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FREE ENERGY ANALYSIS OF CO_2, H_2S, AND CH_4 IN CYANO-FUNCTIONALIZED IONIC LIQUIDS: EFFECT OF TEMPERATURE AND ANION STRUCTURE

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Annotatsiya. Ushbu tadqiqotda 298 K va 373 K haroratlarda [EMIM][SCN] va [EMIM][DCA] ion suyuqliklarida karbonat angidrid (CO_2), vodorod sulfidi (H_2S) va metan (CH_4) gazlarining permeatsiya termodinamikasi molekulyar dinamika modellashtirish va umbrella sampling usuli yordamida o‘rganildi. Vakuum-suyuqlik interfeysi bo‘ylab erkin energiya profillari hisoblandi. Natijalar shuni ko‘rsatadiki, H_2S har ikkala ion suyuqlikda eng qulay solvatsiya xususiyatiga ega bo‘lib, chuqur manfiy erkin energiya minimumlari bilan tavsiflanadi va [EMIM][SCN] da 298 K da deyarli to‘siqsiz bulk fazaga o‘tadi. CO_2 o‘rtacha darajada barqarorlashadi va interfeysga aniq moyillik ko‘rsatadi, CH_4 esa musbat erkin energiya to‘siqlari (+6 dan +9 kJ mol^{-1} gacha) bilan tavsiflanib, suyuqlik ichida noqulay solvatsiyani bildiradi. Harorat oshishi barcha gazlar uchun erkin energiya minimumlarini kamaytiradi, eng katta ta’sir CO_2 uchun kuzatiladi, bu esa harorat asosidagi desorbsiyani osonlashtiradi. Anionlar taqqoslanganda, SCN^- H_2S absorbsiya jarayonini kuchaytiradi, DCA^- esa CO_2 uchun biroz kuchliroq interfeys barqarorligini ta’minlaydi. Har ikkala ion suyuqlik CH_4 ni bulk fazaga kirishini samarali ravishda cheklaydi. Ushbu natijalar gaz–ion suyuqlik o‘zaro ta’sirlarini molekulyar darajada tushuntiradi va selektiv kislota gazlarini ajratish uchun ion suyuqliklarni loyihalashda anion tuzilishining muhimligini ko‘rsatadi.

Kalit so‘zlar: ion suyuqliklar; molekulyar dinamika; umbrella sampling; erkin energiya profili; gazlarni ajratish

Аннотация. В данной работе исследована термодинамика проницаемости газов - диоксида углерода (CO_2), сероводорода (H_2S) и метана (CH_4) - в ионных жидкостях [EMIM][SCN] и [EMIM][DCA] при температурах 298 K и 373 K с использованием молекулярно-динамического моделирования и метода umbrella sampling. Профили свободной энергии были рассчитаны вдоль границы вакуум-жидкость. Полученные результаты показывают, что H_2S демонстрирует наиболее благоприятное поведение солватации в обеих ионных жидкостях, характеризуясь глубокими отрицательными

ISSN 3030-3907

минимумами свободной энергии, а в случае [EMIM][SCN] - практически безбарьерным переходом в объемную фазу при 298 K. CO_2 проявляет умеренную стабилизацию и выраженную склонность к интерфейсной области, тогда как CH_4 характеризуется положительными барьерами свободной энергии (+6…+9 кДж·моль$^{-1}$), что свидетельствует о неблагоприятной солватации в объеме жидкости. Повышение температуры приводит к уменьшению глубины минимумов свободной энергии для всех газов, причем наиболее выраженный эффект наблюдается для CO_2, что указывает на благоприятные условия для температурной десорбции. Сравнение анионов показывает, что SCN^- усиливает поглощение H_2S, тогда как DCA^- обеспечивает несколько более сильную стабилизацию CO_2 в интерфейсной области. Обе ионные жидкости эффективно препятствуют проникновению CH_4 в объемную фазу. Полученные результаты дают молекулярное представление о взаимодействиях газ-ионная жидкость и подчеркивают важность структуры аниона при разработке ионных жидкостей для селективного извлечения кислых газов.

Ключевые слова: ионные жидкости; молекулярная динамика; метод зонтичной выборки; профиль свободной энергии; разделение газов.

