

**REACTION OF SULFUR DIOXIDE (SO₂) WITH REVERSIBLE
IONIC LIQUIDS (REVILS) FOR CARBON DIOXIDE (CO₂)
CAPTURE**

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**REACTION OF SULFUR DIOXIDE (SO₂) WITH REVERSIBLE
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– To Ammu, Apu, Fati, Naseem, & Tanvir –
for your unconditional love and support

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SUMMARY

Silylated amines, also known as reversible ionic liquids (RevILs), have been designed and structurally modified by our group for potential use as solvents for CO₂ capture from flue gas. An ideal CO₂ capture ionic liquid should be able to selectively and reversibly capture CO₂ and have tolerance for other components in flue gas, including SO₂, NO₂, and O₂. In this project, we study the reactivity, selectivity, uptake capacity, and reversibility of RevILs in the presence of pure SO₂ and mixed gas streams to simulate flue gas compositions. Tripropylsilylamine (TPSA), a candidate CO₂ capture RevIL, reacts with pure SO₂ to form an ionic liquid consisting of an ammonium group and a sulfamate group, supported by IR and NMR results. The resulting IL with pure SO₂ partially reverses when heated to temperatures of up to 500 °C in the TGA. TGA analysis of the ionic liquid formed from a 4 vol% SO₂ in CO₂ mixture indicates a possible reversal temperature in the 86-163 °C range.

CHAPTER 1

INTRODUCTION

Selective absorption of a target compound by a solvent is an attractive approach for the separation of gases from a multi-component gas stream¹. This can occur via selective chemisorption and physisorption of the gas by the solvent. Physisorption occurs due to van der Waal forces between the solvent and the gaseous species, without perturbing the electronic structures of the molecules², and depends on the void volume of the solvent. In contrast, chemisorption is defined by the capture of the targeted compound by the solvent via chemical reaction². Preferably, the interactions between a solvent and a gas should be neither too strong nor too weak, thus allowing both absorption and desorption to occur easily³. Additionally, the solvent should have tolerance for the high temperatures of gas streams, have relatively low vapor pressures to prevent solvent loss via evaporation, high absorption capacities, low reversal temperatures, and high selectivity towards targeted compounds in a mixed gas stream³.

Capture and subsequent sequestration of carbon dioxide (CO₂) from fossil fuel fired power plants and from large point sources is an established method for controlling greenhouse gas emissions. The post-combustion mixed gas waste stream, also known as flue gas, goes through several control chambers prior to entering the CO₂ control chamber. Proportions of flue gas components vary with the source of the fuel. For instance, as reported by DOE, Illinois No. 6 coal yields a flue gas consisting of 15.9 vol% CO₂, 81.3 vol% Nitrogen (N₂) + Argon (Ar), 2.8% O₂, 80 ppmv NO_x, 45 ppmv SO_x, 9 ppmw particulate matter, and 1.2 ppbw mercury, based on a dry basis⁴.

Several methods to separate CO₂ selectively include solid absorbents, membrane technologies⁵, cryogenic separation, and solvent absorbents⁶. Among solvent sorbents, aqueous amine solutions are the more mature technology. One of the most widely used and extensively studied alkanolamines in industry is monoethanolamine (MEA)⁷. The amine functionality in MEA reacts with CO₂ to enable its effective capture (Figure 1) from natural gas and the air in submarines⁷. However, it is yet to be deployed for larger scale CO₂ capture processes, such as in a 500 MW coal fired power plant. This is because regeneration of water is energy intensive, and would require an estimated 30% of the energy of an entire power plant⁸.



Figure 1: Reaction of MEA with CO₂ and H₂O⁹

Furthermore, MEA degrades in flue gas streams due to irreversible side reactions with CO₂ and with other flue gas components, mainly sulfur dioxide (SO₂), nitrogen dioxide (NO₂), oxygen (O₂), and water vapor¹⁰. This results in solvent loss, foaming, fouling, and increased viscosity of the amine, requiring replacement of approximately 2.2 kg of MEA per ton of CO₂ captured¹¹.

Many research groups are currently investigating the application of ionic liquids (ILs) as solvents for absorbing gases such as carbon dioxide (CO₂) and sulfur dioxide (SO₂) from gas mixtures – potential cost effective and energy-efficient processes which do not require water and can be regenerated at modest temperatures.

