## **Evidence of Facilitated Transport in Crowded Nano-Pores**

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**Supplementary Information** 

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## **Methods and Algorithms**

**Simulation Setup.** Organic-rich shale formations are source rocks as well as the reservoir basement and caprocks that trap oil and gas. To build nano-pores representative of those found in model organic-rich shales, we considered an 13.4×13.4×15 Å<sup>3</sup> hydroxylated amorphous silica substrate with 4.5 OH nm<sup>-2</sup> on its surface, taken from those published by Ugliengo et al.,<sup>1</sup> as a unit cell. We duplicated this unit-cell to create two parallel silica slabs placed at a distance such to yield a slit-shaped nano-pore of width ~20 Å. The *X* and *Y* dimensions of this substrate were  $L_{x,p} = 53.55$  Å and  $L_{y,p} = 53.15$  Å, respectively. We saturated the pore edge surfaces with OH groups to achieve a surface density of 4.5 OH nm<sup>-2</sup>, which is consistent with experiments.<sup>2</sup> The simulation box is periodic in the three directions. Its *Y* dimension (53.15 Å) reflects the periodicity of the silica substrate; the *X* and *Z* dimensions were set to 193.55 and 31.71 Å, respectively. Due to periodic boundary conditions, the model pore is effectively infinite along the *Y* direction. Conversely, the pore is finite along the *X* direction, along which it is exposed to the fluid reservoirs, as illustrated in **Figure S1**, panel A. The pore obtained following this procedure could represent nano-pores existing in some shale gas plays with tectosilicates (> 30 wt% of quartz) as main components.<sup>3.4</sup>

To model organic content trapped within the amorphous silica pore, we filled the slit-shaped silica pore with 400 benzene molecules, resembling aromatic oil trapped in sedimentary rocks. This model is meant to represent organic-rich shale caprocks that contain significant amount of organic carbon (> 11.7 wt %).<sup>4</sup> The number of benzene molecules introduced were sufficient to fill the pore volume and form thin layers on the solid substrate outside the pore (see **Figure S1**, panel A).

**Force Fields.** The CLAYFF force field was implemented to simulate the SiO<sub>2</sub> substrates.<sup>5</sup> Silicon and oxygen atoms were tethered to their initial positions by applying a harmonic restraint force with a spring constant of 100 kcal/mol.Å. The surface hydroxyl hydrogen atoms were allowed to vibrate. The transferable potentials for phase equilibria (TraPPE) force field was implemented to model CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> molecules.<sup>6-8</sup> The TraPPE models for CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> were found to reproduce experimental results of vapour-liquid phase equilibria for the pure components as well as CO<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>S-CH<sub>4</sub> binary mixtures,

achieving high accuracy.<sup>6-7</sup> Benzene molecules were modelled using the second generation of general AMBER force field (GAFF2),<sup>9</sup> which exhibits a moderate improvement with respect to GAFF1 in its ability to reproduce intermolecular energy, liquid density, heat of vaporization, and hydration free energy for organic molecules.<sup>10</sup> Non-bonded molecular interactions were modelled by means of dispersive and electrostatic forces. The electrostatic interactions were modelled by the Coulomb potential, with long-range corrections treated using the particle-particle particle-mesh method (PPPM).<sup>11</sup> Dispersive interactions were determined by Lorentz-Berthelot combining rules from the values of like components.<sup>12</sup> The cut-off distance for all interactions was set to 12 Å. No corrections were applied for long-range LJ interactions because it was found that such corrections do not affect significantly the amount of fluid adsorbed in the pore used here.

Algorithms. We conducted both equilibrium and boundary-driven non equilibrium MD (BD-NEMD)<sup>13</sup> for studying CO<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>S-CH<sub>4</sub> binary mixtures passing through the benzene-filled pore. Initially, we equilibrated the system containing benzene in the presence of (a) pure CH<sub>4</sub>, and (b) CO<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>S-CH<sub>4</sub> binary mixtures. The equilibration simulations lasted for 50-100 ns, with no external force applied. The simulations conducted for pure CH<sub>4</sub> served as a base case against which to quantify the effect of CO<sub>2</sub> or H<sub>2</sub>S on CH<sub>4</sub> transport. Several mixtures were considered, as listed in Figure S1, panel B. The numbers of CO<sub>2</sub> and H<sub>2</sub>S molecules were varied from 50 to 800. The number of CH<sub>4</sub> molecules in each binary system was also changed, to maintain the pressure outside the pore for all systems at ~13.9 MPa at equilibrium. The amount of CH<sub>4</sub> needed for each system was calculated using the Peng-Robinson equation of states (EOS), based on the molecular density of CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> outside of the pore, and the customary mixing rules for multi-component mixtures.<sup>14-16</sup>