Abstract. This study investigates the thermodynamics of gas permeation for carbon dioxide (CO_2), hydrogen sulfide (H_2S), and methane (CH_4) in the ionic liquids [EMIM][SCN] and [EMIM][DCA] at 298 K and 373 K using molecular dynamics simulations with umbrella sampling. Free energy profiles were calculated along the vacuum-liquid interface. The results show that H_2S exhibits the most favorable solvation behavior in both ionic liquids, with deep negative free energy minima and, in [EMIM][SCN], nearly barrierless transfer into the bulk phase at 298 K. CO_2 displays moderate stabilization and a clear preference for the interfacial region, whereas CH_4 is characterized by positive free energy barriers (+6 to +9 kJ mol^{-1}), indicating unfavorable solvation in the liquid interior. Increasing temperature reduces the magnitude of free energy minima for all gases, with the strongest effect observed for CO_2, suggesting favorable conditions for temperature-driven desorption. Comparison of the two anions shows that SCN^- enhances H_2S absorption, while DCA^- provides slightly stronger interfacial stabilization for CO_2. Both ionic liquids effectively exclude CH_4 from the bulk phase.

These findings provide molecular-level insight into gas-ionic liquid interactions and highlight the importance of anion structure in designing ionic liquids for selective acid gas separation.

Keywords: ionic liquids; molecular dynamics; umbrella sampling; free energy profile; gas separation.

ISSN 3030-3907

1. INTRODUCTION

Natural gas remains one of the primary feedstocks for global energy production, yet raw gas streams routinely contain acid gas impurities principally CO_2 and H_2S that must be removed prior to downstream utilization [1, 2]. The presence of CO_2 reduces the calorific value of the fuel, while H_2S poses acute toxicological risks and initiates severe corrosion of steel infrastructure [3-5]. The benchmark technology for sour gas removal, aqueous alkanolamines, has been in industrial service for decades; however, these systems are burdened by solvent degradation, corrosive byproducts, substantial regeneration energy penalties, and significant volatility losses [6, 7]. These well-documented limitations continue to motivate the search for alternative capture media with superior thermochemical properties.

Room-temperature ionic liquids (RTILs) have attracted sustained interest as solvent platforms for gas capture and separation, driven by their negligible vapor pressure, high thermal and chemical stability, wide liquid-phase temperature windows, and the structural tunability afforded by the independent selection of cation and anion building blocks [8, 9]. Among the broad RTIL chemical space, imidazolium-based ILs bearing cyano-functionalized anions particularly thiocyanate (SCN^-) and dicyanamide (DCA^-), occupy a privileged position owing to their exceptionally low dynamic viscosities (~15–25 mPa·s at 298 K), which facilitate mass transfer and reduce pumping costs compared to more viscous RTIL families [10-12]. The structural distinction between these two anions - the monovalent thiocyanate carrying a single cyano group and a sulfur terminus versus the bifurcated dicyanamide bearing two equivalent cyano arms which gives rise to measurable differences in gas solvation thermodynamics and IL microstructure that are not yet fully resolved at the molecular level.

Experimental investigations by Lim et al. and others established that CO_2 solubility in imidazolium ILs with cyanide-based anions increases with the number of cyano groups, placing DCA^- systems above SCN^- in CO_2 absorption capacity [13, 14]. These macroscopic observations, however, provide limited mechanistic insight into the free energy barriers governing gas transfer across the vacuum–liquid interface, the depth and location of solvation energy minima, and the role of the anion in structuring the local solvent environment around dissolved gas molecules. Molecular dynamics (MD) simulations with enhanced sampling techniques offer a powerful route to access this microscopic detail at both thermodynamically and kinetically relevant resolution [15, 16].

In this work, molecular dynamics simulations combined with umbrella sampling are used to investigate the free energy profiles of CO_2, H_2S, and CH_4 in

ISSN 3030-3907

[EMIM][SCN] and [EMIM][DCA] at 298 K and 373 K. The calculated free energy profiles provide insight into the thermodynamics of gas transfer from the vapor phase into the ionic liquid and help clarify how anion structure and temperature influence gas solvation behavior.

