Combined Superbase Ionic Liquid Approach to Separate CO₂ from Flue Gas

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ABSTRACT: Superbase ionic liquids (ILs) with a trihexyltetradecylphosphonium cation and a benzimidazolide ([P₆₆₆₁₄][Benzim]) anion were investigated in a dual-IL system allowing the selective capture and separation of CO₂ and SO₂, respectively, under realistic gas concentrations. The results show that [P₆₆₆₁₄][Tetz] is capable of efficiently capturing SO₂ in preference to CO₂ and thus, in a stepwise separation process, protects [P₆₆₆₁₄][Benzim] from the negative effects of the highly acidic contaminant. This results in [P₆₆₆₁₄][Benzim] maintaining >53% of its original CO₂ uptake capacity after 30 absorption/desorption cycles in comparison to the 89% decrease observed after 11 cycles when [P₆₆₆₁₄][Tetz] was not present. Characterization of the ILs post exposure revealed that small amounts of SO₂ were irreversibly absorbed to the [Benzim]⁻ anion responsible for the decrease in CO₂ capacity. While optimization of this dual-IL system is required, this feasibility study demonstrates that [P₆₆₆₁₄][Tetz] is a suitable sorbent for reversibly capturing SO₂ and significantly extending the lifetime of [P₆₆₆₁₄][Benzim] for CO₂ capture.

KEYWORDS: ionic liquids, CO₂ capture, SO₂ capture, flue gas, scrubber

INTRODUCTION

Gas capture sorbents such as alkanolamines, metal–organic frameworks, porous liquids, and ionic liquids (ILs) are being increasingly studied in the literature for CO₂ capture due to combat rising greenhouse gas emissions.¹⁻⁶ While CO₂ emissions are subject to legislation in the UK, in line with achieving net zero by 2050, other components of waste gas streams such as SO₂ and nitrogen oxides (NOₓ) also require removal due to their contribution to acid rain and smog formation.⁷

For CO₂ removal from flue gas streams, aqueous alkanolamine scrubbers are the benchmark carbon capture technology commercially available. The production and regeneration of these sorbents are energy intensive, and the loss of the amine sorbent during operation, due to degradation and evaporation, brings additional environmental considerations along with the production of highly corrosive waste solutions.⁸ In terms of CO₂ capture, the addition of contaminants such as SO₂ has been demonstrated to degrade current capture sorbents like alkanolamines; however, consideration of the effect of such impurities has not been widely considered in the literature when investigating the viability of new CO₂ capture sorbents.⁹⁻¹¹

Currently, approximately 85% of power plant desulfurization occurs via a wet limestone–gypsum process which has a high desulfurization rate and a low cost of operation.⁵,¹²,¹³ This process requires waste water treatment, and while gypsum (formed as a by-product) has a number of applications such as in wallboard manufacturing and the cement industry, globally, a large proportion goes to landfill.¹⁴⁻¹⁵ The efficiency of such desulfurization processes (and other purification stages) before CCS (Carbon Capture and Storage) significantly impacts the sorbent lifetime and the overall process efficiency and cost.

ILs have received substantial interest for gas capture due to a tunable structure through the pairing of different cations and anions and favorable physical properties (high thermal stability, low melting point, and low vapor pressure).⁶ In addition, reported calculations show reductions in energy consumption (lower temperature/pressure sorbent regeneration conditions) and overall costs for IL-based gas separation processes, compared to commercial amine-based CO₂ absorbents, which are additional drivers for their use.¹⁶,¹⁷,¹⁸ The ability of an IL to interact either physically or chemically with different gases allows the process to be tailored to optimize the gas uptake capacities through a knowledge of the absorption enthalpies and physiochemical properties of the ILs.¹⁹⁻²¹ Therefore, the available data can now be used to

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identify a wide range of structure—activity relationships for selective gas capture by ILs. In the majority of cases, the anion has been shown to have the largest effect on gas uptake capacities, where there is now an increasing trend in investigating the consequence of altering the anion basicity. In particular, superbase ILs (SBILs) with aprotic heterocyclic anions have been shown to reversibly capture large amounts of CO$_2$ (>1 nCO$_2$/nIL) with minimal increases in viscosity, an important consideration in the industrial application of ILs. For SBILs, where it has been demonstrated that the basicity of the anion can affect the absorption enthalpies, the presence of acidic gases such as SO$_2$ in the feed can significantly affect the recyclability of the sorbent.

