Evidence of Facilitated Transport in Crowded Nanopores

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ABSTRACT: Fluid transport in nature often occurs through crowded nanopores, where a number of phenomena can affect it, because of fluid–fluid and fluid–solid interactions, as well as the presence of organic compounds filling the pores and their structural fluctuations. Employing molecular dynamics, we probe here the transport of fluid mixtures (CO2−CH4 and H2S−CH4) through silica nanopores filled with benzene. Both CO2 and H2S are strongly adsorbed within the organic-filled pore, partially displacing benzene. Unexpectedly, CO2/H2S adsorption facilitates CH4 transport. Analysis of the trajectories suggests that both CO2 and H2S act as vehicle-like carriers and might swell benzene, generating preferential transport pathways within the crowded pore. The results are useful for identifying unexpected transport mechanisms and for developing engineering approaches that could lead to storage of CO2 in caprocks.

Carbon dioxide (CO2) injection in geologic reservoirs could provide one solution for carbon capture and storage (CCS).1−3 Fine-grained sedimentary rocks (shales and mudstone) can provide caprocks in CCS sites.4,5 These rocks also play important roles in shale gas production.6 As-produced shale gas from Haynesville and Barnett shales in the United States and Horn River in western Canada contains various amounts of CO27−11 and up to several hundred parts per million of hydrogen sulfide (H2S), even in sites in which H2S was absent in initial assessments.12 The produced gas is “sweetened”8,10 to avoid harmful effects on health, safety, and the environment.13 In some cases, it might be attractive to reinject both H2S and CO2 into the formation.14

A comprehensive understanding of the fundamental mechanisms responsible for carbon bearing-fluid migration in the presence of CO2/H2S is crucial for risk assessment and site selection for geologic CCS, monitoring H2S emissions, and perhaps identifying innovative enhanced oil recovery (EOR) processes that use CO2 and H2S.15,16 Because a thorough quantification of the phenomena that govern fluid transport in the complex heterogeneous pore networks found in organic-rich shale caprocks, which consist of crowded nanopores that provide poor connections between dispersed pockets of organic matter, remains elusive, because of practical difficulties in observing fluid transport in such complicated systems, computational approaches could be helpful.17−20

This study probes transport of systems containing CO2, H2S, and methane (CH4), through a realistic ~2 nm amorphous silica nanopore saturated with benzene molecules, a model to mimic organic-rich shale caprocks. The number of benzene molecules introduced in the system (400) was sufficient to fill the pore volume and form thin layers on the solid substrate outside the pore (see Figure S1 of the Supporting Information, panel A). The transport results are complemented by careful analysis of mutual solubility, free-energy profiles, and structure of the confined systems. Atomistic molecular dynamics (MD) simulations are conducted at geological temperature (300 K) and pressure (~13.9 MPa) conditions.21−23 Various system compositions in the bulk reservoirs are considered, as shown in Figure S1, panel B. Once equilibrium was achieved, system properties such as density profiles for CO2, H2S, CH4, and benzene molecules were determined within the pore as well as in the bulk reservoirs (see Table 1). Details regarding simulation models, algorithms, methods, and computational procedures are reported in the Supporting Information.

We calculated the solubility of CO2, H2S, and CH4 in confined benzene as a function of system composition. The results (Figure 1A, left panel) suggest that CO2 and H2S solubility increase linearly when the respective bulk mole fractions increase to 0.21 and 0.12. H2S (yellow) is more soluble in confined benzene than CO2 (blue), achieving a solubility coefficient of 7.26 (0.33 MPa−1) compared to 2.38 (0.13 MPa−1) for CO2. For comparison, H2S is more soluble in bulk benzene than CO2, with experimental solubility coefficients being 0.56 MPa−1 for H2S and 0.15 MPa−1 for CO2 at ~300 K.25−26 Because bulk simulations overestimate the experimental solubility, the results in Figure 1A suggest that confinement strongly reduces the solubility of H2S and CO2 in benzene, which is contrary to many results for other confined systems, in which confinement increases solubility.25,26 It is possible that
confined benzene cannot solvate CO2 and H2S molecules as effectively as it does in the bulk, a mechanism similar to the one invoked to explain the lower H2S solubility in confined water.27

Our results show that loading H2S into the benzene-filled SiO2 pore enhances the solubility of CH4 in the same pore, while adding CO2 reduces CH4 solubility (Figure 1A, right panel). This observation could have ramifications for improving shale gas extraction. Our simulations also suggest that CH4 is less strongly adsorbed in the SiO2 pore compared to H2S and CO2 (see Figure S2).