2. COMPUTATIONAL METHODS

2.1. Force Field Parameterization and System Preparation

All MD simulations were carried out with GROMACS 2021.4 utilizing GPU acceleration. Force field parameters for these ILs [17], and for CO_2 [16], H_2S [18], and CH_4 [19] were taken from previous studies. Each bulk IL model consisted of 500 cation–anion pairs assembled using the PACKMOL software [25]. Initial configurations were subjected to steepest-descent energy minimization, after which the systems were equilibrated for 40 ns in the isothermal–isobaric (NPT) ensemble at 298 K and 1 bar. Pressure was controlled with a semi-isotropic Parrinello–Rahman barostat [26] using a relaxation time of 1.0 ps and a compressibility of 4.5×10^{-5} bar^{-1}. Temperature was maintained with a Nosé–Hoover thermostat (relaxation time 1.0 ps). A real-space cutoff of 1.3 nm was applied to non-bonded interactions, and long-range electrostatics were handled by the particle mesh Ewald (PME) method with a reciprocal-space grid spacing of 0.15 nm. The density profiles of equilibrated IL models were compared with experimental literature data to validate the force field accuracy before proceeding to production simulations.

2.2. Vacuum–Liquid Interface and Umbrella Sampling

To construct a well-defined vacuum–IL interface, the equilibrated bulk systems were extended along the z-direction and placed at the center of a tetragonal simulation box of dimensions x = 5.0 nm, y = 5.0 nm, z = 15.0 nm, generating two equivalent liquid–vacuum boundaries. The extended systems were equilibrated in the NVT ensemble for 40 ns at each target temperature (298 K and 373 K) before FEP production. Umbrella sampling (US) was employed to compute the potential of mean force (PMF) along the z-axis as a function of gas position relative to the IL slab center. Six gas molecules per simulation were arranged on a regular xy-grid and distributed at 1.3 nm intervals along the z-axis, spanning the range −3.8 to +3.8 nm. A harmonic position restraint of 2000 kJ mol^{-1} nm^{-2} was applied along z to each gas molecule. Lateral diffusion was suppressed by flat-bottomed cylindrical position restraints (radius 0.4 nm, force constant 500 kJ mol^{-1} nm^{-2}) to reduce computational expense without compromising thermodynamic accuracy. Each US window was simulated for 5 ns, of which the final 4 ns were retained for analysis. Three independent starting configurations (extracted at 30, 35, and 40 ns of the NVT equilibration) and four independent simulation replicas per configuration were used per gas per IL, yielding 12 individual PMF curves whose average

ISSN 3030-3907

constitutes the reported FEP. A total of 576 US windows were used per system–temperature combination, corresponding to approximately 1.44 μs of aggregate simulation time. PMFs were reconstructed with the weighted histogram analysis method (WHAM) [29].

3. Results and Discussion

3.1. Free Energy Profiles of Gas Permeation

3.1.1. CO_2 Permeation

The FEPs for CO_2 in [EMIM][SCN] and [EMIM][DCA] at both temperatures are shown in Figure 1a and 1b. In both ILs, the profile exhibits two symmetrically placed negative minima located near the vacuum–liquid interface, flanked by a plateau-like region of near-constant free energy within the IL bulk. At 298 K, the interfacial minimum for [EMIM][SCN] reaches approximately -7.7 kJ mol^{-1}, while [EMIM][DCA] displays a marginally deeper well of about -7.9 kJ mol^{-1}. This ordering is consistent with prior experimental reports demonstrating that the DCA^- anion affords slightly higher CO_2 solubility than SCN^- at ambient temperature [20], a trend attributed to the greater charge delocalization of DCA^- and the consequent enhancement of electrostatic and induction interactions with the CO_2 quadrupole moment.

The bulk region of both FEPs at 298 K lies between -3.1 and -3.3 kJ mol^{-1}, indicating that once CO_2 has crossed the interface, its further translocation into the IL interior involves no additional free energy barrier. However, the interface minimum is substantially deeper than the bulk plateau, suggesting that CO_2 preferentially accumulates at the liquid–vacuum boundary rather than distributing uniformly throughout the bulk. This interfacial preference is corroborated by the density profile simulations, where CO_2 density near the interface is approximately four times higher than in the bulk.

At 373 K, both FEPs shift upward toward zero: the interfacial wells become significantly shallower and the bulk plateau approaches ≈0 kJ mol^{-1}. This strong temperature sensitivity reflects the unfavorable entropic cost of immobilizing a gas molecule within the structured ionic environment at elevated thermal energies. The substantial reduction in CO_2 solvation free energy between 298 K and 373 K implies that temperature-swing regeneration of CO_2-loaded [EMIM] ILs is thermodynamically straightforward, since the solvation driving force is nearly eliminated at the higher temperature.