The BD-NEMD simulations were conducted by applying a force along the *X*-axis to all CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> molecules located in a thin slab of width  $d_{ext} = 20$  Å outside of the pore (within the permeate) to establish and maintain a constant pressure difference across the pore. In each simulation, 100 ns of simulations were required to reach steady state. Equilibration was confirmed by examining the variations

in the energy and temperature as a function of simulation time, as well as  $CO_2$ ,  $H_2S$ , and  $CH_4$  density profiles along the pore. Once steady state was achieved, production simulations were conducted for 50-150 ns.

**Implementation**. Equilibrium and BD-NEMD simulations were conducted using the package LAMMPS.<sup>17</sup> Simulations were performed in the canonical ensemble (NVT), where the number of particles, volume, and temperature are kept constant. The equations of motion were solved by implementing the leapfrog algorithm<sup>18</sup> with 1.0 fs time steps. The simulated temperature was maintained at 300 K by Nosé-Hoover thermostats<sup>19-20</sup> with a relaxation time of 100 fs. We applied separate thermostats to fluid molecules (CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub>), solvent molecules (benzene), and to the atoms in the silica substrates.<sup>21-22</sup> This allowed us to reduce the perturbations on the dynamics of the system due to the application of the external force, which causes a constant energy input on fluid molecules.



System	n <sub>co2</sub>	n <sub>CH4</sub>	n <sub>CH4</sub> x <sub>CO2</sub>	
0		1100	0.0	1.0
1C	50	1080	0.04	0.96
2C	100	1060 0.09		0.91
3C	200	1000 0.17		0.83
4C	400	900 0.31		0.69
5C	500	860	0.37	0.63
6C	600	830	0.42	0.58
7C	700	800	0.47	0.53
8C	800	750	0.52	0.48
System	n <sub>H2S</sub>	n <sub>CH4</sub>	x <sub>H2S</sub>	x <sub>CH4</sub>
1H	50	1090	0.04	0.96
2H	100	1080	0.09	0.91
3H	200	1050	0.16	0.84
4H	400	1010	0.28	0.72
5H	500	995	0.33	0.67
6H	600	980	0.38	0.62
7H	700	960	0.42	0.58

Figure S1. (A) Representative simulation snapshots for the filled pore exposed to the bulk reservoirs along the X direction. The amorphous silica nano-pore is filled with 400 benzene molecules, providing a model for oil trapped in sedimentary rocks. (B) Compositions of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S in the bulk reservoirs for all systems simulated before equilibration.

## **Computational Procedures and Results**



**Figure S2.** Adsorption isotherms of CO<sub>2</sub> (blue, top), H<sub>2</sub>S (yellow, top), and CH<sub>4</sub> in CO<sub>2</sub>-CH<sub>4</sub> (blue, bottom) and H<sub>2</sub>S-CH<sub>4</sub> (yellow, bottom) mixtures inside the benzene-filled pore at 300 K.

Adsorption Isotherms. In Figure S2, we present the adsorption isotherms for  $CO_2$  (blue, top panel),  $H_2S$  (yellow, top panel), and  $CH_4$  in  $CO_2$ - $CH_4$  (blue, bottom panel) and  $H_2S$ - $CH_4$  (yellow, bottom panel) mixtures inside the benzene-filled pore at 300K using equilibrium MD simulations. Assuming that in the range of compositions considered the Henry's law is applicable, the solubility coefficient might be obtained as the slope of the adsorption isotherms shown in Figure S2 at the limit of zero mole fraction of  $CO_2$  and

 $H_2S$  (or the mole fraction of CH4 approaches 1). From the simulation results we estimate that the solubility coefficient for methane in the crowded pore is lower in CO<sub>2</sub>-CH<sub>4</sub> (~3.8×10<sup>-3</sup> Å<sup>-3</sup>) and  $H_2S$ -CH<sub>4</sub> (~4.6×10<sup>-3</sup> Å<sup>-3</sup>) mixtures, compared to that of CO<sub>2</sub> (11.6×10<sup>-3</sup> Å<sup>-3</sup>) and  $H_2S$  (32.2×10<sup>-3</sup> Å<sup>-3</sup>). Note that solubility coefficients are calculated based on the volume available to the fluids in the pore.

