**Selective CO2 separation through physicochemical absorption by triazole-functionalized ionic liquid binary absorbents**

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**Abstract**

The selective separation of CO2 from CH4-containing gases is crucial to produce clean energy gases. In this study, triazole anion-functionalized ionic liquids (TAFILs) were designed by combining low molecular weight cations with triazole anions containing N electronegative site, and further mixed with physical solvents to form physicochemical absorbents. The results indicated that [Cho][Triz]/TMS (80 wt%/20 wt%) not only absorb 0.125 g CO2/g absorbent equal to that of 30 wt% MEA solution at 40 °C and 1 bar, but also have low enthalpy of -35.76 kJ/mol less than half of 30 wt% MEA solution. Simultaneously, superhigh CO2/CH4 selectivity of 191.0 higher than most of reported absorbents is obtained for [Cho][Triz]/TMS solvents. Such great performance of CO2 separation was attributed to relatively weak chemical and physical interaction between CO2 and TAFIL binary absorbents. This study may provide novel promising IL absorbents for CO2 capture applications from clean energy gases.

**Keywords:** Ionic liquids, triazole anion, CO2/CH4 separation, thermodynamic analysis

**Highlights:**

* TAFILs were combined with physical solvents to form the physicochemical absorbents.
* TAFIL absorbent exhibited excellent CO2/CH4 selectivity up to 191.0.
* CO2 mass solubility of TAFIL absorbent was equal to that of 30 wt% MEA solution.
* Absorption enthalpy of TAFIL absorbent was less than half of 30 wt% MEA solution.

# INTRODUCTION

The continuous emission of carbon dioxide (CO2) in the atmosphere is directly associated with global warming. In recent, the total emissions of CO2 have been raising very quickly to 36.3 gigatons (Gt)1,2. Environmental concerns regarding the accumulation of fossil-fuel-based energy sources have prompted a shift towards exploiting and utilizing sustainable energy sources such as clean energy gases, including natural gas, shale gas, biomethane and so on3. The main component of these gases is methane (CH4), and others are 30~70% CO2 and trace amounts of hydrogen (H2), nitrogen (N2), sulfuretted hydrogen (H2S), and other gases1,4. The calorific value and quality of crude natural gas were reduced due to the presence of CO2, and CO2 is acidic and corrosive to equipment and pipelines in the presence of moisture, which increases the cost of transportation5-7. The common methods of CO2 separation are absorption8, adsorption5 and cryogenic technologies9. Amine aqueous solutions were considered as the preferred method for CO2 capture, but it could cause high energy consumption during regeneration due to strong chemical interaction between the amine group and CO2 as well as a number of water evaporation10,11. In order to realize efficient and energy-saving CO2 separation, the development of new absorbents with high CO2 selectivity and CO2 capacity, easy desorption and regeneration is desirable for gas purification.