The amount of benzene confined in the nanopore decreases as the bulk mole faction of CO2 (blue) and H2S (yellow) increases (Figure 1B). In particular, our analysis suggests that 10 H2S molecules displace 4 CH4 molecules from the pore, while 10 CO2 molecules displace 3 CH4 molecules (see Figure S3). These results suggest that varying the minority fluids mixed with CH4 strongly affects the structure of organics trapped in caprock nanopores and might also be responsible for the pronounced differences observed for CH4 solubility in confined benzene (Figure 1A, right panel).

To assess whether the results shown in Figure 1A,B are representative of equilibrated systems, we carried out adsorption−desorption cycles. By employing the “evaporate” and “deposit” procedures available in the software package,28 we extracted CO2/H2S molecules and simultaneously inserted CH4 molecules into the simulated systems. The results in Figure 1A,B show negligible adsorption−desorption hysteresis, suggesting that all simulated processes are reversible and that the results represent equilibrated systems. The results show (Figure 1B) that reducing the bulk CO2/H2S mole fraction prompts benzene readsoption into the SiO2 nanopore.

To document the molecular structure of benzene inside the crowded pore, we calculated in-plane surface density distributions of benzene carbon atoms within layers parallel to the pore surfaces. The results for CO2−CH4 (left) and H2S−CH4 (right) mixtures are shown in Figure 1C. Details regarding the layer positions are presented in Figure S4. The first and fourth layers are near the bottom and top silica surfaces, respectively, while the second and third layers are approximately in the middle of the pore. The high-density areas (red-yellow spots) of the contour plots indicate positions where the benzene molecules preferentially reside. The results strongly suggest that the distributions of benzene molecules in the first and fourth layers are not altered by the presence of CO2 and H2S, indicating that the adsorbed CO2/H2S molecules are not able to displace the benzene molecules adsorbed on the pore surfaces. Rather, they displace the benzene molecules accumulated in the middle of the pore, with the result that the distribution of corresponding benzene molecules changes significantly as the CO2/H2S bulk mole fraction increases. The density profiles suggest that H2S displaces more benzene than CO2 does, which is consistent with the results of Figure 1B. We conducted additional simulations for some systems in which the SiO2 pore was initially exposed to CO2/H2S and subsequently to benzene. The results for the distributions of benzene molecules near the silica surfaces were similar to those shown in Figure 1C, which suggests preferential adsorption of benzene on silica for the systems considered here.

To understand the results shown in Figure 1, we calculated the adsorption energy of benzene, CH4, CO2, and H2S in the nanopore filled with benzene and CH4 (system 0 in Table 1 and Figure S1) using the two-box approach proposed by Heinz.29 This method involves the simulation of the adsorbate within the pore and in bulk (Figure 2A). The results in Figure 2B show that H2S is more strongly adsorbed than the other species, achieving an adsorption energy of −2.13 eV. To compare the values in Figure 2, we refer to ab initio studies of H2S−benzene, CO2−benzene, CH4−benzene, and benzene−benzene dimers.30−33 The corresponding interaction energies are approximately −2.83, −2.55, −1.47, and −1.81 to −2.78 kcal/mol, respectively.30−33 The results in Figure 2 explain why benzene is displaced more effectively by H2S than by CO2. The interaction energies for benzene−benzene dimers with the T-shaped and parallel-displaced configurations are −2.74 and −2.78 kcal/mol,32 both stronger than that reported for CO2−benzene dimers (−2.55 kcal/mol).30 The highly positive adsorption energy calculated here (0.44 eV, see Figure 2B) suggests that benzene is unlikely to be adsorbed in the nanopore considered, probably because the pore is already filled.

