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4	Supplementary Information					
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8	Elucidating Molecular Scale Interactions Underlying the					
9	Freezing Behavior of Salt Solutions in Silica Nanopores					
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1 S1. The Hydroxylation Reaction of Non-bridging Oxygens on the Pore Surface

The protonation of non-bridging oxygens on the silica surface in contact with water is resolved 2 using reactive forcefield molecular dynamics simulations implemented in the Amsterdam density 3 functional (ADF) software. The silica surface is solvated with 1 g/cm³ of water and the initial 4 configurations undergo NVT simulations of 250 ps under 300 K, controlled by Nose-Hoover 5 thermostat with a time constant of 1 fs. Silica surface and water molecules are modeled using the 6 forcefield developed by Fogarty and co-workers.¹ The snapshot shown in **Figure S1** are taken from 7 different frames in the trajectory file to show the progress in the hydroxylation reactions that occur 8 between water molecules and the non-bridging oxygens on the silica surface. The nonbridging 9 oxygens undergo a progressive hydroxylation reaction that results in OH group formation on the 10 silica surface and the surface density of these groups increases with time. With a sufficiently long 11 simulation time, all the non-bridging oxygens are being protonated and resulting in OH group. The 12 protons are released from the water molecules surrounding the silica surface. The number of water 13 molecules and the total energy of the system as a function of the simulation time are shown in 14 15 Figure S2. The number of water molecules decrease dramatically from 180 to about 130 molecules in the first 5 ps due to the reaction with the oxygens on the silica surface. The hydroxylation 16 reaction reduces the total energy of the system. Based on these simulations, all the non-bridging 17 oxygens on the pore surface used in the classical MD simulations are protonated forming OH 18 groups. 19

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2 Figure S1. Snapshots showing the progressive hydroxylation of nonbridging oxygen on the silica

3 surface with the simulations time.



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Figure S2. The number of water molecules and the corresponding energy of the silica in the water
system as a function of the simulation time.

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5 S2. MD Simulation Setup

- 6 Silica, TIP5P water and ions are modeled using ClayFF, TIP5P and OPLSAA forcefields. ClayFF
- 7 accounts for non-bonding interactions and OH bond stretching, while TIP5P and OPLSAA account
- 8 for nonbonded and all bonded interactions. The parameters used to describe the atoms in the MD
- 9 simulations are depicted in Table S1.

10 Table S1. The non-bonded forcefield parameters for silica, water and ions that are used in the 11 molecular dynamics simulations (see ref. 48, 49 and 50 in the main text).

Molecule	Atomic description	Atom	σ (Å)	ε (kJ/mol)	<i>q</i> (e)
	Silicon	Si	3.30200	7.70065×10 ⁻⁶	2.1000
Silica	Bridging Oxygen	Ob	3.16557	0.65017	-1.0500
	Nonbridging Oxygen	Oh	3.16557	0.65017	-0.9500
	Hydrogen	Н	0.00000	0.00000	0.4250
	Oxygen	0	3.12000	0.669440	0.0000
Water	Hydrogen	Н	3.09700	0.744752	0.2410
	Virtual Site	LP	0.00000	0.00000	- 0.2410
	Magnesium	Mg	1.64447	3.66118	2.0000
Ions	Calcium	Ca	2.41203	1.88136	2.0000
	Potassium	Κ	4.93463	1.37235×10 ⁻³	1.0000
	Chloride	Cl	4.41724	0.492833	- 1.0000

1 S3. Heterogeneous Crystallization of Confined Water

The onset and growth of ice crystals in the nanopores are probed using 2D density maps averaged over the xy plane from MD trajectories (Figure S3). The emerged hexagons dominate the pore space at low temperatures, indicating the formation of stable hexagonal polymorphs which is consistent with the observations of WAXS measurements.





Figure S3. 2D density maps show the onset and growth of crystalline ice in the nanopores at (a)
245 K, (b) 235 K, (c) 225 K and (d) 200 K, obtained from MD simulation trajectories.

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1 S3. Water-Pore Surface Interactions



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Figure S4. The hydrogen bonding profile of water with the hydroxyl groups on the pore surface
normalized by the number of OH groups attached to the pore surface. The inset shows a water
molecule interact with surface OH by a hydrogen bond.

6 The interaction of interfacial water with the pore surface is characterized by hydrogen bonding

7 (Figure S4) and the radial distribution functions of OH groups with the water oxygen (Figure S5).

8 The hydrogen bonding profile shows a slight and continuous increase with the simulation time,

9 indicating a distinct behavior of the interfacial water compared to bulk water in the nanopores.

10 Further, the coordination number obtained by integrating the radial distribution function of OH_{silica}

11 and Owater shows that water exhibits a preserved number of molecules around OH groups,

12 suggesting a temperature-independent structure of interfacial water. These observations are

13 consistent with the premelted behavior of interfacial water.

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Figure S5. The radial distribution function (g(r)) and the corresponding coordination number (n(r))
of OH groups on the pore surface and water oxygen as a function of the applied temperature. The
RDFs are averaged over the last 5 ns of the temperature segment to ensure equilibrated profiles.

- 5 S4. Translational Dynamics
- 6 The translational diffusion coefficient is calculated along the pore length using the mean square
- 7 displacement (MSD) approach as a function of the applied temperature (Figure S6)^{2,3}.

$$MSD = \frac{1}{N} \sum_{i=1}^{N} |x(t)^{(i)} - x(0)^{(i)}|^2 = 6Dt \qquad (1)$$

9 'N' is the total number of particles, x(t)⁽ⁱ⁾ and x(0)⁽ⁱ⁾ are the position at time 't' and the reference
position of the *i*-th particle respectively, and 'D' is the translational diffusion constant in threedimension.



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Figure S6. The mean square displacement of water along the vector parallel to the pore length as
a function of the applied temperature.

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5 S4. Ions Hydration Shells

6 The structure and interaction of the hydration shells with the ions are characterized by the radial 7 distribution function (RDF) of ions-water oxygen (Figure S7). The RDFs show that the density of 8 hydration water is preserved at all the applied temperatures and the distinct gap between the first 9 and second hydration shells predicts the lack of water exchange between the hydration shell and 10 bulk water at low temperatures.





Figure S7. The radial distribution function and the corresponding coordination number of cationswater oxygen and anions-water oxygen as a function of the applied temperature. The radial distribution functions are averaged over the last 5 ns of each temperature segment to ensure

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7 References

equilibrated profiles.

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