TRANSPORT BEHAVIOR OF CO_2, H_2S, AND CH_4 IN [BMIM][TCM] IONIC LIQUID: A MOLECULAR DYNAMICS STUDY

Akbar Kodirov
Institute of Fundamental and Applied Research, National Research University TIIAME, Kori Niyoziy 39, 100000 Tashkent, Uzbekistan
Shakhzod Tojiev
Institute of Material Sciences, Academy of Sciences, Chingiz Aytmatov 2b, 100084 Tashkent, Uzbekistan
Javokhir Khursandov
Laboratory of Experimental Biophysics, Centre for Advanced Technologies, Universitet 7, Tashkent 100174, Uzbekistan
Jamoliddin Razzokov
Institute of Fundamental and Applied Research, National Research University TIIAME, Kori Niyoziy 39, 100000 Tashkent, Uzbekistan

Abstract. The removal of acid gases such as CO_2 and H_2S from natural gas is essential to meet environmental and processing standards, yet conventional amine solvents suffer from high energy demand and degradation. In this study, molecular dynamics simulations with umbrella sampling were used to explore the interaction and diffusion of CO_2, H_2S, and CH_4 in the ionic liquid [BMIM][TCM]. Free-energy and MSD analyses show that CO_2 and H_2S are favorably solvated, while CH_4 is excluded. The results clarify temperature-dependent solvation and diffusion mechanisms relevant to selective acid-gas capture.

Keywords: Ionic liquids, Gas solubility, Free energy profile, CO_2 capture; H_2S removal; CH_4 separation.

Annotatsiya. Tabiiy gazdan co₂ va H_2S kabi kislota gazlarini olib tashlash atrof-muhit va qayta ishlash standartlariga javob berish uchun juda muhimdir, ammo an'anaviy omin erituvchilari yuqori energiya talabi va degradatsiyadan aziyat chekmoqda. Ushbu tadqiqotda [BMIM][TCM] ionli suyuqlikdagi CO_2, H_2S va CHEFFNING o'zaro ta'siri va tarqalishini o'rganish uchun soyabon namunalari bilan molekulyar dinamika simulyatsiyalari ishlatilgan.avhum. Tabiiy gazdan co₂ va H_2S kabi kislota gazlarini olib tashlash atrof-muhit va qayta ishlash standartlariga javob berish uchun juda muhimdir, ammo an'anaviy omin erituvchilari yuqori energiya talabi va degradatsiyadan aziyat chekmoqda. Ushbu tadqiqotda [BMIM][TCM] ionli suyuqlikdagi CO_2, H_2S va CHEFFNING o'zaro ta'siri va tarqalishini o'rganish uchun soyabon namunalari bilan molekulyar dinamika simulyatsiyalari ishlatilgan. Erkin energiya va MSD tahlillari shuni ko'rsatadiki, CO_2 va h₂ lar ijobiy solvatlangan, CHOMETRIK esa bundan mustasno. Natijalar haroratga bog'liq bo'lgan solvatsiyani va diffuziya selektiv kislota-gazni olish bilan bog'liq mexanizmlar.

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Kalit so'zlar: ionli suyuqliklar, gazda eruvchanligi, Erkin energiya profili, CO_2 olish; H_2SNI olib tashlash; CHOGLOBNI ajratish.

Аннотация. Удаление кислых газов, таких как CO_2 и H_2S, из природного газа необходимо для соблюдения экологических стандартов и стандартов переработки, однако обычные аминные растворители требуют больших затрат энергии и подвергаются деградации. В этом исследовании для изучения взаимодействия и диффузии CO_2, H_2S и CH_4 в ионной жидкости [BMIM] [TCM] было использовано моделирование молекулярной динамики с использованием зонтичной выборки. Анализ свободной энергии и MSD показывает, что co_2 и H_2S положительно сольватируются, в то время как ch_4 исключается. Полученные результаты проясняют зависящие от температуры механизмы сольватации и диффузии, имеющие отношение к селективному улавливанию кислых газов.