Ionic liquids (ILs) have been proposed as promising solvents for gas separation because of their low volatility, high gas affinity and tunable properties12-14. Wang et al.15 reported CO2/CH4 selectivity of four conventional ILs including [N2222][PF6], [N4444][PF6], [C12mim][PF6] and [C16mim][PF6] from 1 to 40 bar at 30 °C. The results showed that the imidazolium ILs have a higher CO2/CH4 selectivity than ammonium ILs due to the larger free volume for CO2 accommodation induced by long alkyl chains of cations. For example, [C12mim][PF6] and [C16mim][PF6] showed CO2/CH4 selectivity ranging from 9.0~19.0, while [N2222][PF6] and [N4444][PF6] had CO2/CH4 selectivity of only 1.0~6.0. Shaahmadi et al.16 investigated two conventional ILs ([Bmim][Ac] and [Bmim][BF4]) and their binary mixtures for CO2/CH4 separation at 25~45 °C and pressures up to 50 bar. The results revealed that the pure IL [Bmim][Ac] shows higher CO2 solubility than [Bmim][BF4], and the ideal CO2/CH4 selectivity of 25 wt% [Bmim][Ac]/75 wt% [Bmim][BF4] is about 24.0 at 25 °C and 1 bar. In addition to non-functionalized ILs, Zeng et al.17 designed and synthesized three ether-functionalized pyridinium ILs [EnPy][NTf2] with low viscosity to improve CO2/CH4 separation performance. Compared to the non-functionalized analogs [CmPy][NTf2] (m= 4, 7, 10), the viscosity of [EnPy][NTf2] (n= 1, 2, 3) greatly reduced due to the introduction of ether groups, and their CO2/CH4 selectivity improved to 16.9~17.2 at 40 °C for pressures up to 22 bar. Among them, CO2/CH4 selectivity of [E3Py][NTf2] was improved by 66.4% over that of [C10Py][NTf2] with the same chains length. The reason was that the incorporation of ether groups in the cation significantly reduces CH4 solubility, while it does not have a substantial influence on CO2 solubility, thus resulting in higher CO2/CH4 selectivity in ether-functionalized ILs. In contrast, the introduction of nitrile groups into ILs was useful in improving CO2 solubility and selectivity due to the polar nature. Carlisle et al.18 measured the CO2/CH4 selectivity of nitrile-functionalized ILs [NC-Cnmim][Tf2N], which was up to 13.0~18.0 at 40 °C and 1 bar.

Besides the above physisorption ILs for CO2 capture, a series of functionalized ILs for chemical absorption of CO2 were also developed to further improve CO2 separation performance, including amino19 and non-amino ILs20. For example, Saravanamurugan et al.21 synthesized four amino acid ILs that comprised ammonium cations and anions of naturally occurring amino acids which contain an additional amine group. Among them, the absorption capacity of [N66614][Lys] was up to 2.10 mol CO2/mol IL (0.125 g CO2/g IL) at 22 °C and 1 bar, but less than 85% of the absorbed CO2 in IL could be released at 80 °C in 4 h during three absorption-desorption cycles, which implies poor desorption efficiency. In order to solve this problem, Wang et al.22 proposed a new strategy to tune the enthalpy of CO2 absorption by basic ILs. The basic ILs could achieve equimolar absorption of CO2, and the absorption enthalpy of [P66614][Triz] was only -56.4 kJ/mol, which is much lower than that of 30 wt% MEA aqueous solution (-85 kJ/mol). However, the IL had a relatively high viscosity of over 810 mPa∙s at 25 °C, and the data on CH4 solubility and CO2/CH4 selectivity were not covered. Alcantara et al.23 synthesized two protic ILs ([m-2HEA][Pr] and [BHEA][Bu]) and studied CO2 and CH4 solubilities from 40 to 80 °C. It was found that the highest CO2/CH4 selectivity is approximately 10.0 at 40 °C under 25 bar, along with the low CO2 mass solubility of 0.005~0.073 g CO2/g IL. Meanwhile, to reduce the viscosity of ILs and enhance the mass transfer, Chen et al.24 studied the solubility of pure CO2, CH4, and N2 in the mixture of [Cho][Pro] and PEG200 as a cosolvent with low viscosity at 35~65 °C and pressures up to 28 bar. It was found that CO2/CH4 selectivity in [Cho][Pro]/PEG200 with the mass ratio of 1:2 is high up to 185.0 at 65 °C and about 3 bar due to the chemical interaction between the anion [Pro]- and CO2, but the relatively low mass solubility of 0.044 g CO2/g absorbent is obtained under the same conditions.

