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Tuning molecular dynamics by hydration and confinement: antiplasticizing effect of water in hydrated prilocaine nanoclusters (Supplementary Material)

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DSC Thermal protocol for 1 nm samples

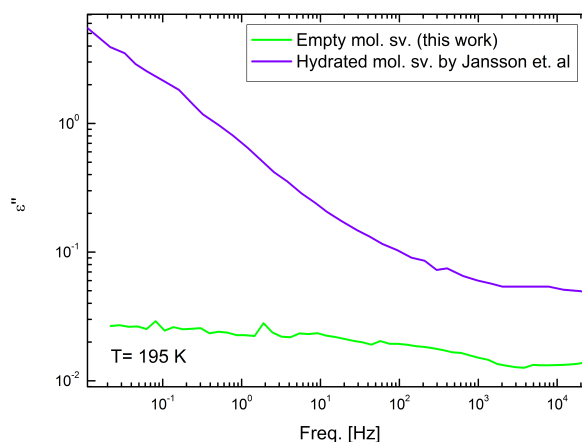
All thermal protocols used included an annealing temperature, in order to have a higher overshoot in T_g and make the transition more visible. Since the T_g samples confined in 1 nm molecular sieves is significantly lower than that of bulk and 0.5 nm confined samples, a different annealing temperature was chosen on the former case. The main difference between the protocol used for bulk and 0.5 nm samples, with that used for 1 nm samples is that on the latter case annealing (steps 5 - 6) was done at 203.15 K, while on bulk and 0.5 nm confinement it was done at 215.5 K. The DSC protocol used for the samples confined in 1 nm molecular sieves is hereby stated.

1. Equilibrate at 313.15 K
2. Isothermal for 5 min
3. Ramp 8 K/min to 193.15 K
4. Isothermal for 1 min
5. Ramp 8 K/min to 203.15 K
6. Isothermal for 60 min
7. Ramp 8 K/min to 193.15 K
8. Isothermal for 1 min
9. Ramp 8 K/min to 423.15 K

Comparison of dielectric relaxations in dried and hydrated 0.5 nm molecular sieves

In order to make sure that the relaxations detected in the empty 0.5 nm molecular sieves did not arise from humidity confined in

the pores, we compare our data with that reported by Jansson et al.¹. These authors studied the dynamics of water under the same confinement using Broadband Dielectric Spectroscopy. Supplementary Figure 1 shows the dielectric loss spectrum measured at 195 K on the hydrated molecular sieves data from Jansson et al., violet trace, and the empty (dried) molecular sieves of the same pore diameter (0.5 nm) analyzed in the current work.



Supplementary Figure 1 Dielectric loss at 195 K in molecular sieves of 0.5 nm pore size. Violet trace: water confined in molecular sieves (data extracted from reference¹). Green trace: Empty (dried) molecular sieves used in the current work.

It may be observed that the presence of water increases significantly the conductivity contribution, visible as an increase of loss signal at low frequency. At the same time, a broad peak was identified in Ref. 1 centered at about 10² Hz at 195 K. It is clear from the data that neither of these processes triggered by water can be observed in our data.

Supplementary Figure 2 shows the Arrhenius plot of the relaxation times τ in the 0.5 nm molecular sieves. Whereas green markers correspond to the Cole-Cole functions used in this work for empty molecular sieves, violet ones indicate the three water-related relaxation processes reported in the hydrated molecular