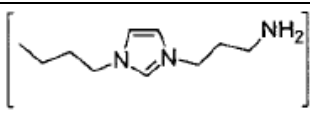
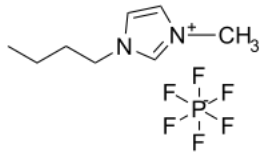
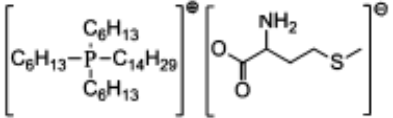
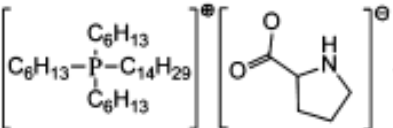
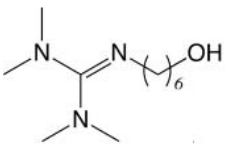
Ionic liquids have very low vapor pressures and are liquids salts at temperatures below 100 °C. They have excellent solvent properties and are often stable at high temperatures.

An ideal CO₂ capture Ionic Liquid should not only be able to reversibly and selectively capture CO₂ from flue gas streams, but also have tolerance for other components in flue gas, including SO₂, NO₂, and O₂, so that frequent solvent degradation is minimized. Therefore, the solvent selected for studying effects of flue gas components on reactivity and selectivity, should primarily have favorable CO₂ capture properties. In this project, we are interested in looking at how mainly SO₂ reacts with CO₂ capture ILs which our group designed. Following is a brief literature review of IL solvents in literature that have been investigated as absorbents for CO₂.

1.1 Literature Overview of Ionic Liquids for CO₂ Capture

Table 1 presents CO₂ uptake capacities of task specific and conventional ionic liquids in literature, at 1 bar and 25 °C. Conventional ionic liquids absorb CO₂ by physisorption alone and have relatively weaker interactions with CO₂ compared to “task specific” ionic liquids (TSIL). They require low reversal energies and undergo minimal degradation. TSILs absorb CO₂ by both chemisorption and physisorption. Therefore, both types of ILs are viable choices for CO₂ capture in mixed gas streams.

Table 1: Absorption capacities of CO₂ capture ionic liquids at 25 °C and 1 bar

Ionic Liquid	Molar Ratio of CO ₂ /IL	Mole CO ₂ /kg solvent	Type of Absorption	Reference
[BMIM][BF ₄]	0.016	0.071	physisorption	Anthony <i>et al.</i> ¹²
 [AMIM] [BF ₄]	0.489	2.128	physi and chemisorption	Bates <i>et al.</i> ¹³
 [BMIM] [PF ₆]	0.017	0.059	physisorption	Anthony <i>et al.</i> ¹²
[BMIM] [Tf ₂ N]	0.333	0.794	physisorption	Anthony <i>et al.</i> ¹²
 [P66614] [Met]	0.830	1.317	physi and chemisorption	Brennecke <i>et al.</i> ¹⁴
 [P66614] [Pro]	0.850	1.426	physi and chemisorption	Brennecke <i>et al.</i> ¹⁴
 N''-(6-Hydroxyhexyl)-N,N,N,N-tetramethylguanidine	0.5	2.315	physi and chemisorption	Heldebrant <i>et al.</i> ¹⁵

Among conventional ILs, [BMIM] [Tf₂N] uptakes 0.794 mole of CO₂ per kg compared to 0.059 and 0.071 moles per kg for [BMIM] [BF₄] and [BMIM] [PF₆] respectively. The interactions are stronger for the Tf₂N based IL because of its larger anion size¹². Therefore changing the nature of the anion influences uptake, but it also comes with the price of having a heavier IL, which corresponds to higher regeneration enthalpies.

Bates *et al.* were the first to incorporate free amine (-NH₂) functional group in ILs, specifically in their imidazolium cation, synthesizing [Amine functionalized imidazolium] [BF₄] or [AMIM] [BF₄]. The resulting IL was able to capture approximately 2.218 mole of CO₂ per kg IL¹³. CO₂ targets the amine group of the cation to form a carbamate (NHCOO⁻) group (Figure 2).