Based on the above [analysis](javascript:;), to develop novel absorbents with high CO2 mass solubility, high CO2/CH4 selectivity, low viscosity and low absorption enthalpy, the triazole anion with the N electronegative site was selected because of its weak chemical interaction with CO2 for equimolar absorption and low absorption enthalpy. Meanwhile, quaternary ammonium cations (e.g. [N2222]+, [Cho]+) with short alkyl chains were chosen due to the low weight of molecules, which could contribute to the high solubility of CO2 mass and easy preparation. Hence, the triazole anion-functionalized ionic liquids (TAFILs) were designed and synthesized by one-step reaction. The organic solvent (e.g. TMS or NFM) with a high boiling point was further added to the TAFILs for preparing the novel physicochemical absorbents, which reduce the viscosity of the TAFIL systems and enhance gas-liquid mass transfer. The CO2 and CH4 solubilities of TAFILs and TAFIL binary absorbents were systematically investigated at 40~60 °C and up to 25 bar. The temperature dependence of CO2 and CH4 solubility was correlated using the modified deactivated model to calculate CO2/CH4 selectivity and the thermodynamic parameters, including enthalpy (Δ*reaH*), Gibbs free energy change (Δ*reaG*) and dissolution entropy (Δ*reaS*). Furthermore, spectroscopic characterizations (NMR and in-situ FTIR), and quantum chemical calculations were combined to deduce the interaction mechanism between CO2 and the TAFIL binary absorbents.

# 2. EXPERIMENTAL

## 2.1. Materials

CH4 (99.999 vol%), CO2 (99.999 vol%), and N2 (99.999 vol%) were purchased from Beijing Yongsheng Co. Ltd, China. Choline hydroxide solution ([Cho][OH], 44.0 wt% in H2O), tetramethylammonium hydroxide ([N2222][OH], 25.0 wt% in methanol), 1, 2, 4-triazole (Triz, 99.0 wt%), sulfolane (TMS, 99.5 wt%), 4-formyl morpholine (NFM, 99.0 wt%), ethanol absolute (99.9 wt%), methanol (99.5 wt%), phosphorus pentoxide (99.0 wt%) were all purchased from Aladdin Industrial Corporation. Double distilled water was used in the experiments, and all the chemical reagents were used as received without further purification.

## 2.2. Preparation and characterizations of TAFILs and TAFIL binary absorbents

In this work, the TAFILs including the choline triazonium salt ([Cho][Triz]) and the tetraethylammonium triazonium salt ([N2222][[Triz]) were synthesized by one-step neutralization reaction as described in the literature25,26. Taking [Cho][Triz] as an example, 0.21 mol 1, 2, 4-triazole dissolved in 100 ml of absolute ethanol. Under the condition of an ice bath (0~5 °C), 0.20 mol [Cho][OH] was slowly added to 1, 2, 4-triazole solution, followed by stirring for 48 h at 25 °C to form a homogenous liquid. Subsequently, water and ethanol were removed by rotary evaporation at 60 °C to obtain the crude product [Cho][Triz]. Since the [Cho][Triz] was soluble and 1, 2, 4-triazole was almost insoluble in ethyl acetate, ethyl acetate was added to the crude product to remove the excess of 1, 2, 4-triazole. Furthermore, the solvent was removed by evaporation at 60 °C, and the TAFIL was dried under a vacuum at 60 °C for 72 h to obtain the final product [Cho][Triz]. The TAFIL binary absorbents were prepared by mixing the TAFILs and physical solvents with high boiling points (e.g. TMS or NFM) in different mass ratios to obtain homogeneous liquids. The structures of two novel TAFILs were shown in Figure 1.

Nuclear Magnetic Resonance (NMR), such as 13C NMR spectra, was performed to confirm the chemical structures of the two TAFILs. NMR spectra were obtained on the Bruker 600 spectrometer with *ԁ6*-DMSO in the capillary tube as the internal standard solvent at 25 °C. In-situ FTIR spectra were carried out on a Mettler iC IR 7.1 spectrometer with the spectral resolution of 4 cm−1 and scan numbers 32, respectively. The density and viscosity of TAFILs and binary mixtures were determined using the Anton Para DMA 5000 type automatic densitometer from 20 to 80 °C. The decomposition temperature was carried out on TGA Q7300 to determine thermal stability at a dry N2 flow rate of 25 ml/min with a heating rate of 10 °C/min. The water content in the TAFILs was determined by Karl Fischer Moisture Titrator (METTLER TOLEDO Coulometric KF Titrator C20), which was less than 4000 ppm.