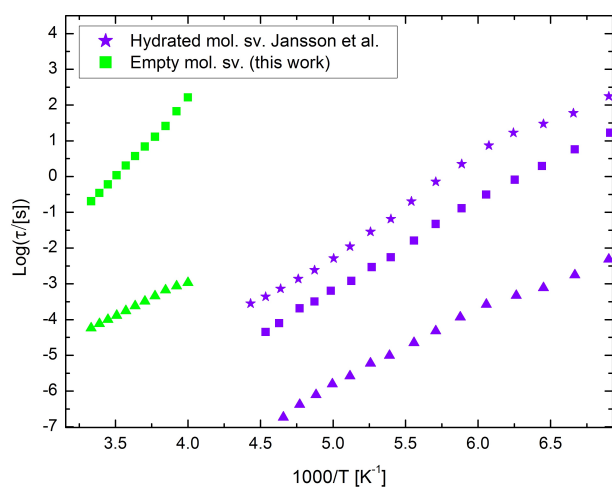
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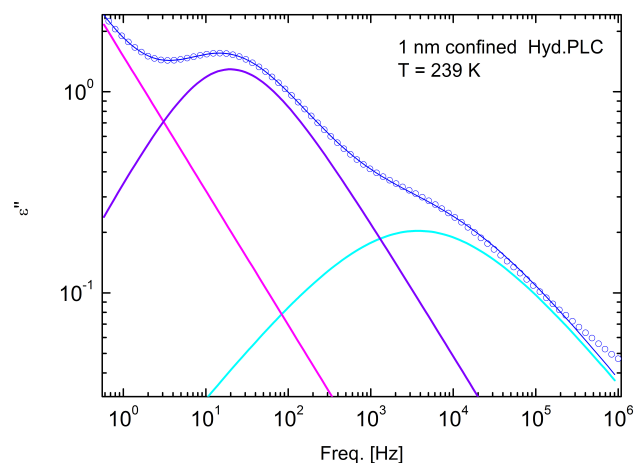


Supplementary Figure 2 Arrhenius plot of the relaxation times τ of the fitting functions. Green markers correspond to the Cole-Cole functions used in this work for empty molecular sieves, as described in the main manuscript. Violet markers portray the relaxation times of the three processes obtained for water confined in such pores by Jansson et al.¹.

sieves (Ref.¹). It is clear from the plot that water confined inside the pores of the molecular sieves shows relaxation times that are quite different from our current observations. Only the longest relaxation times of the molecular sieves indicated by the green triangles could maybe coincide with an extrapolation of the relaxation times indicated by violet stars at higher temperatures. However, the dielectric signal of the dried molecular sieves of the present work is about 15 times smaller than that of Jansson et al. Hence our fastest signal (green triangles) might correspond to a tiny fraction of pores (less than 7%) with water trapped inside, while the large majority of pores are empty. This relaxation is too slow to correspond to a molecular dynamics of the water molecules, and must be ascribed instead to a space-charge effect associated with charge carriers associated with or present in water, which accumulate at the pore-water interface.

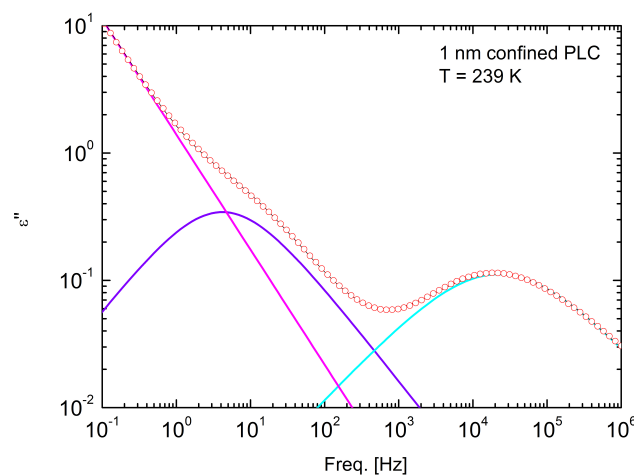
Fit functions employed for 1 nm pore size MS

The loss spectra of PLC and hydrated PLC under 1 nm confinement were fitted as the sum of a HN function, one Cole-Cole function and dc conductivity contribution. Supplementary Figure 3 shows the experimental loss spectrum (empty markers) of hydrated PLC under 1 nm confinement at 239 K, together with the fit as well as all three spectral contributions.



Supplementary Figure 3 Data (empty blue circles) and fit (full blue line) of the dielectric loss spectra of hydrated PLC confined in molecular sieves of 1 nm pore size obtained at 239 K. The violet trace portrays the Cole-Cole function used to fit the data, while the light blue and pink traces show the HN and conductivity contributions respectively.