The effect of the anion on the capture of CO$_2$ and SO$_2$ is displayed in Table 1 for two SBILs: trihexyltetradeylyphosphonium benzimidazolide, [P$_{66614}$][Benzim], and trihexyltetradeylyphosphonium tetrazolide, [P$_{66614}$][Tetz]. [P$_{66614}$][Benzim] has been used in a series of studies investigating the effect of flue gas contaminants on CO$_2$ uptake and was also shown to capture significantly more CO$_2$ per mole of IL in comparison to [P$_{66614}$][Tetz] (1.20 vs 0.08 nCO$_2$/nIL) due to a higher absorption enthalpy (−52.1 vs −19.1 kJ/mol·1). Importantly, when SO$_2$ capture is considered, both ILs can absorb large amounts. However, [P$_{66614}$][Benzim] does so irreversibly, which has been shown to have a negative effect on its ability to simultaneously absorb CO$_2$. In contrast, a small residue following desorption (0.06 nSO$_2$/nIL) was reported for [P$_{66614}$][Tetz] after exposure to 0.2 vol % SO$_2$ which may be due to a weaker binding affinity when compared to [P$_{66614}$][Benzim] (−89.4 vs −123.9 kJ/mol·1). However, a study of the recyclability of [P$_{4442}$][Tetz] showed that the working absorption capacity remained constant.

The differing absorption enthalpies of these SBILs toward CO$_2$ and SO$_2$ could allow the possibility of using the two SBILs in series for stepwise gas separation, with [P$_{66614}$][Tetz] used to selectively absorb SO$_2$. In this case, [P$_{66614}$][Tetz] acts as a scrubber and extends the lifetime of [P$_{66614}$][Benzim] for the reversible capture of CO$_2$. Previous studies on the gas absorption of SO$_2$ by [P$_{66614}$][Benzim] showed that in the presence of realistic flue gas amounts of SO$_2$ (0.2 vol %), an 89% decrease in CO$_2$ capacity was observed over 11 absorption/desorption cycles. Herein, the feasibility of using [P$_{66614}$][Tetz] with [P$_{66614}$][Benzim] in a dual-IL system has been investigated to assess the effect on the lifetime and recyclability of the [P$_{66614}$][Benzim] sorbent for CO$_2$ uptake. This study has utilized the previously developed mass spectrometry-based gas absorption rig with the ILs after exposure characterized using NMR and elemental analyses to determine their recyclability. This paper is a feasibility study for the use of ILs in a stepwise separation process and shows [P$_{66614}$][Tetz] to increase the lifetime of [P$_{66614}$][Benzim] as a CO$_2$ capture sorbent.

### EXPERIMENTAL SECTION

#### Materials

Trihexyltetradeylyphosphonium chloride (97.7 wt %, CAS: 258864-54-9) was obtained from IoLiTec; benzimidazole (98 wt %, CAS: 51-17-2) and tetrazole (CAS: 288-94-8) were purchased from Sigma-Aldrich. [P$_{66614}$][Superbase] was prepared using a previously reported two-step synthesis method. The structure and purity of the ILs, after synthesis and post-exposure, were analyzed using $^1$H NMR and $^{13}$C NMR with a Bruker AVANCE II 500 MHz Ultra shield Plus spectrometer and carried out as neat ILs in the presence of a glass capillary insert containing DMSO-d$_6$ purchased from Cambridge Isotope Laboratories Inc. (CAS: 2206-27-1). The halide content was determined to be <5 ppm using a silver nitrate test, and water content was measured to be <0.1 wt % using a Metrohm 787 KF Titrino Karl Fischer machine. The following gases were obtained from BOC: argon (99.998%, CAS: 7440-37-1), carbon dioxide (99.99%, CAS: 124-38-9), and sulfur dioxide (1% in argon, CAS: 7446-09-5).

