td>
</tr>
<tr>
<td>4</td>
<td>12.404445021</td>
<td>-0.16337</td>
<td>$8.56 \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>15.579236410</td>
<td>0.129447</td>
<td>$3.42 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
FIG. S1. Dielectric relaxation of protons in a sphere: change in the concentration of protons in water ($D = 9.3 \times 10^{-9} \, \text{m}^2\text{s}^{-1}$) confined in a 4 nm diameter sphere after switching on an electric field in the $z$ direction at $t = 0$. Cross section through the center of the sphere, calculated using the first 10 terms of eq. 12. Red denotes $n(r,\theta,t) - n_0 > 0$, blue denotes $n(r,\theta,t) - n_0 < 0$. The color scale has been normalized at each time point $t$.

Density $P(t) = p(t)/V$. By definition, $P(t) = \varepsilon_0 \int_{-\infty}^{t} dt' \chi(t-t')E(t')$, and comparing with eq. 13 we find

$$\chi_R(t) = \frac{n_0 e^2 R^2}{5 \varepsilon_0 kT} e^{-t/\tau}.$$

(16)

The corresponding dielectric function is found by Fourier transformation and using definitions 3.3.1, 3.3.2 and 3.3.5 of Ref. 11, and is given by

$$\varepsilon_R(\omega) = 1 + \chi_R(\omega) = 1 + \frac{n_0 e^2 R^2}{5 \varepsilon_0 kT} \frac{1}{1 - i\omega \tau},$$

(17)

where the dependence on the radius of the sphere has been indicated explicitly.
III. ADDITIONAL RESULTS

FIG. S2. (a) Small angle x-ray scattering curves (scattering intensity $I(q)$ versus the modulus of momentum transfer vector $q$ from spherical reverse micelles for different $w_0$ ($w_0$ of 2.5, 5, and 8 at $c_s = 0.333$ and $w_0$ of 10 and 15 at $c_s = 0.282$) obtained from the aqueous phase—Igepal—cyclohexane system on a double logarithmic scale. Successive scattering curves are displaced upwards by one logarithmic unit for better visualization. Reverse micelles containing water are displayed as filled symbols and those containing 1M HCl as open symbols. The solid lines present fits to the water data. The shape of the curves is typical for spherical scatterers at concentrations high enough to clearly visualize the structure factor peak. The scattering data were fitted with a multi-component model for hard spheres and the refined values are given in the Table below. (b) SAXS curves from the tubular system aqueous phase—Igepal—hexane for $w_0 = 5$ at $c_s = 0.37$ on a double logarithmic scale. Filled circles present reverse micelles containing water, open circles 1M HCl and open squares 1M LiCl.
TABLE S2. Structure parameters for spherical reverse micelles in the water—Igepal—cyclohexane system obtained from the refinement of the SAXS scattering curves using the multi-component model for hard spheres at different $w_0$ and RT. The spherical reverse micelles are characterized by the droplet radius $r_0$, polydispersity parameter $\sigma_0$ of the log-normal size distribution and droplet concentration $c_0$. The droplet volume that is seen by the x-rays corresponds to the ethylene oxide shell built up by the hydrophilic surfactant moiety and the interior water pool. The hydrophobic tail stays invisible since the electron densities of the nonylphenyl and cyclohexane are similar. For all droplet sizes a constant surface to surface distance $D_0$ is found from the hard sphere structure factor, where $D_0/2 = 0.91(1)\text{ nm}$ corresponds to the shell thickness built up by the surfactant tails.

<table>
<thead>
<tr>
<th>$w_0$</th>
<th>2.5</th>
<th>5</th>
<th>8</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_s$</td>
<td>0.333</td>
<td>0.333</td>
<td>0.333</td>
<td>0.282</td>
<td>0.282</td>
</tr>
<tr>
<td>vol fraction</td>
<td>0.300</td>
<td>0.3184</td>
<td>0.337</td>
<td>0.300</td>
<td>0.328</td>
</tr>
<tr>
<td>$c_0 (10^{-3}\text{ nm}^{-3})$</td>
<td>2.641(1)</td>
<td>1.743(1)</td>
<td>1.235(1)</td>
<td>0.725(1)</td>
<td>0.422(1)</td>
</tr>
<tr>
<td>$r_0 (\text{nm})$</td>
<td>1.93(1)</td>
<td>2.50(1)</td>
<td>2.97(1)</td>
<td>3.53(1)</td>
<td>4.50(1)</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>0.198(2)</td>
<td>0.166(2)</td>
<td>0.168(2)</td>
<td>0.148(8)</td>
<td>0.160(8)</td>
</tr>
</tbody>
</table>

FIG. S3. Imaginary (a) and real (b) parts of the dielectric difference spectra $\Delta\varepsilon = \varepsilon_{ionic} - \varepsilon_{H_2O}$ of $w_0=5$ for tubular reverse micelles for 1M HCl, LiCl, NaCl and KCl.
FIG. S4. Imaginary (a) and real (b) parts of the dielectric response of \( w_0 = 5 \) spherical reverse micelles prepared with neat water and 1M HCl, LiCl, NaCl and KCl, respectively.

FIG. S5. Imaginary (a) and real (b) parts of the dielectric response of \( w_0 = 15 \) spherical reverse micelles prepared with neat water and 1M HCl, LiCl, NaCl and KCl, respectively.
FIG. S6. The average reorientation rate $<k_{H_2O}> = \tau_{\text{surface}}^{-1} \cdot (1 - S) + \tau_{\text{core}}^{-1} \cdot S$ versus reverse-micelle radius extracted from DRS measurement of reverse micelles containing neat water. Data from Ref. 6.
REFERENCES

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13The functions $j_n(a_{ni}x)$ with $a_{ni}$ the $n$th root of $j_n'(a) = 0$ are orthogonal in the sense that $\int_0^1 x^2 j_n(a_{ni}x) j_n(a_{nj}x) = 0$, as can be derived from eq. 37 on p. 493 of Ref. 14.