Ключевые слова: ионные жидкости, растворимость в газах, профиль свободной энергии, улавливание CO_2; удаление H_2S; разделение ch_4.

1. Introduction

The continuous rise in global energy consumption and the dominance of fossil fuels in energy production have intensified concerns over greenhouse gas emissions, particularly carbon dioxide (CO_2) and hydrogen sulfide (H_2S). These gases, often found as impurities in natural gas streams, not only diminish fuel quality but also contribute to corrosion and severe environmental impacts (1,2). Conventional purification methods, including amine-based absorption, face major limitations such as high energy requirements, toxicity, and solvent degradation, prompting the search for more sustainable and efficient alternatives (3).

Ionic liquids (ILs), with their tunable physicochemical properties, negligible vapor pressure, and superior chemical stability, have emerged as promising candidates for gas separation and capture processes (4–6). Among these, imidazolium-based ILs have attracted significant attention owing to their structural flexibility, low volatility, and potential to selectively absorb acid gases like CO_2 and H_2S. The solubility and transport behavior of gases in ILs are strongly influenced by the choice of anion, with cyanide-based systems showing particular promise due to their low viscosity and enhanced gas affinity.

Previous studies have demonstrated that introducing cyano-functional groups into the anion framework significantly improves gas solubility and diffusivity. For instance, ILs containing thiocyanate or dicyanamide anions have exhibited favorable CO_2 and H_2S permeation characteristics (7,8). However, the tricyanomethanide ($[TCM]^-$) anion, despite its high electron-withdrawing capacity and ability to stabilize guest molecules through multiple CN interactions, remains less explored in this context. Its unique molecular configuration offers a distinctive

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environment for gas interaction, potentially improving the thermodynamic and kinetic parameters governing permeation.

In this study, we employ molecular dynamics (MD) simulations using the umbrella sampling approach to investigate the permeation behavior of CO_2, H_2S, and CH_4 gases in the [BMIM][TCM]. By analyzing the free energy profiles and interfacial behavior across different conditions, we aim to elucidate the molecular mechanisms governing gas transport in this system. The results are expected to deepen our understanding of how cyano-rich anions influence gas solvation and provide valuable insights for designing next-generation ILs optimized for efficient gas capture and separation technologies.

2. Computational method

All MD simulations were conducted using the GROMACS 2021.4 package with GPU acceleration [55]. The system under investigation consisted of a single imidazolium-based ionic liquid, 1-butyl-3-methylimidazolium tricyanomethanide ([BMIM][TCM]). The force field parameters for the [BMIM][TCM] IL were obtained from previously validated studies (9), while gas molecule parameters for CO_2 (10), H_2S (11), and CH_4 (12) were adopted from established literature sources.

The initial configuration of the IL was constructed using the Packmol software, containing 500 $[BMIM]^+$ cations and 500 $[TCM]^-$ anions. The system was first minimized using the steepest descent algorithm to remove any unfavorable contacts, followed by equilibration for 100 ns in the isothermal–isobaric (NPT) ensemble at 298 K and 1 bar. The pressure and temperature were maintained using a semi-isotropic Parrinello–Rahman barostat (13) with a compressibility constant of 4.5×10^{-5} bar^{-1} and a Nose–Hoover thermostat (14) with a coupling constant of 1.0 ps. Nonbonded interactions were truncated at 1.3 nm, and long-range electrostatics were treated with the particle-mesh Ewald (PME) method using a grid spacing of 0.15 nm. The resulting equilibrium densities were in good agreement with experimental data, confirming the validity of the chosen parameters.