The IL samples post exposure to the gases were stored in an argon-filled glovebox before analysis. Elemental analysis was carried out using a Thermo Scientific Flash 2000 elemental analyzer.

#### Methods

In previous work, a novel gas absorption technique utilizing mass spectrometry was developed to allow the study of mixed component gas feeds that resemble realistic flue gas conditions. This experimental setup was modified, herein, to allow the inclusion of two reactors connected in series, and this is shown in Figure 1. Two reactors connected in series, and this is shown in Figure 1. In this case, [P$_{66614}$][Tetz] acts as a scrubber and extends the lifetime of [P$_{66614}$][Benzim] for the reversible capture of CO$_2$. Previous studies on the gas absorption of SO$_2$ by [P$_{66614}$][Benzim] showed that in the presence of realistic flue gas amounts of SO$_2$ (0.2 vol %), an 89% decrease in CO$_2$ capacity was observed over 11 absorption/desorption cycles. Herein, the feasibility of using [P$_{66614}$][Tetz] with [P$_{66614}$][Benzim] in a dual-IL system has been investigated to assess the effect on the lifetime and recyclability of the [P$_{66614}$][Benzim] sorbent for CO$_2$ uptake. This study has utilized the previously developed mass spectrometry-based gas absorption rig with the ILs after exposure characterized using NMR and elemental analyses to determine their recyclability. This paper is a feasibility study for the use of ILs in a stepwise separation process and shows [P$_{66614}$][Tetz] to increase the lifetime of [P$_{66614}$][Benzim] as a CO$_2$ capture sorbent.

### Table 1. CO$_2$ Capacity, SO$_2$ Capacity, and Absorption Enthalpy of the Two SBILs Investigated in This Work; Trihexyltetradeylyphosphonium Benzimidazolide, [P$_{66614}$][Benzim], and Trihexyltetradeylyphosphonium Tetrazolide [P$_{66614}$][Tetz]

|        | [P$_{66614}$][Benzim] | [P$_{66614}$][Tetz] |
|--------|----------------------|---------------------|
| CO$_2$ Uptake (nCO$_2$/nIL) | 1.20 | 0.08 |
| Absorption Enthalpy of CO$_2$ (kJ/mol·1) | -52.1 | -19.1 |
| SO$_2$ Uptake (nSO$_2$/nIL) | 1.18 | 0.87 |
| Absorption Enthalpy of SO$_2$ (kJ/mol·1) | -123.9 | -89.4 |

In the majority of cases, the anion has been shown to have the largest effect on gas uptake capacities, where there is now an increasing trend in investigating the consequence of altering the anion basicity. In particular, superbase ILs (SBILs) with aprotic heterocyclic anions have been shown to reversibly capture large amounts of CO$_2$ (>1 nCO$_2$/nIL) with minimal increases in viscosity, an important consideration in the industrial application of ILs. For SBILs, where it has been demonstrated that the basicity of the anion can affect the absorption enthalpies, the presence of acidic gases such as SO$_2$ in the feed can significantly affect the recyclability of the sorbent.

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Herein, the feasibility of using [P$_{66614}$][Tetz] with [P$_{66614}$][Benzim] in a dual-IL system has been investigated to assess the effect on the lifetime and recyclability of the [P$_{66614}$][Benzim] sorbent for CO$_2$ uptake. This study has utilized the previously developed mass spectrometry-based gas absorption rig with the ILs after exposure characterized using NMR and elemental analyses to determine their recyclability. This paper is a feasibility study for the use of ILs in a stepwise separation process and shows [P$_{66614}$][Tetz] to increase the lifetime of [P$_{66614}$][Benzim] as a CO$_2$ capture sorbent.
atm) under feed conditions of 14% CO$_2$ in Ar or 14% CO$_2$ + 0.2% SO$_2$ in Ar, followed by a 2 h desorption step at 90 °C under Ar.