To assess whether all simulated processes are reversible and that the results presented are representative of equilibrated systems (see **Figure 1A** and **1B** in the main text), we carried out CO<sub>2</sub>/H<sub>2</sub>S adsorption-desorption cycles. By employing the 'evaporate' and 'deposit' procedures available in the software package,<sup>17</sup> we extract CO<sub>2</sub>/H<sub>2</sub>S molecules and simultaneously insert CH<sub>4</sub> molecules randomly into the benzene-filled pore as well as the bulk reservoirs starting from the configuration of system 8C/7H (see **Figure S1**, panel B for system composition), respectively, to slowly retrieve the compositions of the other binary mixtures. The results for solubility of CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> and adsorption and re-adsorption of benzene during CO<sub>2</sub>/H<sub>2</sub>S adsorption-desorption cycles are shown in **Figure 1A** and **1B** in the main text.



Figure S3. Amount of benzene molecules displaced out of the SiO<sub>2</sub> pore per adsorbed CO<sub>2</sub>/H<sub>2</sub>S in the pore.

**Benzene Displacement.** In **Figure S3**, we report the number of benzene molecules displaced out of the SiO<sub>2</sub> nano-pore upon changing the composition of the binary mixtures simulated. Focus is on the number of CO<sub>2</sub> (blue) and H<sub>2</sub>S (yellow) molecules adsorbed within the pore. The results suggest that H<sub>2</sub>S is more effective than CO<sub>2</sub> in displacing benzene. Our results suggest that ten H<sub>2</sub>S molecules displace four C<sub>6</sub>H<sub>6</sub> molecules from the pore, while ten CO<sub>2</sub> molecules displace only three C<sub>6</sub>H<sub>6</sub> molecules.



Figure S4. Density profiles of CH<sub>4</sub> (blue), benzene (green), and CO<sub>2</sub>/H<sub>2</sub>S (yellow) molecules as a function of the distance *z* across the ~20 Å amorphous silica pore. The results are obtained for 200CO<sub>2</sub>-1000CH<sub>4</sub> (3C) and 200H<sub>2</sub>S-1050CH<sub>4</sub> (3H) systems from equilibrium MD simulations at 300K. The reference (z = 0) is the plane formed by the oxygen atoms of the surface hydroxyl groups of the bottom silica slab.

Fluid Density Profiles at Equilibrium and During Flow. In Figure S4, the density profiles of CH<sub>4</sub> (blue), benzene (green), and CO<sub>2</sub>/H<sub>2</sub>S (yellow) are reported as a function of the vertical distance z from the surface of the bottom slab of the amorphous silica nano-pore. The reference (z = 0) corresponds to the plane formed by the oxygen atoms of the surface hydroxyl groups of the bottom silica slab. The results are obtained for 200CO<sub>2</sub>-1000CH<sub>4</sub> (3C) and 200H<sub>2</sub>S-1050CH<sub>4</sub> (3H) systems from equilibrium MD simulations at 300K as shown in top and bottom panels, respectively. The density profiles of center of mass of benzene molecules in both systems indicate the formation of four well-defined benzene layers at locations z = 0 - 5.3 Å, 5.3 - 9.1 Å, 9.1 - 14.3 Å and 14.3 - 20 Å.



**Figure S5.** Top: Representative simulation snapshots for the final configuration of 200CO<sub>2</sub>-1000CH<sub>4</sub> mixtures moving across the pore filled with benzene at 300 K. An external force of 0.01 kcal/mol.Å is applied to CO<sub>2</sub> (grey and red spheres) and CH<sub>4</sub> (green spheres) molecules in the shaded region on the left to drive the flow along the direction of the blue arrow. Bottom: Resultant density profiles for CO<sub>2</sub> (blue) and CH<sub>4</sub> (green) along the length of simulation box in the *X* direction.