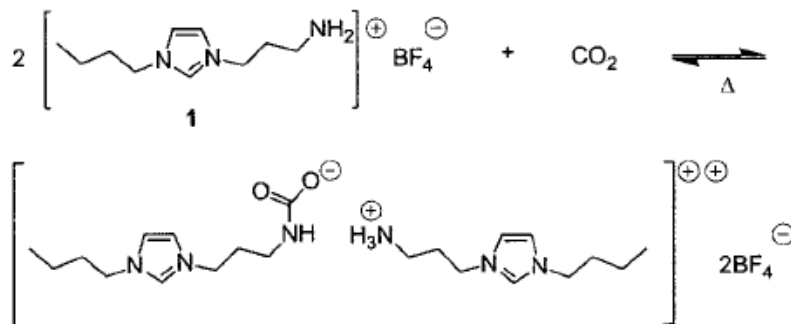


Figure 2: Reaction of [AMIM] [BF₄] with CO₂ (Reprint)¹³

The IL synthesized was quite viscous before reacting with CO₂. Further increase in viscosity upon reaction of the IL with CO₂ was therefore expected. The Bates group acknowledges this challenge and the possibilities of designing variants in their ILs structures to cut down solvent viscosity.

Task-specific ILs [P66614] [Met] and [P66614] [Pro] were designed by the Breneckke group with CO₂ uptake capacities of 1.317 and 1.426 moles per kg IL respectively and a reaction stoichiometry of 1:1 CO₂: IL (Figure 3), which is unique with respect to other amine based ILs that react with CO₂ in a 1:2 ratio. Despite their uptakes being higher than conventional ILs, these ILs consists of non-participating, heavy counter ions [P6614]⁺. Furthermore, the solvents remain in the ionic form before and after reaction and thus are significantly viscous. Ionic liquids generally have high viscosities.

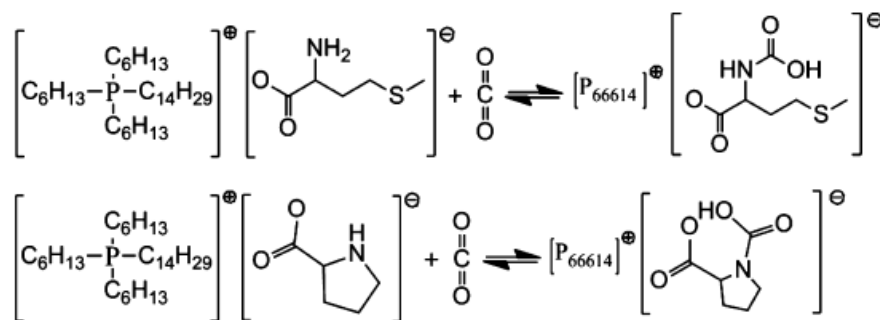


Figure 3: Reaction of [P6614] containing ILs with CO₂ (Reprint)¹⁴

Other groups use solvents which change form upon reacting with CO₂. For instance, Heldebrant *et al.* designed solvents which change from a neutral molecule to a zwitterion upon reaction with CO₂ (Figure 4). It has a reasonable weight (Mol. Wt. of 216 g/mol) and a high CO₂ capacity of 2.315 moles per kg IL. As the alkyl chain lengths in these compounds increases, so does the viscosity of the compounds.

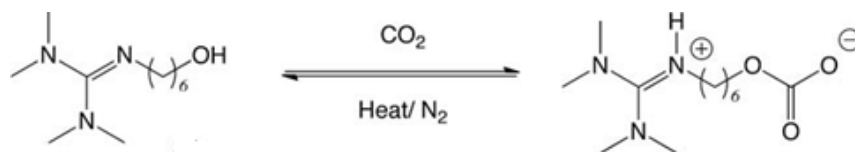


Figure 4: Reaction of N,N,N,N -(6-Hydroxyhexyl)- N,N,N,N -tetramethylguanidine with CO_2 (Reprint)¹⁵

Most of the ILs shown in Table 1, such as the amine functionalized imidazolium tetrafluoroborate IL, [AMIM] [BF₄], remains in the ionic form before and after absorbing CO_2 ¹³. Tackling high solvent viscosity may therefore become an issue in a real flue gas CO_2 capture and solvent regeneration system. Considering challenges of high viscosity of ILs, and low CO_2 capture capacities in terms of CO_2 uptake per kg of solvent, we bring to the plate, a series of neutral, low molecular weight solvents, which switch to ionic liquids upon reacting with CO_2 . Their viscosities can be tuned based on the extent of conversion to their ionic forms. These solvents are known as reversible ionic liquids or “RevILs” and will be discussed further in section 1.3.