A pressure gradient is imposed through the benzene-filled nanopore via implementing boundary driven nonequilibrium simulations (see Figure S5). As a function of the pressure gradient, a molecular flux is established. Once the steady-state flow is achieved, we extracted molar fluxes, permeability, and transport diffusivity (D). The latter is quantified in the limit of the external force approaching zero, when the structure of the benzene-filled pore should remain unchanged in response to the applied pressure. This is confirmed via in-plane density distributions at equilibrium and during flow (Figure S6).

In Figure 3A, the permeabilities are shown for CO2 and H2S (left panel, blue and yellow, respectively) as well as CH4 mixed with CO2/H2S (right panel, blue/yellow) as a function of system composition. We considered only those systems with CO2 (H2S) mole fraction <0.21 (0.12) as these exhibit linear changes in the adsorption isotherms (see Figure 1A) and because the CH4 mole fraction in shale gas is typically >0.8.34,35 The results in Figure 3A show that H2S permeates the pore much faster than CO2 and CH4. Increasing both CO2 and H2S bulk mole fraction enhances the permeability of all species, probably because CO2 and H2S displace benzene from the pore, opening preferential pathways across the crowded nanopore.

Table 1. Mole Fraction of CH4, CO2, and H2S in the Bulk Reservoirs as Well as Number of CH4, CO2, H2S, and Benzene Molecules Confined in the Pore for All Systems Simulated after Equilibration Was Achieved

| system | xCH4 | xCO2 | xH2S | nCH4 | nCO2 | nH2S | nCH4_H2S |
|--------|------|------|------|------|------|------|----------|
| 0      | 0.0  | 1.0  | 0    | 97   | 0    | 97   | 236      |
| 1C     | 0.03 | 0.97 | 0.03 | 98   | 0.97 | 98   | 231      |
| 2C     | 0.05 | 0.95 | 0.05 | 96   | 0.95 | 96   | 227      |
| 3C     | 0.10 | 0.90 | 0.10 | 88   | 0.90 | 88   | 220      |
| 4C     | 0.21 | 0.79 | 0.21 | 77   | 0.79 | 77   | 204      |
| 5C     | 0.27 | 0.73 | 0.27 | 72   | 0.73 | 72   | 192      |
| 6C     | 0.30 | 0.70 | 0.30 | 72   | 0.70 | 72   | 184      |
| 7C     | 0.34 | 0.66 | 0.34 | 72   | 0.66 | 72   | 176      |
| 8C     | 0.40 | 0.60 | 0.40 | 67   | 0.60 | 64   | 175      |

\[ \text{adsorption energy of benzene, CH4, CO2, and H2S in the nanopore filled with benzene and CH4 (system 0 in Table 1 and Figure S1)} \]
Figure 1. (A) Solubility of CO$_2$/H$_2$S (blue/yellow, left panel) and CH$_4$ (blue/yellow, right panel) inside the benzene-filled pore at 300 K as a function of CO$_2$/H$_2$S and CH$_4$ mole fractions, respectively, in the bulk reservoirs. (B) Amount of confined benzene per adsorbed CO$_2$/H$_2$S molecule as a function of CO$_2$ (blue) and H$_2$S (yellow) bulk mole fractions. Closed and open symbols represent data obtained during adsorption and desorption of CO$_2$/H$_2$S, respectively. (C) In-plane surface density distributions of benzene molecules within first, second, third, and fourth layers formed within the amorphous silica pore. Results are obtained for CO$_2$−CH$_4$ (left) and H$_2$S−CH$_4$ (right) mixtures at various CO$_2$/H$_2$S bulk mole fractions, as indicated above the panels. Details on computational procedures are available in the Supporting Information.
The permeability of CO$_2$, H$_2$S, and CH$_4$ depends linearly on CO$_2$/H$_2$S bulk concentrations. Notably, the results show a decline in the rates of permeability increase for CH$_4$ mixed with CO$_2$ at CO$_2$ bulk mole fractions $>0.05$. The permeability of CH$_4$ mixed with H$_2$S is greater than that of CH$_4$ mixed with CO$_2$ at $x_{CO2/H2S} > 0.05$, indicating that utilizing H$_2$S could be advantageous for improving shale gas extraction.