To model the vacuum–ionic liquid interface, the equilibrated [BMIM][TCM] system was extended in the z-direction and centered in a rectangular simulation box of $5.8 \times 5.8 \times 15$ nm^3 (Fig. 1a). The system was further equilibrated for 100 ns under the canonical (NVT) ensemble to ensure stable distribution between bulk and vacuum phases. This configuration was then used for subsequent umbrella sampling (US) simulations to evaluate the permeation behavior of CO_2, H_2S, and CH_4.

Free energy profiles (FEPs) for gas permeation through [BMIM][TCM] were computed using the US technique (8,15). Three independent configurations were extracted from the final 100 ns of the NVT equilibration at 90, 95, and 100 ns to

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ensure statistical reliability. For each gas species, six molecules were placed along the z-axis at intervals of 1.3 nm, spanning the interface region from −3.8 to 3.8 nm (Fig. 1). The gas molecules were restrained along the z-direction with a harmonic potential of 2000 $kJ \cdot mol^{-1} \cdot nm^{-2}$, while lateral (xy-plane) motion was confined within a flat-bottom potential of 0.4 nm radius using a force constant of 500 $kJ \cdot mol^{-1} \cdot nm^{-2}$. Each umbrella window was simulated for 5 ns, with the last 4 ns used for data collection. In total, 576 sampling windows were generated for each gas type, corresponding to a cumulative simulation time of 1.44 μs. The weighted histogram analysis method (WHAM) was applied to reconstruct the FEPs from the biased trajectories. The symmetric profiles obtained confirmed adequate sampling and convergence. Representative snapshots and system configurations were visualized using the VMD software package (16).

Diffusion coefficients of CO_2, H_2S, and CH_4 were determined by inserting 24 gas molecules into the bulk [BMIM][TCM] system. Following equilibration, 100 ns production runs were carried out at 298 and 373 K. Mean squared displacement (MSD) data were collected over the final 10 ns of each trajectory, and diffusion coefficients were extracted using the Einstein relation from the linear regime of the MSD curves.

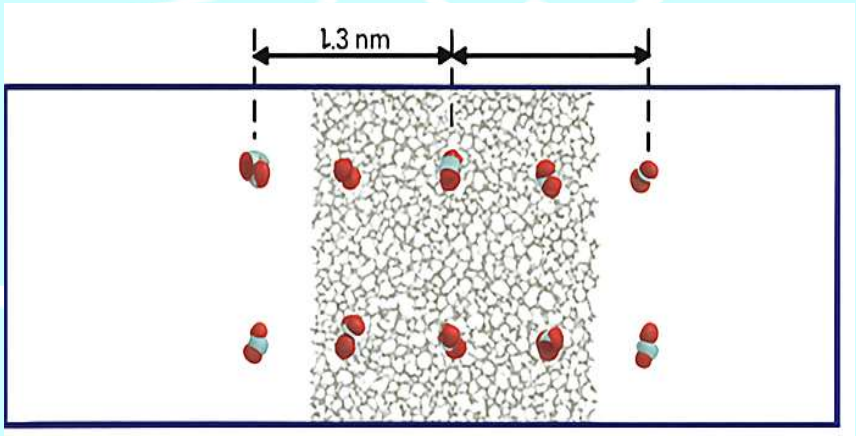


Figure 1. Side view of the [BMIM][TCM] ionic liquid with CO_2 molecules positioned along the z-axis at 1.3 nm intervals.