1.2 Literature Review of Ionic Liquids for SO₂ Capture

Ionic liquids have also been examined for the selective capture of SO₂. Table 2 presents SO₂ uptake capacities of task specific and conventional ionic liquids.

Table 2: Absorption capacities of SO₂ capture ionic liquids at 25 °C and 1 bar

Ionic Liquid	Molar Ratio of SO ₂ /IL	Type of Absorption
[BMIM] BF ₄	1.5	physisorption
[TMG] BF ₄ ^{16,17}	1.27	physisorption
[BMIM] Tf ₂ N	1.33	physisorption
[TMGH] lactate	0.976	physisorption
[TMGH] BF ₄	1.267	physisorption
[hmim] [Tf ₂ N] ¹⁹	0.916	physisorption
BMIM BTA ^{16,17}	1.33	physisorption
TMG BTA ^{16,17}	1.18	physisorption
[TMGB ₂] [BTA]	1.60	physisorption
[TMG]lactate*40 C ³	0.978	chemi and physisorption
MEA lactate*45C	0.903	chemisorption
Ether functionalized IL ²⁰	2.3-6.3	chemi and physisorption
DBUA ¹⁸	2.45	chemi and physisorption

Wu et al. synthesized 1,1,3,3-tetraethylguanidinium lactate, (TMG)Lactate IL, for capturing SO₂ from dilute 8 vol% SO₂ streams. The temperature of the stream and the concentration of SO₂ were chosen to simulate flue gas conditions.

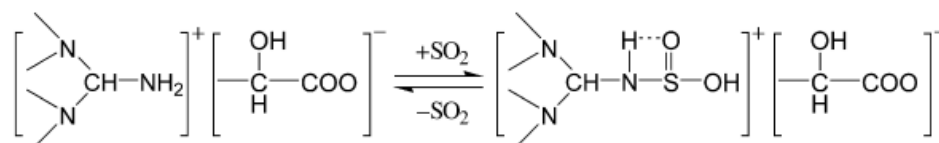


Figure 5: [TMG] [lactate] reaction with SO₂ (Reprint)³

The uptake capacity at 40 °C and 1 bar was 0.978 mole of SO₂ per mole of IL. SO₂ absorbs by reacting with the amine group attached to the cation (Figure 5). The products formed were characterized using FT-IR spectroscopy; characteristic S=O and S-O stretch bonds were identified at wave numbers of 1230 cm⁻¹ and 957 cm⁻¹ respectively indicating successful SO₂ absorption³. TMG-lactate is not a thermally stable IL but has been the basis for other thermally stable ILs designed.

Riisager *et al.*^{16,17} synthesized ILs with [BMIM] and [TMG] cations, which absorb SO₂ via physisorption, with demonstrated high capacities, within the 1.1-1.6 mole SO₂ per mole IL range. Table 2 presents these four ILs: [BMIM] [BTA], [TMG] [BF₄], and [TMG] [BTA], and their respective SO₂ capacities.^{16,17} Interestingly, compared to TMG Lactate, which absorbs SO₂ via chemi and physisorption, these ILs have higher uptake capacities, despite absorbing SO₂ via physisorption alone. Absorption occurs at 20 °C, 1 bar, with a 50 mL.min⁻¹ SO₂ flow rate for 1 hour, and 200 rpm stirring. Complete desorption occurs when SO₂-IL is heated to 140 °C or at room temperature under 20 Pa vacuum. The Heldebrant group's approach is a little different – upon absorption of SO₂, their nonionic solvent, DBUA, switches to its zwitterionic form (Figure 6)¹⁸.