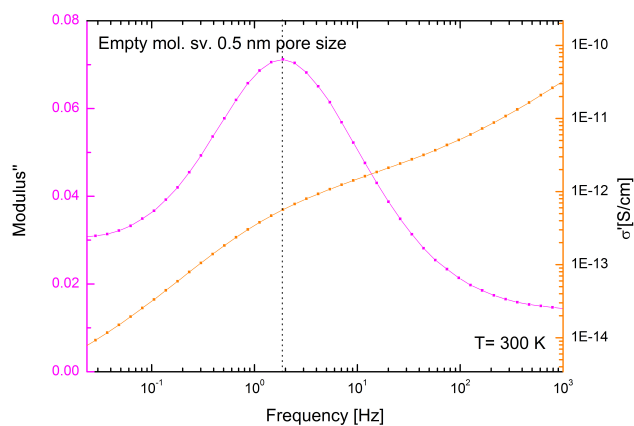
Supplementary Figure 4 shows the analogous fit and fit components for pure PLC confined in the same pores.



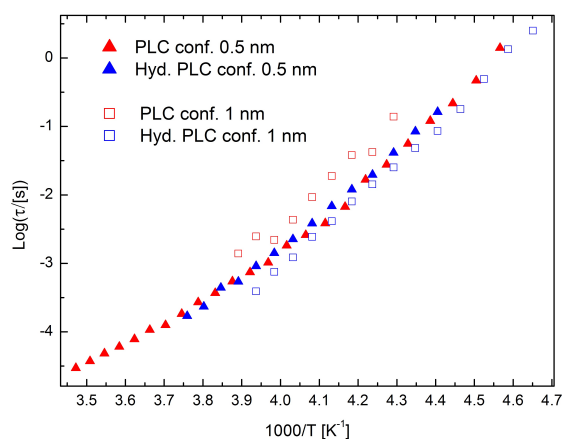
Supplementary Figure 4 Dielectric loss spectrum (empty orange circles) and fit (full orange line) of PLC confined in molecular sieves of 1 nm pore size, obtained at 239 K. The violet trace portrays the Cole-Cole function, while the light blue and pink traces show the HN and conductivity contributions respectively.

Modulus and conductivity in molecular sieves

The complex dielectric modulus is defined as $M = 1/\epsilon$, and in the frequency domain, it is a complex function of the frequency ($M(\omega) = M'(\omega) + iM''(\omega)$)². It is related to the relaxation of the electric field within the material and it was originally introduced by Macedo et al. to study space charge relaxation phenomena³.



Supplementary Figure 5 Comparison between the ac conductivity spectrum ($\text{Log}(\sigma')$, orange axis and trace) and the imaginary modulus spectrum (M'' , pink axis and trace) of empty molecular sieves at $T=300$ K. The latter exhibits a maximum at the (temperature-dependent) frequency indicated with a dotted line that coincides with the cross-over point in σ' .



Supplementary Figure 6 Arrhenius plot of the relaxation times τ of the interfacial relaxations in the filled molecular sieves. Full red and blue triangle markers correspond to pure and hydrated PLC in the pores of 0.5 nm diameter, respectively, whereas empty square markers of the same colors portray pure and hydrated PLC in the pores of 1 nm diameter, respectively.

Notes and references

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Supplementary Figure 5 shows the imaginary part of the modulus (M'' , pink left axis) and ac conductivity ($\log(\sigma')$, orange right axis) spectra of 0.5 nm empty molecular sieves at 300 K. It can be observed that the maximum of the modulus (the so-called conductivity relaxation^{4,5}) occurs at a frequency that coincides with the cross-over between two different σ' regimes (resembling the cross over between a σ_{dc} plateau and the electrode polarization effect) the conductivity spectrum. This is a signature feature of a space-charge (conductivity) relaxation³.

Supplementary Figure 6 shows the Arrhenius plot of the relaxation times τ of the fast CC fitting functions used to model the interfacial relaxation processes of the molecular sieves filled with pure or hydrated prilocaine. It can be observed that, as in the case of the 0.5 nm pores analyzed in the main article, the relaxation times coincides reasonably with those observed for 1 nm pores. For this reason, we hypothesize the CC fast relaxation arises in both MS from accumulation of free charges (ions) of the confining material taking place in the interfaces of the pores.