## 2.3. Gas solubility measurements

The vapor-liquid equilibrium apparatus was used to measure the CO2 or CH4 solubility in the TAFIL binary absorbents. To verify the reliability of the apparatus, the experiments of CO2 solubility in [Bmim][BF4] at 25 °C17,27,28 and CH4 solubility in [Cho][Cl]/urea with the molar ratio of 1:2 at 45 °C29 were carried out and compared with the literature. As shown in Figure 2, the experimental results were in good agreement with those reported by the literature, demonstrating that the experimental apparatus is creditable.

## 2.3. Density functional theory (DFT) calculation details

The interaction energies between the gas (CO2 or CH4) and TAFILs or other absorbents were calculated by density functional theory (DFT) through GAUSS 09 software with Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP), and the structures of TAFIL-gas (CO2 or CH4) were optimized by B3LYP-D3BG/6-311++G\*\* level. At the same time, the solvation effect was considered with the SMD model. Based on the optimized structures, the electrostatic potential (ESP) was analyzed with Mulliken charges. The charge distribution was calculated using Multiwfn30. The interaction energy was calculated with different absorbents and gas molecules according to Equation (1)31.

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|  | *ΔE* = *E*absorbents-gas - *E*absorbents – *Egas* | (1) |

where *ΔE* is the interaction energy (kJ/mol) between absorbents and gas; *E*absorbents-gas, *E*absorbents, and *Egas* represent the energies (kJ/mol) of the absorbent-gas system, absorbents and gas molecules, respectively.

## 2.4. Data availability and reproducibility statement

Experimental operations and data analysis were described in detail in Support Information (SI). All the above equilibrium pressure data were performed three times, and the standard relative deviation (RSD) was within 3%.

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|  | (2) |

where *S* represents the gas solubility (mol gas/mol absorbent) that was calculated by the Peng-Robinson equation (P-R) as Equations (S1) in SI.

A comparison between our measurements and these previous data was discussed in Figure 2 and Table S1, which showed that our results are consistent with these previously reported results. The experimental data from Figure 2, Figure 3(a), and 3(b) were tabulated in Table S1, S2, and S3, respectively. The experimental data from Figures 4~8 and Figure 13 were tabulated in Tables S4~S7, respectively. The TGA data from Figure 3(c), the in-situ FTIR and NMR spectra from Figures 9~10, and the extensive simulation data in Figures 11~12, and Table 4 were available as a zip file in the Supplementary Material. These input files also included the calculation parameters that were used in the DFT in this work.

## 3. RESULTS AND DISCUSSION

## 3.1. Physicochemical properties of TAFIL binary absorbents

Physicochemical properties, such as the density, viscosity, and thermal stability of the absorbents are fundamental parameters. The densities and viscosities of these TAFILs and TAFIL binary absorbents at different temperatures (20~80 °C) were depicted in Figure 3 (a) and 3(b), respectively. The results showed that the densities of TAFILs and TAFIL/TMS binary absorbents have linear behaviors and decrease with increasing temperatures, which range from 1.00 to 1.25 g/cm3. The viscosity of TAFILs and TAFIL/TMS binary absorbents had a significant effect on CO2 mass transferduring absorption. As shown in Figure 3 (b), the addition of TMS obviously decreased viscosity, which is favorable for promoting CO2 diffusion. In addition, the decomposition temperatures (*Td*) of the TAFILs and TAFIL/TMS binary absorbents as shown in Figure 3 (c) all exceed 100 °C, which were higher than the absorption and desorption temperatures. In addition, the densities, viscosities, and *Td*of TAFILs and the TAFIL/NFM binary absorbents were depicted in Figure S1 and showed similar trends. In the following study, combined with low viscosity and excellent thermal stability, the TAFIL/TMS binary absorbents were chosen as the research target.

