Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Surface Hydration Drives Rapid Water Imbibition into Strongly Hydrophilic Nanopores

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1. Schematic of the simulation system for studying water imbibition

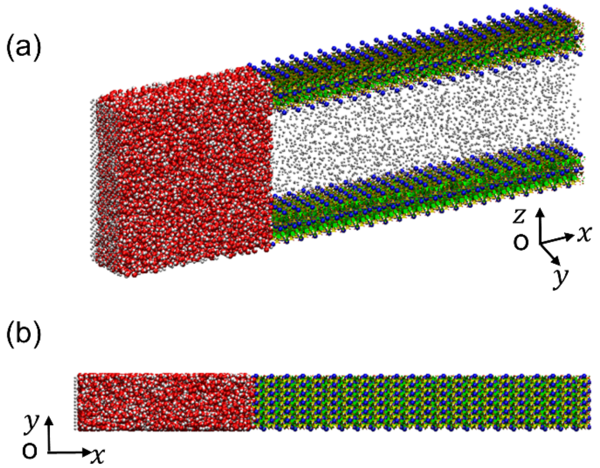

Figure S1. Schematics of the MD system used in Fig. 1 in the main text. (a) A 3D view of the MD system. (b) An *xy*-plane view of the system.

2. Equilibrium MD simulations for characterizing hydration layers of mica surfaces

To understand the dynamics of water molecules in the hydration layer on mica surfaces, we performed separate equilibrium MD simulations. The MD system in these simulations features two mica walls separated by a slab of methane measuring 6nm in thickness. The dimension of the mica walls is 3.67 and 3.15nm in the *x*- and *y*- direction, respectively. The system is periodical in the *xy*-plane, and its center is located at (0, 0, 0). A layer of water molecules is placed on each wall so that the water area density matches the asymptotic density of the water molecules in the *monolayer* water film on pore walls shown in Fig. 3b. The system is equilibrated for 2ns, which is followed by a 5ns equilibrium run. The mean square displacements

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of water molecules in the x- and y-directions are used to determine their diffusion coefficients, e.g., the self-diffusion coefficient in the x-direction, D_x, is computed using the Einstein relation $D_x = \lim_{t\to\infty}\langle|x_i(t) - x_i(0)|^2\rangle/2t$, where x_i is the x-position of water molecule i and t is the time. To compute the PMF of water molecules on the mica surface, the average density of the water molecules in the xy-plane, $\rho_s(x,y)$, is first computed by binning their positions during the equilibrium run. The PMF is next computed using $\mathrm{PMF}(x,y) = -k_B T \ln(\rho_s(x,y)/\rho_0)$, where ρ_0 is the average water density in the monolayer water film.

3. System used for calculating potential energy of water molecules

As described in the main text, to qualitatively understand $E_{\downarrow}$ and $W_{\leftarrow}$, the potential energy of water molecules at four different positions in water-mica systems are calculated (see Fig. S2):

1. In bulk water. The potential energy of the water molecule is denoted as E_1
2. In the first water layer near a mica wall hydrated by a thick slab of water (slab thickness: ~6nm). The potential energy of the water molecule is denoted as E_2.
3. In the monolayer water film adsorbed on a mica surface. The water film is exposed to methane (pressure: 250bar). The potential energy of the water molecule is denoted by E_3.
4. Isolated water molecules on a mica surface. The potential energy of the water molecule is denoted as E_4. In this simulation, eight water molecules are placed on a mica surface measuring 3.7×3.15nm^2 laterally so that water-water interactions are very weak. Periodical boundary condition is adopted in directions parallel to the mica surface.

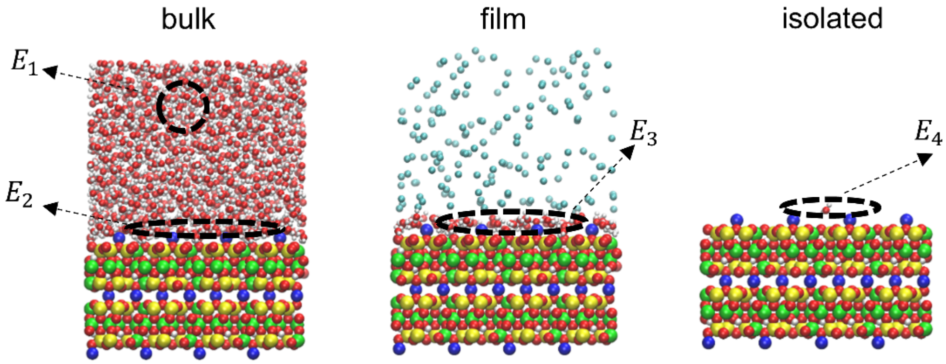

Figure S2. Schematics of the MD system used for studying the potential energy of water molecules in various water-mica systems. In the middle panel, the cyan balls denote methane molecules.

4. Radial density distribution around water molecules

In the main text, to understand why it is energetically favorable for a water molecule at the imbibition front to hop forward, we compute the potential energy of a single water molecule in two scenarios: when it resides in a monolayer water film adsorbed on mica surface (E_3, middle panel in Fig. S2) or when it is isolated on a mica surface (E_4, right panel in Fig. S2). It was found that E_4 is lower than E_3 by $3k_BT$. To understand this result, we compute the distribution of mica surface atoms around a water molecule in these two scenarios. Since water molecules often interact strongly with the bridging oxygen atoms with tetrahedral substitution (OBST) on mica surfaces, we compare the distribution of OBST atoms around water molecules in the above two scenarios. Figure S3 shows that, compared to the water molecules in a monolayer film, water molecules isolated on mica surface are coordinated by more OBST atoms. Since OBST atoms interact with water molecules via attractive electrostatic interactions, this result helps explain why the potential energy of a water molecule is lower when it is isolated on a mica surface.

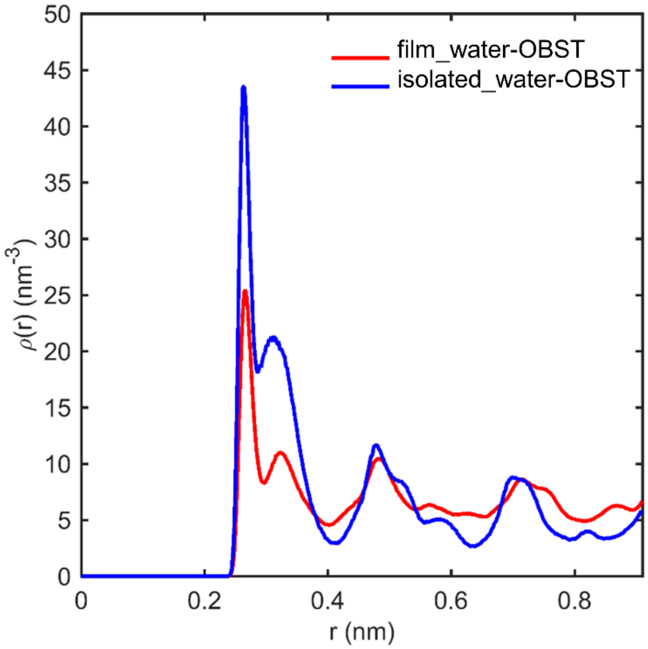

Figure S3. Radial density distribution of OBST atoms of mica near water molecules in a monolayer water film adsorbed on mica surface and isolated on mica surfaces. OBST atoms are the bridging oxygen atoms with tetrahedral substitution in mica.