The transport diffusivity for the various gases can be extracted by dividing the permeability by the solubility within the nanopore. We report solubility data for each species in Table S1. In interpreting those results, it should be noted that, as the bulk mole fraction of CH$_4$ decreases, the amount of benzene in the pore also decreases (see Figure 1B). We also computed the self-diffusivity for the various species inside the crowded pore using the Green–Kubo formulation.

In Figure 3B, we present transport- (closed circles) and self- (open squares) diffusivity for CO$_2$ and H$_2$S (left panel, blue and yellow, respectively) and for CH$_4$ (right panel) for the various systems simulated. Similar to the permeability results, we observe a linear relation between transport (/self) diffusivities of CO$_2$/H$_2$S and the corresponding bulk mole fractions. However, the transport (/self) diffusivity of CH$_4$ first decreases upon loading CO$_2$/H$_2$S and then increases. The results show that CH$_4$ diffuses faster than CO$_2$ and H$_2$S, achieving transport (/self) diffusivity of $\sim$2.4 $\pm$ 6.8 $\times$ 10$^{-9}$ m$^2$/s, as opposed to $\sim$2.25 $\div$ 3.5 $\times$ 10$^{-9}$ m$^2$/s for CO$_2$ and H$_2$S when the CO$_2$ (/H$_2$S) mole fraction is $<0.21$ (/0.12). This is probably a consequence of the weaker attraction between CH$_4$ and the benzene-filled pore (see Figure 2). In contrast, although H$_2$S is more strongly adsorbed inside the pore than CO$_2$, it moves faster than CO$_2$, possibly because H$_2$S displaces more benzene from the pore than CO$_2$ does (see Figure 1B). At infinitely dilute conditions ($x_{CO2/H2S} \rightarrow 0$), the transport diffusivity of CO$_2$ and that of H$_2$S are similar ($\sim$2.3 $\times$ 10$^{-9}$ m$^2$/s). Recently, An et al. conducted nuclear magnetic resonance experiments to measure methane diffusion in seven organic-rich shale samples from a Middle Eastern source rock. At $\sim$13.9 MPa and ambient temperature, the methane diffusion coefficient was found to be $\sim$2 $\div$ 6 $\times$ 10$^{-9}$ m$^2$/s, comparable to the results obtained here.

Figure 2. (A) Representative simulation snapshots for the calculation of average energies (one benzene, CH$_4$, CO$_2$, and H$_2$S molecule) within the SiO$_2$ pore filled with benzene and CH$_4$ (top) and in the bulk reservoirs containing only CH$_4$ (bottom) at 300 K. (B) Adsorption energies of benzene, CH$_4$, CO$_2$, and H$_2$S in the pore filled with benzene and CH$_4$. For isothermal mass transfer of pure species through a porous medium, transport diffusivity is generally greater than self-diffusivity, because interparticle correlations affect collective diffusivity, positively contributing to transport. Our results differ from this general trend, because the transport diffusivity of all gases considered is slower than the corresponding self-diffusivity. This unexpected result is probably due to molecular clustering. Molecular clustering within pores is often ascribed to hydrogen bonding. A recent experimental study provided evidence that the H$_2$S dimer has an anisotropic structure exhibiting one S–H···S hydrogen bond (HB). In addition, the interactions between benzene and H$_2$S are due to SH···π interactions, a type of HB abundant in biological systems. Preferential interactions between benzene and CO$_2$ (ref 30) could lead to clustering. Indeed, the surface density distributions for H$_2$S and CO$_2$ within various layers inside the crowded nanopore (Figure S8) provide conclusive proof of the existence of molecular clusters in our systems. These clusters appear to be more pronounced in the presence of H$_2$S rather than CO$_2$.

Although the value for the transport diffusivity of CO$_2$ (/H$_2$S) should approach the corresponding self-diffusivity, $D_s$, at low mole fraction, we observe a small deviation between $D_t$ and $D_s$ at $x_{CO2/H2S} \rightarrow 0$. This discrepancy is ascribed to uncertainties in the calculation of self-diffusivity using the Green–Kubo method, which is based on the integration of velocity–velocity autocorrelation functions over infinite times.
Although the transport diffusivity of CH₄ in the presence of either CO₂ or H₂S is slower than that for pure CH₄ (Figure 3B, right panel), we observe an increase of CH₄ molar flux when loading CO₂ or H₂S (Figure 3C). This confirms that CO₂ and H₂S play the role of carriers, facilitating CH₄ transport through the crowded nanopore. The facilitated transport factors are estimated to be ∼1.46 and 1.77, respectively.