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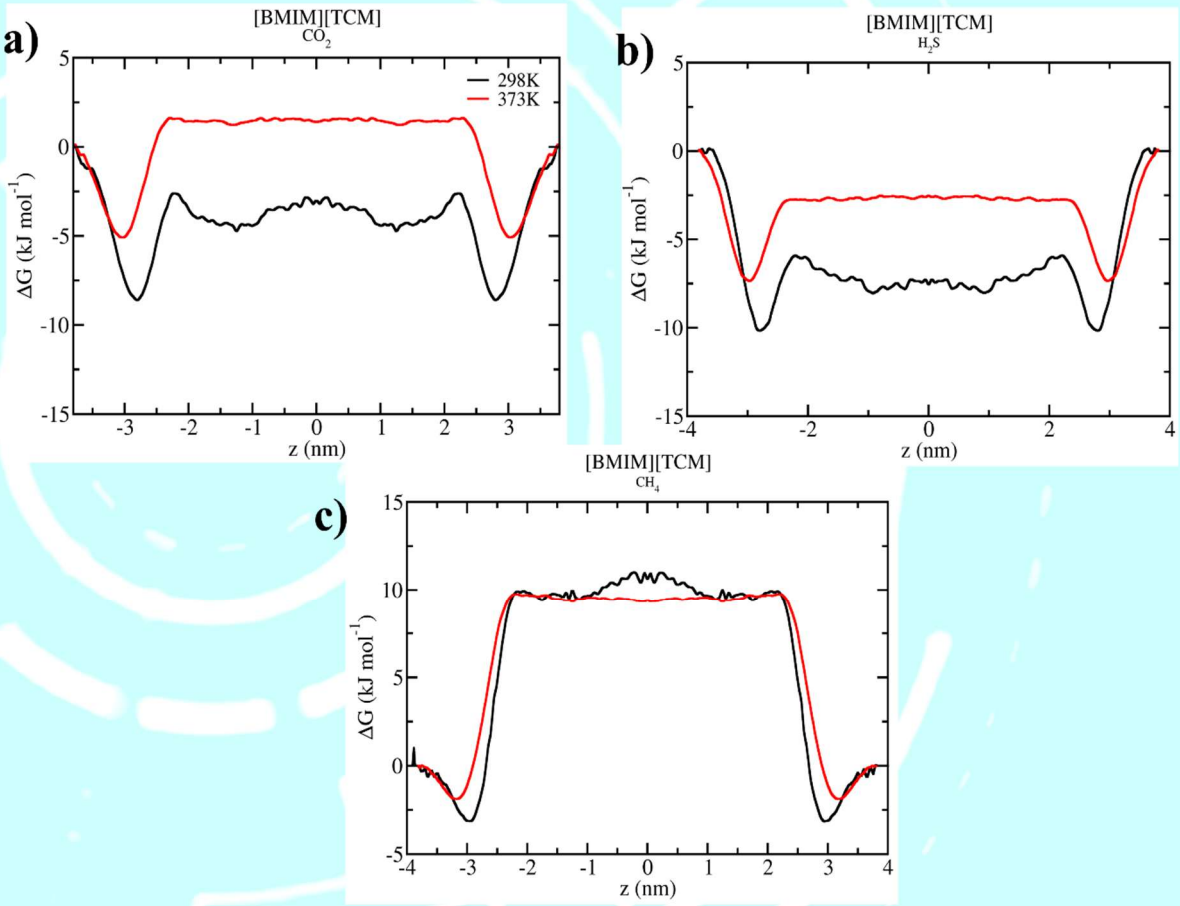


Figure 2. FEPs for CO_2 (a), H_2S (b) CH_4 (c) in [BMIM][TCM].

3. Results and discussion

3.1 Free Energy Profiles and Temperature Dependence

At 298 K, the FEPs for CO_2 exhibits two pronounced interfacial minima around $|z| \approx 3$ nm (≈ -8.5 kJ mol^{-1}) and a moderately negative bulk region (≈ -2.2 kJ mol^{-1}). These features indicate thermodynamically favorable adsorption at the IL surface and diffusion into the bulk. The stabilization arises mainly from quadrupole–anion interactions between CO_2 and $[TCM]^-$, as well as cation–π interactions with the imidazolium ring of $[BMIM]^+$. Upon heating to 373 K, the FEPs profile becomes shallower, with the bulk ΔG approaching 0 kJ mol^{-1} and interfacial wells decreasing to about −5 kJ mol^{-1}, reflecting entropic weakening of these directional interactions and consistent with the easier desorption of CO_2 at elevated temperatures.