To prevent the exposure of [P$_{66614}$][Benzim] to SO$_2$ during the desorption step, a four-way valve was used to direct the outlet from the reactor containing [P$_{66614}$][Tetz] to the vent, while the outlet of [P$_{66614}$][Benzim] was directed to the mass spectrometer. Initially, a baseline for the absorption of CO$_2$ by the two ILs was found by flowing a feed of 14% CO$_2$ in Ar through both reactors consecutively. Six cycles were performed, yielding an average CO$_2$ uptake of 0.77 nCO$_2$/nIL, agreeing with previously published work. Three cycles with a feed of 14% CO$_2$ in Ar were then carried out after every five consecutive 14% CO$_2$ + 0.2% SO$_2$ in Ar cycles to monitor the CO$_2$ capacity of the ILs. The breakthrough curve from the mass spectra was used to calculate the CO$_2$ uptake with an error of ±0.04 nCO$_2$/nIL.

**RESULTS AND DISCUSSION**

The gas absorption rig developed was used to determine whether the use of [P$_{66614}$][Tetz] as a SO$_2$ scrubber would protect the CO$_2$ recyclability of [P$_{66614}$][Benzim] under a realistic gas feed (14% CO$_2$ + 0.2% SO$_2$ in Ar). It should be noted that the design of the scrubber was not optimized to maximize SO$_2$ removal in this feasibility study. The results are shown in Figure 2 and are presented in comparison to earlier work without the presence of [P$_{66614}$][Tetz].

Initial observations revealed that the CO$_2$ capacity of [P$_{66614}$][Benzim] dropped from 0.77 to 0.71 nCO$_2$/nIL after one cycle under the CO$_2$ + SO$_2$ in Ar feed. As this is outside the error of the measurement (0.04 nCO$_2$/nIL), the decrease could either be attributed to the influence of SO$_2$ on [P$_{66614}$][Benzim] and/or the loss of a small CO$_2$ contribution from [P$_{66614}$][Tetz] due to the stronger absorption enthalpy of SO$_2$. This is because the initial CO$_2$ only value of 0.77 nCO$_2$/nIL includes contributions from both [P$_{66614}$][Benzim], and [P$_{66614}$][Tetz]. As the number of cycles increases, both ILs are exposed to increasing amounts of SO$_2$ and it can be seen that the CO$_2$ capacity of [P$_{66614}$][Benzim] decreases further. For this 1:1 ratio of [P$_{66614}$][Tetz] to [P$_{66614}$][Benzim] (by mass), the decreasing CO$_2$ capacity of [P$_{66614}$][Benzim] suggests that the reactor containing [P$_{66614}$][Tetz] was unable to fully...
remove SO$_2$ from the mixed gas feed and allowed the exposure of a reduced amount of SO$_2$ to interact with [P$_{66614}$][Benzim]. After 11 absorption/desorption cycles, the CO$_2$ capacity of [P$_{66614}$][Benzim] had reduced to 0.54 nCO$_2$/nIL, a 30% decrease. Conversely, when the gas feed was not scrubbed by [P$_{66614}$][Tetz], an 89% decrease (to 0.09 nCO$_2$/nIL) in the CO$_2$ capacity of [P$_{66614}$][Benzim] was observed, demonstrating the significant impact [P$_{66614}$][Tetz] has on extending the lifetime of the sorbent. As such, a total of 30 cycles were carried out on the new system, after which it was found that [P$_{66614}$][Benzim] still maintained >53% of its original capacity (0.41 nCO$_2$/nIL). For comparison, the theoretical maximum CO$_2$ uptake by the benchmark alkanolamine sorbent is 0.5 nCO$_2$/nMEA. The CO$_2$ uptake capacity demonstrated herein shows potential for dual-IL systems even after numerous regenerative treatments.