For solute transport through pores filled with solvents (i.e., our crowded SiO₂ pore), the local distribution of solvent molecules yields preferential transport pathways for the solute. To better understand the transport behavior of CO₂, H₂S, and CH₄, we quantified free-energy (FE) landscapes by implementing well-tempered metadynamics. The results for CO₂ and H₂S (panels A and B of Figure 4, respectively), show that the path connecting neighboring FE wells for CO₂ is longer and more tortuous than the one encountered by H₂S. However, to traverse the pore, H₂S molecules can jump only from one FE well to another, across barriers of ∼9 kcal/mol, whereas CO₂ encounters barriers of only ∼6.4 kcal/mol. This suggests that the CO₂ molecule can travel more easily,

Figure 3. (A) Permeability and (B) transport diffusivity as determined by boundary driven nonequilibrium MD simulations across the benzene-filled pore for CO₂ and H₂S (blue and yellow closed symbols in the left panels, respectively) and CH₄ (right panels) for the various systems considered. Self-diffusivity data (open symbols), as determined by the Green–Kubo formulation, are also reported for CO₂/H₂S and CH₄ in panel B. (C) Molar flux of methane in CO₂–CH₄ (blue) and H₂S–CH₄ (yellow) mixtures across the benzene-filled SiO₂ nanopore as a function of CO₂/H₂S bulk mole fraction.
notwithstanding the more tortuous path, compared to H2S. In our systems, it appears that the longer path length that characterizes CO2 transport is balanced by the lower FE barriers, as the pore diffusivity of CO2 is similar to that for H2S (∼2.3 × 10^{-9} m^2/s) at x_{CO2/H2S} → 0.

In Figure 4C,D we found similar patterns connecting FE wells as experienced by CH4 in systems 1C and 1H (in the presence of CO2 and H2S, respectively); however, in the presence of CO2, deep FE wells appear, within which CH4 molecules accumulate. Lower FE barriers are found in system 1C (∼4.4 kcal/mol) compared to those observed for system 1H (∼6.3 kcal/mol), likely due to the benzene–CO2 interactions, which are weaker than those between benzene and H2S. This difference in barriers seems to be correlated and potentially explains why the diffusivity of CH4 in the pore of system 1C (50CO2−1080CH4) is greater than that in system 1H (50H2S−1090CH4) (Figure 3B, right panel).

In conclusion, our simulations demonstrate that adding fluids such as CO2 or H2S impacts significantly fluid transport mechanisms in organic-rich sedimentary rocks. Particularly, CO2/H2S adsorption displaces and perhaps swells the organics, leading to noticeable differences for CH4 solubility in confinement. More importantly, CO2 and H2S facilitate CH4 transport through organic-rich caprock pores, acting as mobile carriers. Our results emphasize the importance of fluid–fluid and fluid–pore interactions, compounded by changes in the structure of confined fluids, in determining transport mechanisms of importance for geo-energy applications such as carbon sequestration in caprocks and enhanced hydrocarbon production and provide a general understanding of fluid transport in crowded pores frequently encountered in nature.

ASSOCIATED CONTENT
* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcllett.9b03751. Details about simulation models, algorithms, implementation methods, calculation procedures and results for properties of interest such as density profiles, in-plane surface density distributions, adsorption isotherms, amount of benzene displaced, cross-sectional area, and solubility of all species (CO2, H2S, CH4, and benzene) (PDF)

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Figure 4. Free-energy landscapes projected onto planes parallel to the pore surface for one CO2 (panel A) and one H2S (panel B) molecule traveling inside the crowded nanopore (system 0, with composition shown in Table 1 and Figure S1), and that for one CH4 molecule moving inside the pore of system 1C (panel C) and 1H (panel D). The results are obtained from well-tempered metadynamics simulations. The collective variables chosen are the components of the distance along the three Cartesian coordinates (x, y, z) between one molecule species i and the center of the benzene-filled pore.
Notes
The authors declare no competing financial interest.

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