In contrast, H_2S shows deeper free-energy minima at 298 K, with interfacial wells of about −10 kJ mol^{-1} and a bulk plateau near −6.7 kJ mol^{-1}, indicating stronger overall stabilization. This originates from hydrogen bonding between H_2S hydrogens and the nitrogen atoms of $[TCM]^-$, complemented by weak electrostatic attraction to the $[BMIM]^+$ cation. At 373 K, both interfacial and bulk wells reduced in depth (≈ -7.3 and -2.6 kJ mol^{-1}, respectively) but remain negative, confirming that H_2S–IL interactions are more thermally robust than those of CO_2.

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For CH_4, the FEPs at both temperatures reveal no significant stabilization. The bulk region remains strongly positive (≈ +9.5 kJ mol^{-1}), with only minor interfacial depressions (≈ −3 kJ mol^{-1}), demonstrating the incompatibility of nonpolar CH_4 with the polar IL matrix.

Overall, both CO_2 and H_2S exhibit negative bulk free energies at 298 K, confirming their favorable solvation, while CH_4 is excluded. Among these gases, H_2S displays the most negative bulk ΔG, implying higher solubility within the IL core. The temperature-dependent flattening of the FEPs reflects the exothermic nature of gas absorption, where enthalpic stabilization decreases as thermal motion increases. The selectivity sequence at 298 K follows: $H_2S > CO_2 \gg CH_4$. At 373 K, CO_2 stabilization nearly vanishes while H_2S retains moderate affinity, suggesting enhanced H_2S selectivity under regeneration conditions. Consequently, [BMIM][TCM] can efficiently capture CO_2 and H_2S at room temperature, while elevated temperature facilitates CO_2 release and suppresses CH_4 co-absorption, improving overall process efficiency.

3.2 Diffusion Coefficient Analysis

MSD calculations from 100 ns NVT trajectories yielded self-diffusion coefficients of 0.758×10^{-6}, 0.993×10^{-6}, and 1.073×10^{-6} $cm^2\ s^{-1}$ for CO_2, H_2S, and CH_4, respectively, at 298 K. The diffusivity trend ($D_{CH_4} > D_{H_2S} > D_{CO_2}$) aligns with the FEPs-derived free-energy landscapes.

CO_2 diffuses slowest due to strong quadrupole–anion and cation–π interactions, which form localized energy wells (≈ −8.5 kJ mol^{-1}) and increase local friction. H_2S, although more stabilized thermodynamically (ΔG ≈ −6.7 kJ mol^{-1}), exhibits slightly higher mobility, indicating that its hydrogen-bond and dipolar interactions are transient and reversible, producing a smoother energy landscape. CH_4, with negligible interactions, diffuses through transient free-volume voids, yielding the highest apparent diffusivity despite poor solvation.

These results establish a clear structure–dynamics correlation: deeper free-energy wells correspond to reduced mobility, whereas weakly interacting species diffuse faster but are thermodynamically unfavorable. Thus, [BMIM][TCM] functions as a selective sorbent for polar gases (CO_2 and H_2S) while restricting the motion of nonpolar CH_4.

Conclusion

Molecular dynamics simulations revealed that the [BMIM][TCM] provides a selective environment for CO_2 and H_2S absorption while excluding CH_4. Free energy analysis demonstrated that both CO_2 and H_2S exhibit favorable solvation at 298 K, whereas CH_4 remains thermodynamically unstable within the liquid phase. Increasing the temperature to 373 K weakened gas–liquid interactions, confirming the exothermic nature of absorption and suggesting efficient CO_2 desorption under

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regeneration conditions. Diffusion results supported the thermodynamic trends, with higher mobility observed for weakly interacting gases. These findings highlight the potential of [BMIM][TCM] as an efficient and regenerable medium for selective acid-gas capture in natural gas purification.

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