## 3.2. Effect of TAFILs on CO2 and CH4 solubility

To screen TAFILs for CO2/CH4 separation, the solubilities of CO2 and CH4 in the TAFIL binary absorbents with 20 wt% TAFIL were determined at 40 °C. As shown in Figure 4, CO2 solubility of the TAFIL binary absorbents was at least two orders of magnitude higher than CH4 solubility, which was attributed to the chemical interaction between CO2 and [Triz]- forming carbamate. The CO2 dissolution curves in TAFIL binary absorbents displayed nonlinearly in the low-pressure ranges but displayed linearly at higher pressures. However, CH4 solubility in TAFIL binary absorbents increased almost linearly with pressures. Obviously, CO2 solubility of [Cho][Triz]/TMS binary absorbents was significantly higher than that of [N2222][Triz]/TMS binary absorbents. Taking into account the choline cation with low toxicity and great biodegradability, [Cho][Triz] was chosen as the optimum IL candidate.

## 3.3. Effect of [Cho][Triz]/TMS mass ratio on gas solubility

The CO2 and CH4 solubilities in different mass ratios of [Cho][Triz]/TMS system were investigated at 40 °C as shown in Figure 5. All the curves indicated that CO2 solubility rises steeply in the pressure range from 0 to 2.5 bar and then grows linearly at higher pressures. The chemical reaction dominated CO2 solubility in the low-pressures lower than 2.5 bar, resulting in a rapid increase in CO2 solubility with increasing CO2 partial pressures. However, the physical solubility of CO2 played the primary role under higher pressures over 2.5 bar. It was demonstrated that the higher the IL concentration in [Cho][Triz]/TMS system, the higher CO2 solubility. The CO2 solubility of pure TMS is very low and only 0.004 g CO2/g TMS (0.012 mol CO2/mol TMS) at 40 °C and about 1 bar. However, CO2 solubility in [Cho][Triz]/TMS (20 wt%/80 wt%) was 0.034 g CO2/g absorbent (0.098 mol CO2/mol absorbent) at 40 °C and 1 bar, and CO2 mass solubility in [Cho][Triz]/TMS (20 wt%/80 wt%) was almost 7.8 times higher than that in TMS.

The CO2 solubility in pure [Cho][Triz] shown in Figure 5 (a) at 40 °C and 1 bar was approximately 0.150 g CO2/g absorbent (0.585 mol CO2/mol absorbent), while CO2 solubility in [Cho][Triz]/TMS (80 wt%/20 wt%) was 0.125 g CO2/g absorbent (0.447 mol CO2/mol absorbent), which is equal to that of 30 wt% MEA aqueous solution (0.120 g CO2/g absorbent) used in industries32. Meanwhile, the CH4 solubility in [Cho][Triz]/TMS systems with different mass ratios was investigated under 40 °C as shown in Figure 5 (b). It was found that CH4 solubility in these [Cho][Triz]/TMS absorbents follows a physical behavior during the entire dissolution process, and the change of [Cho][Triz] concentration had little effect on CH4 solubility. CH4 solubility in pure [Cho][Triz] and [Cho][Triz]/TMS (80 wt%/20 wt%) was about 0.0002 g CH4/g absorbent (0.0024 mol CH4/mol absorbent) at 40 °C and 1 bar. That implied that the increased CO2/CH4 selectivity is accompanied by a higher IL concentration in [Cho][Triz]/TMS binary absorbents. Meanwhile, the viscosity and absorption enthalpy were also reduced due to the addition of TMS. Therefore, the mass ratio of 80 wt%/20 wt% for [Cho][Triz]/TMS was selected as the optimum concentration.

Further, the solubilities of CO2 and CH4 and CO2/CH4 selectivity at about 1 bar in different IL systems reported in the literature were summarized for comparison. As shown in Table 1, due to high CO2 solubility and low CH4 solubility in [Cho][Triz]/TMS, the higher [Cho][Triz] concentrations, the larger CO2/CH4 selectivity. The values of SCO2/CH4 in pure [Cho][Triz] and [Cho][Triz]/TMS (80 wt%/20 wt%) were 235.1 and 191.0 at 40 °C and 1 bar, respectively, which are much higher than most of the reported ILs and IL-based absorbents. When the [Cho][Triz] concentration was more than 80 wt% in [Cho][Triz]/TMS binary absorbents, the CO2 mass solubility was 0.125~0.150 g CO2/g absorbent, and CO2/CH4 selectivity was greater 165.0 at 40 °C and 1 bar. These results showed that [Cho][Triz]/TMS binary absorbents have not only high mass CO2 solubility but also high CO2/CH4 selectivity, which indicated that the [Cho][Triz]/TMS system can be potentially used for highly efficient and selective separation of CO2 from the gas mixtures of CO2 and CH4.