In **Figure S5** we show one representative simulation snapshot (top panel) and the averaged density profiles (bottom panel) for  $CH_4$  and  $CO_2$  molecules distributed along the length of the simulation box along the *X* direction when the applied external force is 0.01 kcal/(mol.Å). The results are shown for the system

3C (see **Figure S1**, panel B, for its composition). The results show that the external force yields a pressurised zone on the right of the porous media, within which an increase in  $CH_4$  and  $CO_2$  densities is observed (**Figure S5**, bottom panel). This is the 'retentate' volume. The external field is considered equivalent to imposing a density (or a pressure) gradient, leading to a macroscopic flux in the direction of the arrow in **Figure S5**, top panel. Once a density gradient is imposed,  $CH_4$  and  $CO_2$  molecules diffuse from the retentate to the 'eluate' volume, located on the left of the pore, where the fluid density is lower.

In Figure S6, we report the in-plane density distributions of benzene carbon atoms within first, second, third and fourth layers at equilibrium (left) and during flow (right) for the system shown in Figure S5, top panel. The high-density areas (red-yellow spots) of the contour plots indicate positions where the benzene molecules preferentially reside. The contour plots for the first and fourth layers at equilibrium and during flow suggest that some benzene molecules in these layers are parallel to the surfaces, as illustrated by the presence of planar hexagonal rings reminiscent of the benzene carbon atoms, while others orient themselves at an angle with respect to the surfaces. The results in **Figure S6** show that the benzene molecules in the middle of the pore manifest a somewhat less ordered structure than those close to the pore surfaces. Our analysis reveals that the positions within the pore where benzene molecules occupy once the external forces are applied are similar to those in which they accumulate at equilibrium, as long as the applied pressures are moderate. The same qualitative results are also observed for the H<sub>2</sub>S-CH<sub>4</sub> binary mixtures. This suggests that the external force of 0.01 kcal/(mol.Å) is not large enough to significantly perturb the structural properties of confined benzene in the presence of CH<sub>4</sub> with either CO<sub>2</sub> or H<sub>2</sub>S. Note that the transport diffusion coefficient  $D_t$  is quantified in the limit of the eternal force to zero, in which case the structure of the benzene-filled pore remains unchanged; hence it is essential to apply such a small external force, which would guarantee that the morphology of pore saturated with benzene is uninterrupted. Upon applying the external force, the density profiles show (see Figure S5, bottom panel) that once the flow is induced, the molecular density profiles show a decreasing gradient from the retentate (right) to the eluate regions (left). For the density profiles, the centres of mass of the various molecules are considered.



**Figure S6**. In-plane surface density distributions of benzene carbon atoms found within first, second, third and fourth layers at equilibrium (left panels) and during flow (right panels) for the 200CO<sub>2</sub>-1000CH<sub>4</sub> mixtures moving across the pore filled with benzene at 300 K.

**Transport Properties.** The molar flux against the concentration difference along the X direction,  $J_i$ , was quantified by counting the number of molecule species *i* which passed through a Y-Z plane at a given X location within the pore as a function of the production similation time, *t*, and the cross sectional area across which the flux occurred, A(x):<sup>13</sup>

$$J_i = \frac{(N_i^+ - N_i^-)_x}{tA(x)}$$
(1)

In Eq. (1),  $N_i^+$  and  $N_i^-$  denote the number of molecule species *i* that have passed the plane from right to left and left to right, respectively, in the representation of **Figure S5**.

Once the flux is known, permeability, K, can be determined based on Darcy's law,<sup>23</sup> which shows a linear relationship between molar flux and pressure drop across a porous medium.

$$J_i = -K_i \frac{dP_i}{dx} \tag{2}$$

The pressure drop, dP, for each species *i* (CH<sub>4</sub>, CO<sub>2</sub>, or H<sub>2</sub>S) was calculated using the Peng-Robinson equation of states using the molecular density of each specie in the feed and permeate regions as inputs.<sup>24-</sup><sup>25</sup> By substituting the molar flux  $J_i$  from Eq. (1), Eq. (2) can be rearranged and integrated to obtain *K*:

$$K_{i} = \frac{1}{\Delta P.t} \int_{0}^{l} \frac{(N_{i}^{+} - N_{i}^{-})_{x} dx}{A(x)}$$
(3)

Note that the cross-sectional area of one plane within the pore A(x) varies along the X direction of the pore because of the roughness of the amorphous silica substrates as well as the non-uniform distribution of benzene inside the pore. Thus, A(x) should be calculated based on the volume available for the various species CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S to occupy.