3.1.2. H_2S Permeation

Among the three gases examined, H_2S demonstrates the most favorable interaction with both ILs across the full z-range (Figure 1c and 1d). At 298 K, the FEP for H_2S in [EMIM][SCN] attains a minimum of approximately −16 kJ mol^{-1} at

ISSN 3030-3907

the interface and remained negative throughout the bulk, with only a negligible barrier (≈1 kJ mol^{-1}) separating the interfacial minimum from the bulk plateau. This near-barrierless entry into the [EMIM][SCN] bulk indicates spontaneous and rapid absorption at room temperature. In [EMIM][DCA], the interfacial minimum was -12 kJ mol^{-1}, but a small yet discernible free energy barrier of approximately 4–5 kJ mol^{-1} existed between the interface and the bulk, suggesting a mild kinetic resistance to full bulk solvation in the DCA^--based system.

The strong solvation of H_2S in both ILs can be explained by several factors. H_2S is a weakly polar protic molecule (μ = 0.97 D) capable of hydrogen-bond-like interactions to basic anion sites. The SCN^- anion offers both a nitrogen acceptor (N···H–S) and a sulfur terminus that participates in soft Lewis base–acid interactions, whereas the DCA^- anion provides two equivalent nitrogen acceptors that can simultaneously interact with H_2S molecules. The deeper interfacial minimum in [EMIM][DCA] is consistent with the higher density of basic nitrogen sites per anion in this system. At 373 K, both FEPs shift upward by 4–6 kJ mol^{-1}, but the bulk free energy in [EMIM][SCN] remains well below zero, confirming that H_2S absorption in this IL is robust even at elevated temperatures. This temperature resilience distinguishes H_2S solvation from that of CO_2 and has direct implications for the design of selective two-stage absorption–regeneration cycles.

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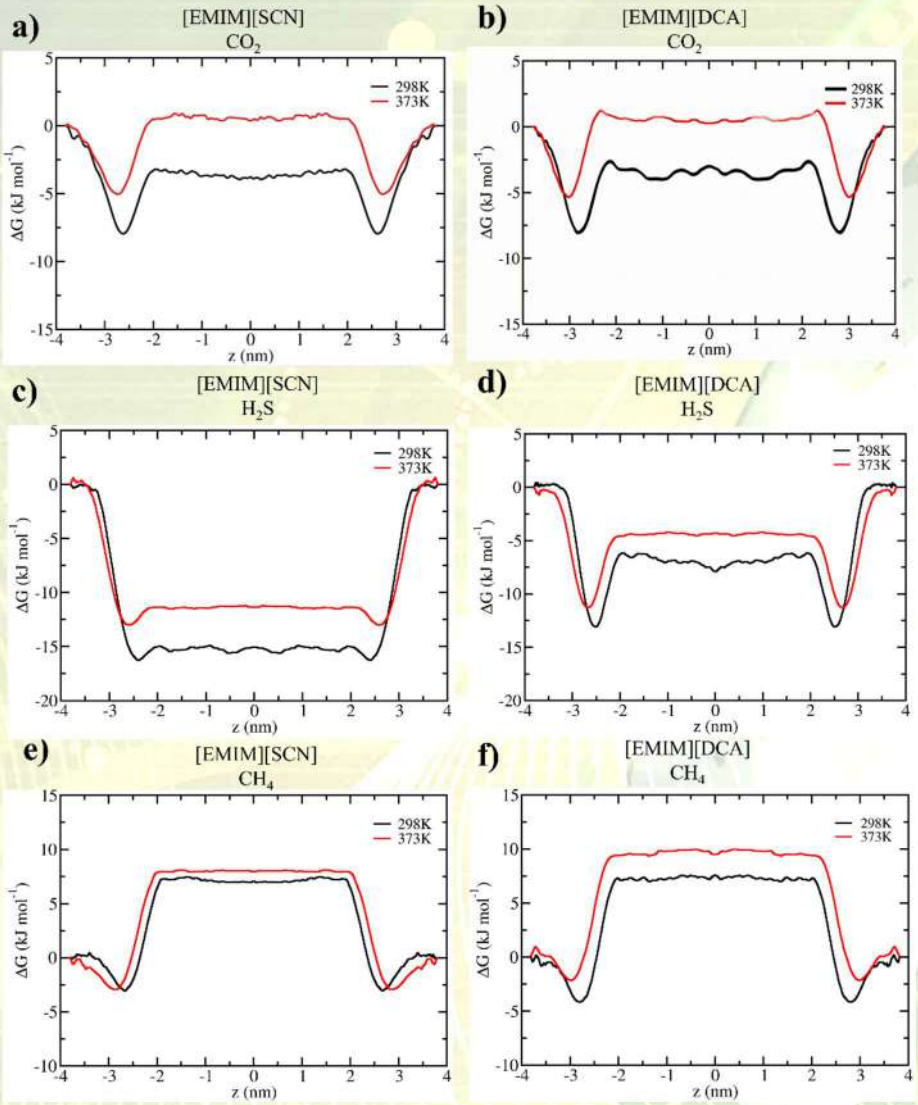