## 3.4 Thermodynamic analysis

To better understand the mechanisms of CO2 and CH4 absorption, the thermodynamic properties (Henry's law constant *H*, reaction equilibrium constant *K*, Δ*reaH*, Δ*reaG*, and Δ*reaS*) were also calculated. As shown in Figure 6, [Cho][Triz] could absorb 0.585 mol CO2/mol TAFIL at 40 °C and about 1 bar. Owing to the possible 1:1 reaction mechanism, the modified deactivated model was used to correlate CO2 solubility at temperatures from 40 to 60 °C33,34. Equation (3) represented the dissolution of CO2 including chemical dissolution and physical dissolution, which was modified by the physical solvent correction factor *N*. The reactive principle and the derivation of Equation (3) were explained in detail in SI.

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|  |  | (3) |

where *Z* is the total molar amount of CO2 solubility including CO2 physical solubility and CO2 chemical solubility in mol CO2/mol absorbent, *P* donates the partial pressure of CO2 in bar, and *H* is the Henry’s law constant in bar. *K* represents the reaction equilibrium constant in bar−1, and *C* is the ratio of reactive TAFIL to total TAFIL binary absorbents.

Equation (3) was based on the assumption of [Cho][Triz]/TMS binary absorbents with different mass ratios as ideal absorbents, which was similar to the agreement of the suppositional solubilities of CO2 in pure [Cho][Triz] with the experimental solubility. Their fitting curves were illustrated in Figure 6 (R2 > 0.99), and the parameters *H*, *K*, and *C* were calculated using this assumption by fitting. The solubility data were summarized in Table 2. *C* was 0.69 at 40 °C in pure [Cho][Triz], demonstrating that the reaction mechanism was 1:1. This could be explained by the anion of [Cho][Triz] reacting with CO2 to form carbamate. The value of *C* decreased with the decreasing proportion of [Cho][Triz] because the chemical complexation between CO2 and the absorbents was compromised. Table 2 showed that *H* increases with the proportion of TMS, which agrees that the higher proportion of [Cho][Triz] in absorbents, the stronger the ability of CO2 dissolution.

To explore the influence of temperature on the gas solubilities of different absorbents, the fitting curves for CO2 or CH4 solubility in pure [Cho][Triz] and [Cho][Triz]/TMS (80 wt%/20 wt%) at different temperatures were plotted in Figure 7. Thermodynamic parameters were shown in Table 3, and *K* varied negatively and dramatically with temperatures, indicating that the increase of temperatures weakens the complexation of CO2 with the anion of [Cho][Triz] because the reaction of [Cho][Triz] with CO2 is exothermic. The physical solubility was related to *H*, and it increased remarkably with the temperature.

As mentioned above, the total molar amount (*Z*) of CO2 solubility in absorbents could be divided into two portions: CO2 physical solubility (nCO2(phy)) and CO2 chemical solubility (nCO2(chem)). To understand the contributions of nCO2(chem) and nCO2(phy), the chemical and physical solubility curves of CO2 in [Cho][Triz]/TMS (80 wt%/20 wt%) at 40 °C were calculated as shown in Figure 8. Due to the stoichiometric limitation of the equilibrium reaction, the chemical CO2 solubility played a major role in the system and leveled off under the pressure of 1.93 bar. On the contrary, the physical solubility increased linearly with the increasing CO2 pressure over 1.93 bar. Therefore, it was demonstrated that CO2 solubility in absorbents is a combination of chemical and physical absorption, and the modified deactivated mode is accurate and suitable to describe the CO2 dissolution behaviors of absorbents.