Additionally, it can be seen that after 21 cycles, the CO$_2$ uptake began to stabilize, suggesting that an equilibrium point was reached. It is possible that at these extremely low uptake would be achievable at lower amounts of IL, which would be favorable to the process costs. Subsequent characterization of [P$_{66614}$][Tetz] (below) indicates that the absorption of SO$_2$ is reversible and demonstrates that the detection of increased amounts of SO$_2$ by mass spectrometry is not caused by incomplete regeneration of the sorbent but may be due to a loss of efficiency due to the ability of [P$_{66614}$][Tetz] to absorb gases on multiple absorption sites with differing binding affinities.

The influence of residual water, present in either the ILs or gas feed, was also considered as a potential mode of deactivation of the ILs as this can lead to the formation of further acidic gas species or protonation of the IL anion. However, no significant impact from water was observed in this work.

The ILs were subsequently removed from the gas absorption rig after 30 cycles and characterized using NMR and elemental analyses. $^1$H NMR indicates a small downfield shift in the protons attached to the [Benzim]$^-$ anion (Figures 3 and S3) from 6.30/6.68/7.28 to 6.41/7.00/7.48 ppm. This agrees with previous literature and indicates the irreversible absorption of a small amount of SO$_2$ as expected from the gas absorption rig results. In the case of the [Tetz]$^-$ anion, a downfield shift was observed from 7.72 to 7.97 ppm, as well as a broadening of the peak. These studies have noted that there is often a desorption residue (0.06 nSO$_2$/nIL) for [P$_{66614}$][Tetz], indicating the irreversible absorption of a small amount of SO$_2$ and explaining the small chemical shift changes; however, a significantly high recyclability was still observed. The $^{13}$C NMR spectra are shown in Figure S3 where shifts were also found for the anionic peaks, agreeing with these findings.

Elemental analysis (Table S1) was performed on both ILs before and after exposure in the gas absorption rig, where

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Figure 3. $^1$H NMR spectra of [P$_{66614}$][Benzim] before (a) and after (b) exposure and [P$_{66614}$][Tetz] before (c) and after (d) exposure to the CO$_2$ and SO$_2$ absorption cycles.
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[P$_{66614}$][Benzim] was found to show a small increase in the sulfur content (to 1.64 wt %). This is in comparison to 4.56 wt % that was found in previous work after 11 cycles with no [P$_{66614}$][Tetz] scrubber, demonstrating a 64% decrease in the sulfur content in [P$_{66614}$][Benzim] after 30 cycles. In contrast, for [P$_{66614}$][Tetz], no change was observed after exposure, in agreement with the indication that the SO$_2$ is reversibly absorbed in this IL. It should be noted that a desorption residue has been observed by other authors and in the NMR results, herein, but was not observed in the elemental analysis results. It is possible that this is a result of the
uncertainty from the elemental analyzer used in this work ($u = 0.3 \text{ wt } \%$) as the contamination is expected to be low from previous studies.²³

The post-exposure characterization reveals that the use of $[P_{66614}][\text{Tetz}]$ as a reversible scrubber to remove SO$_2$ from the feed and protect $[P_{66614}][\text{Benzim}]$ was not completely effective, with the results indicating the incorporation of a small amount of SO$_2$ into the structure of $[P_{66614}][\text{Benzim}]$ and a subsequent decrease in the CO$_2$ capacity. Optimization of the dual-IL system in terms of the ratio of $[P_{66614}][\text{Tetz}]$ to $[P_{66614}][\text{Benzim}]$ and the flow rate/residence time of the gases in the ILs could feasibly increase the SO$_2$ uptake and, therefore, the CO$_2$ uptake and lifetime of $[P_{66614}][\text{Benzim}]$, improving the overall efficiency of the process for longer-term operation. Furthermore, stepwise processes for the capture and separation of SO$_2$ and CO$_2$ have been reported to save $\sim$50% of the energy compared to simultaneous separation processes.²⁸