Figure 1. Free energy profiles (PMFs) of CO_2, H_2S, and CH_4 across the vacuum–liquid interface in [EMIM][SCN] and [EMIM][DCA] at 298 K and 373 K.

3.1.3. CH_4 Permeation

The FEPs for CH_4 display a qualitatively distinct topology (Figure 1e and 1f). Both [EMIM][SCN] and [EMIM][DCA] present large positive free energy barriers within the IL bulk at 298 K, reaching approximately +7.5 kJ mol^{-1} and +7.4 kJ mol^{-1}, respectively. Near the interface, shallow negative minima of −3 to −3.1 kJ mol^{-1} are observed, indicating that interfacial adsorption can occur without significant resistance; however, penetration into the IL bulk is strongly disfavored. This behavior is mechanistically consistent with the nonpolar, spherically symmetric character of CH_4: the absence of a permanent multipole moment and low polarizability preclude the specific interactions that stabilize CO_2 and H_2S in the ionic environment. Instead, the positive solvation free energy reflects the

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dominant cavity formation cost, which is not compensated by solute–solvent van der Waals attractions.

Collectively, the FEPs for all three gases establish a clear solvation hierarchy: H_2S > CO_2 > CH_4. H_2S enters both ILs spontaneously and retains negative free energies throughout the bulk, CO_2 preferentially accumulates at the interface with limited bulk penetration, and CH_4 is effectively excluded from the IL interior by large positive barriers. These results demonstrate that both [EMIM][SCN] and [EMIM][DCA] possess inherent thermodynamic selectivity for acid gases over methane, making them promising candidates for natural gas sweetening applications.

4. CONCLUSIONS

This study presents a molecular-level analysis of gas permeation in [EMIM][SCN] and [EMIM][DCA] ionic liquids based on free energy profiles obtained from molecular dynamics simulations with umbrella sampling. The results clearly demonstrate that gas solvation behavior is strongly dependent on both gas identity and anion structure.

H_2S exhibits the most favorable thermodynamics in both ionic liquids, characterized by deep interfacial minima and, in the case of [EMIM][SCN], nearly barrierless transfer into the bulk phase. In contrast, CO_2 shows moderate stabilization, with a clear preference for the interfacial region and limited driving force for bulk solvation. CH_4 displays unfavorable thermodynamics, with positive free energy barriers in the bulk phase, indicating effective exclusion from the ionic liquid interior.

Temperature has a significant impact on gas solvation. Increasing the temperature from 298 K to 373 K reduces the magnitude of free energy minima for all gases, with the most pronounced effect observed for CO_2. This behavior suggests that temperature-swing processes may be effective for CO_2 desorption, while H_2S remains relatively stable within the ionic liquid phase.

Comparison between the two anions highlights their distinct roles in gas absorption. The SCN^- anion promotes stronger interactions with H_2S and enables efficient bulk solvation, whereas the DCA^- anion provides slightly enhanced interfacial stabilization for CO_2. For CH_4, both ionic liquids exhibit similar behavior, confirming that methane rejection is primarily governed by unfavorable cavity formation.

Overall, these findings indicate that cyano-functionalized imidazolium ionic liquids can provide selective separation of acid gases from methane, with anion choice serving as a key parameter for tuning absorption performance. The results

ISSN 3030-3907

contribute to a clearer understanding of gas–ionic liquid interactions and may assist in the rational design of improved absorbents for natural gas sweetening.

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