To better understand the chemical and physical dissolution behaviors of CO2 and CH4 in TAFILs and the TAFIL binary absorbents, thermodynamic properties including Δ*reaH*, Δ*reaG*, and Δ*reaS* were investigated. The detail of the calculation was explained in Equations (S23)~(S29). In the above results, CO2 and CH4 solubility data in pure [Cho][Triz] and [Cho][Triz]/TMS (80 wt%/20 wt%) were performed at different temperatures by the modified deactivated model as shown in Figure 7. The calculation results of *H*, *K*, and thermodynamic properties were summarized and compared in Table 3. The Δ*reaH* of pure [Cho][Triz] was -47.27 kJ/mol, approximately comparable to the half of the CO2 absorption enthalpy in aqueous organic amines32,35. The Δ*reaH* of [Cho][Triz]/TMS (80 wt%/20 wt%) was -35.76 kJ/mol, which implies that CO2 dissolution can be easily desorbed. As shown in Figures 7 (b) and 7 (d), the R2 values of the linear relationship between *P* and *x* were 0.99, respectively. CH4 solubility decreased with the increasing temperatures, agreeing well with the increased *H* of CH4 as the temperatures increase. The negative value of *ΔsolH* indicated that the process is exothermic. The Δ*reaH* of CO2 dissolution in (−35.76 kJ/mol) was more negative than the *ΔsolH* of CH4 solubility (−3.60 kJ/mol) for [Cho][Triz]/TMS (80 wt%/20 wt%), which indicated that [Cho][Triz]/TMS binary absorbents have high CO2/CH4 selectivity in the experiment.

## 3.5 CO2 dissolution mechanism of TAFIL binary absorbents

## 3.5.1 Spectroscopic studies

To gain a deep understanding of the CO2 dissolution mechanisms, the structures of [Cho][Triz]/TMS (80 wt%/20 wt%) before and after CO2 dissolution were studied using spectroscopic characterizations. Spectral changes during CO2 bubbling into [Cho][Triz]/TMS (80 wt%/20 wt%) were monitored by in-situ FTIR spectrometry in 90 min, as depicted in Figure 9. Compared to the spectra of fresh [Cho][Triz]/TMS (80 wt%/20 wt%), one new peak appeared at 1662 cm−1 during CO2 dissolution, which was attributed to the asymmetrical stretching vibration of C=O belonged to N−COO−36. The other peak at 1268 cm−1 attributed to the bending vibration of C-N in the [Triz]- ring became stronger, which indicated that the N−COO− formation enhances the vibration of the C−N. In-situ FTIR spectra for pure [Cho][Triz] during CO2 dissolution and desorption were also depicted in Figure S2.

Meanwhile, the 13C NMR spectra of [Cho][Triz]/TMS (80 wt%/20 wt%) after CO2 dissolution and desorption were examined and compared with fresh [Cho][Triz]/TMS in Figure 10. The new peak in 13C NMR appeared at 159.58 ppm that represented a carbon signal in N−COO−, but the other signals of [Cho][Triz] and TMS remained unchanged. All these results demonstrated the strong complexation of the nitrogen atom in [Triz]- with CO2. After CO2 desorption, the structure of the [Cho][Triz]/TMS (80 wt%/20 wt%) was almost consistent with the fresh solvent. The 13C NMR for pure [Cho][Triz] before CO2 dissolution and after CO2 desorption was shown in Figure S3.

## 3.5.2 Quantum chemical calculations

To confirm the experimental results, the relative affinity of TAFILs for interacting with CO2 and CH4 was calculated using DFT simulation37-39. As shown in Figure 11, the interaction energies between absorbents and CO2 were higher than those between absorbents and CH4, indicating these absorbents had a stronger interaction with CO2. For example, the interaction energy of [Cho][Triz]-CO2 (-48.73 kJ/mol) was higher than that of [Cho][Triz]-CH4 (-12.81 kJ/mol). Similarly, the interaction energy of TMS-CO2 (-20.61 kJ/mol) was higher than that of TMS-CH4 (-9.18 kJ/mol). The difference in interaction energies meant that it is easier to selectively capture CO2 than CH4 for these absorbents, which is consistent with the gas solubilities in the absorbents.