The results for A(x) as a function of system composition are reported in Figure S7.



Figure S7. Cross-sectional area distribution along the *X* direction A(x) in the benzene-filled pore as a function of system composition. A(x) is calculated based on the volume available for the various species CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S to occupy.

Knowing the permeability, the transport diffusivity of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S can be extracted by<sup>26</sup>

$$D_{t,i} = \frac{K_i}{S_i} \tag{4}$$

where  $S_i$  is the solubility of species *i* within the pore. The solubility of species *i* is calculated as the ratio of its density in the pore,  $\rho_i$ , and its partial pressure in the bulk feed side,  $p_i$ , using the slope of the simulated adsorption isotherms (see **Figure S2**) obtained in the linear regime, at high CH<sub>4</sub> mole fraction:

$$S_i = \frac{\rho_i}{p_i} \tag{5}$$

We report the solubility for CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S in the pore filled with benzene in Table S1 in the SI.

Table S1. Solubility for CO<sub>2</sub>, H<sub>2</sub>S, and CH4 in CO<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>S-CH<sub>4</sub> mixtures in the pore filled with benzene at 300 K.

	CO <sub>2</sub> -CH <sub>4</sub>		H <sub>2</sub> S-CH <sub>4</sub>	
	$CO_2$	CH4	$H_2S$	$CH_4$
Solubility (1/(Å <sup>3</sup> .MPa)	8×10 <sup>-4</sup>	4×10 <sup>-4</sup>	20×10 <sup>-4</sup>	4.8×10 <sup>-4</sup>

We also computed the self-diffusivity, which describes the motion of individual species within the pores filled with benzene, using the Green-Kubo formulation:<sup>27</sup>

$$D_{s,i} = \frac{1}{dN_i} \int_0^\infty \langle \sum_{k=1}^{N_i} v_k^i(t) . v_k^i(0) \rangle dt$$
 (6)

In Eq. (6),  $v_k^{i}$  is the centre of mass velocity of molecule k of species i.

The results of permeability, transport- and self-diffusivity of  $CH_4$ ,  $CO_2$  and  $H_2S$  are reported in the main text.



Figure S8. In-plane surface density distributions of  $CO_2$  (top) and  $H_2S$  (bottom) molecules found within first, second, third and fourth layers for the representative 100CO<sub>2</sub>-1060CH<sub>4</sub> and 100H<sub>2</sub>S-1080CH<sub>4</sub> mixtures in the pore filled with benzene at 300 K, respectively.

**Molecular Clustering.** To gain insights into the molecular structure of  $CO_2$  and  $H_2S$  molecules inside the pore filled with benzene when injecting  $CO_2$ -CH<sub>4</sub> and  $H_2S$ -CH<sub>4</sub> mixtures, we calculated the in-plane surface density distributions of  $CO_2$  and  $H_2S$  molecules found in the first, second, third and fourth layers formed in the SiO<sub>2</sub> pore. The projections are obtained along the *X*-*Y* plane. The results are shown for  $CO_2$  (top panels) and  $H_2S$  (bottom) in the representative 100CO<sub>2</sub>-1060CH<sub>4</sub> and 100H<sub>2</sub>S-1080CH<sub>4</sub> mixtures in the pore filled with benzene at 300 K, respectively, in **Figure S8**. Details regarding the positions of the layers within the nano-pore are presented in **Figure S4**. The first and fourth layers of CO<sub>2</sub>/H<sub>2</sub>S are near the bottom and top silica slabs, respectively, while the second and third layers are located approximately in the middle of the pore. The high-density areas (shown as red-yellow spots) of the contour plots indicate positions where the CO<sub>2</sub>/H<sub>2</sub>S molecules preferentially reside. The results show the existence of CO<sub>2</sub>/H<sub>2</sub>S molecular clusters in the middle of the pore. These clusters appear to be more pronounced in the presence of H<sub>2</sub>S within the pores rather than CO<sub>2</sub>.

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