In addition, such a dual-IL system, with stepwise separation of SO$_2$ and CO$_2$ from flue gas, could provide pure gas streams (albeit diluted in an inert gas) during desorption and regeneration of the IL. The pure SO$_2$ gas streams could be utilized as feedstocks for processes such as conversion to elemental sulfur and/or used in a sulfuric acid production,³⁸ and the CO$_2$ stream could be used in the production of chemicals and fuels such as urea, a major agricultural fertilizer, or methane (dry reforming or hydrogenation), as well as in the food and beverage industries.³⁹ In situ utilization of gases absorbed (and activated) by ILs is also a continually developing research area.⁴⁰–⁴⁵ However, barriers to the deployment of IL systems for gas capture include their high viscosity (with consideration to viscosity changes upon gas absorption required) and the cost of IL production on an industrial scale. In the development of such task-specific ILs for gas separation processes, the toxicology and environmental impact of the chosen ILs require evaluation alongside the energy consumption and techno-economic calculations/modeling of the desired process.⁴⁶

This technology has the potential to be applied to NO$_x$ removal, as well as SO$_2$. A number of ILs, including $[P_{66614}][\text{Tetz}]$, have been shown to display large “working” capacities for NO removal opportunities for removing both contaminants simultaneously through multi-site absorption capability.³⁶,³⁷–⁵¹ However, it is essential to study conditions that are representative of real-world environments to assess the impact of realistic amounts of flue gas contaminants on the ability of IL sorbents to reversibly capture CO$_2$.³²–³⁴ Gas capture in thin films of ILs, such as $[P_{66614}][\text{Benzim}]$, is also being investigated as studies have shown that their behavior differs in comparison to bulk solution.³²

Finally, it is important to consider the advantages and disadvantages that ILs present in comparison to other CO$_2$ capture solvents for a commercial process, both in terms of performance and also economic feasibility, presenting an area for future exploration.⁵²–⁵⁶

**CONCLUSIONS**

This work has demonstrated that the use of $[P_{66614}][\text{Tetz}]$ as a SO$_2$ scrubber enables the extended lifetime of a CO$_2$ capture sorbent, $[P_{66614}][\text{Benzim}]$, where after 30 absorption/desorption cycles, $>53\%$ of its original CO$_2$ uptake capacity remains. Further design engineering offers the potential to limit the degradation of $[P_{66614}][\text{Benzim}]$ by increasing the efficiency of SO$_2$ removal. Deactivation of $[P_{66614}][\text{Benzim}]$ to the absorption of CO$_2$ was characterized using NMR and elemental analyses, showing the irreversible uptake of sulfur into the IL, blocking the active sites. However, analysis of $[P_{66614}][\text{Tetz}]$ showed that this IL was largely unaffected by SO$_2$ absorption, offering the capability of reversibly absorbing SO$_2$ under the studied conditions.

By tuning the basicity of the anion ([(Tetz)$^-$]) to initially and selectively capture SO$_2$, an anion with a higher affinity for gas capture ([(Benzim)$^-$]) was able to be used to remove CO$_2$ from a multicomponent gas feed. Anion effects have been well investigated for gas capture, but this is the first time, to the best of the authors’ knowledge, that a dual system has been proposed and investigated. However, it is also important to consider the effect of the cation on basicity by tuning the cation–anion interactions, and this offers an area for continued exploration.⁵³

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c01848.

Averaged CO$_2$ uptakes; mass spectrometry breakthrough curves for SO$_2$; $^1$H NMR; $^{13}$C NMR; and elemental analysis of ILs before and after exposure (PDF)

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Notes

The authors declare no competing financial interest.

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