It is essential to find potential sites for TAFILs that can interact with gases by the nucleophilic site and the electrophilic site. Therefore, the electrostatic potential (ESP) of the surface for optimized geometry of the TAFILs was also plotted and shown in Figure 12. Different colors represent the different values of ESP at the surface, and the order of decreasing potential is blue > green > yellow > orange > red40. The results demonstrated that positive charges of quaternary ammonium cations with different side chains are mainly concentrated on the neighboring regions of the central nitrogen atom, and the positive charge regions gradually decrease as the alkyl side chains extend longer. It could be seen from Figure 12 that the apparent nucleophilic site in the anion [Triz]- plays a vital role in interaction with CO2, therefore affecting CO2 solubility. From Mulliken charges in Table 4, N-1 in [Cho][Triz] and [N2222][Triz] had the lowest negative charge, indicating that N-1 may be the strongest interaction site, which is consistent with the above results.

## 3.5 Regeneration behaviors

Recyclability is an essential criterion for estimating the performance of absorbents. To evaluate the reversibility of CO2 absorption and desorption in [Cho][Triz]/TMS binary absorbents, CO2-saturated [Cho][Triz]/TMS (80 wt%/20 wt%) was heated at 80 °C and swept by dried N2 gas stream at 150 mL/min to desorb CO2. Figure 13 showed the absorption-desorption performance of CO2 at 40 °C and about 1 bar during five cycles. It could be seen that there is no obvious decrease in CO2 solubility, and [Cho][Triz]/TMS (80 wt%/20 wt%) is easily regenerated by heating and reducing pressures. These results revealed that CO2 absorption in [Cho][Triz]/TMS (80 wt%/20 wt%) is reversible, which implies excellent recyclability.

## 4. CONCLUSIONS

In this work, to obtain novel IL-based absorbents with excellent performance for CO2 separation from the CH4-containg gas, two TAFILs [Cho][Triz] and [N2222][Triz] with chemical sites were synthesized, and further mixed with the physical solvent to form the novel physicochemical absorbents. CO2 and CH4 solubility and the ideal CO2/CH4 selectivity in TAFIL binary absorbents were investigated at 40~60 °C and 0~25 bar by vapor-liquid equilibrium apparatus. The dissolution mechanism was analyzed by in-suit FTIR, NMR, the modified deactivated model, and quantum chemical calculations. The results demonstrated that [Cho][Triz]/TMS binary absorbents with IL content above 80 wt% show high CO2 mass solubility of more than 0.125 g CO2/g absorbent at 40 °C and 1 bar that is close to that of 30% MEA aqueous solution, and CO2/CH4 selectivity exceeds 191.0, which is higher than most reported absorbents. Meanwhile, [Cho][Triz]/TMS (80 wt%/20 wt%) also showed low CO2 absorption enthalpy of -35.76 kJ/mol less than half of 30 wt% MEA aqueous solution, resulting in low regeneration consumption and good reversibility. The great performance of [Cho][Triz]/TMS solvents was mainly attributed to the combination of relatively weak chemical and physical interaction between CO2 and TAFIL binary absorbents. Hence, TAFIL binary absorbents are competitive alternatives for CO2 separation from clean energy gases.

## ACKNOWLEDGEMENTS

This work is financially supported by the National Key R&D Program of China (2022YFB4101701), the National Natural Science Foundation of China (22122814 and 21890764), the Youth Innovation Promotion Association of the Chinese Academy of Sciences (Y2022024), and State Key Laboratory of Multiphase complex systems, Institute of Process Engineering, Chinese Academy of Sciences (MPCS-2022-A-03). We sincerely appreciate Prof. Suojiang Zhang (IPE, CAS) for his careful academic guidance, suggestions, and great support.

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