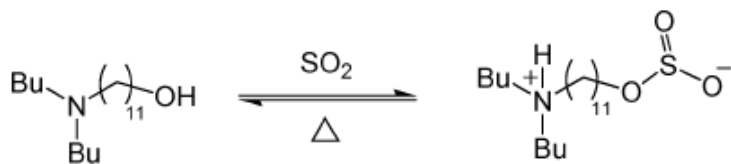
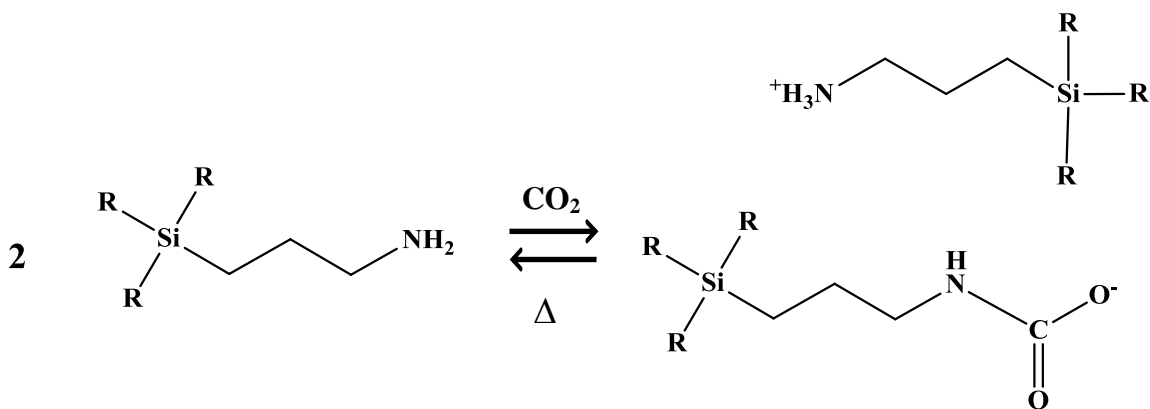


Figure 6: Reaction of DBUA with SO₂¹⁸

SO₂ targets the alcohol group of DBUA, since the amine group is sterically hindered by the alkyl chains. The chemisorption capacity is high- 2.45 mole of SO₂ per mole of DBUA IL¹⁸. Ionic liquids from Anderson *et al.* (hmim Tf₂N)¹⁹ and Hong *et al.* (ether functionalized IL)²⁰ are also presented in Table 2. Most of the above groups developed or studied SO₂ capture solvents with the objective of replacing the current flue gas desulfurization (FGD) technologies in industry.

1.3 Review of Ionic Liquids for CO₂ Capture

The Eckert-Liotta group has developed reversible ionic liquids, as solvents for post-combustion recovery of CO₂ from fossil fuel-fired power plants. Reversible Ionic Liquids are formed from silylated amines and have low vapor pressures in their ionic state, high absorption capacities, and demonstrated solvent reversibility²¹⁻²². Silylated amines are neutral molecules which absorb CO₂ by both chemisorption and physisorption (Figure 7). Subsequently, modest elevations in temperature reverse the reaction and yields pure CO₂ for sequestration²¹⁻²². Due to this dual-mode capture ability, CO₂ uptake capacities by silylated amines can be large; our group has done extensive studies in modifying the precursor structures using structure-property relationships to optimize both physical and thermodynamic properties of these solvents. A series of silylated amines with varying substituent were designed, including (3-aminopropyl) triethylsilane (TEtSA), (3-aminopropyl) tripropylsilane (TPSA), and (3-aminopropyl) trihexylsilane (THSA) respectively.



R – ethyl, propyl, hexyl

Figure 7: Reaction scheme for CO₂ capture by silylated amines²¹

The theoretical CO₂ uptake capacities for TEtSA, TPSA, and THSA are 2.89 mol CO₂/kg, 2.32 mol CO₂/kg, and 1.46 mol CO₂/kg respectively. The overall experimental CO₂ uptake capacity at 25 °C and 200 mL.min⁻¹ pure CO₂ flow rate, decreases from TEtSA (3.20 moles CO₂ /kg) to TPSA (2.71 mol CO₂ /kg) and then increases for THSA (1.78 moles CO₂ /kg)²¹. This is a result of two simultaneously occurring phenomena: with increasing size of the substituent, increasing physisorption and decreasing chemisorption. The physisorption of CO₂ by silylated amines is small at 1 bar, but significant higher at high partial pressures of CO₂²¹.

The reversion temperature of these compounds transitions from 70.5 °C for TEtSA to 64 C for TP50.5 °C for THSA²². Viscosities of RevILs at 25°C are 7600 cP for TEtSA, 4000 cP for TPSA, and 1650 cP for THSA. At flue gas operating conditions, the viscosities of these solvents decrease nearly by a factor of four. Viscosity of TPSA upon reaction with CO₂ depends on the extent of conversion. At approximately 60% conversion of the molecular liquid to its ionic form, hence we believe that the unreacted amine acts as a solvent and solvates the salt causing dissociation of the ions (Figure 8). At

higher conversions, even small changes in composition (on the order of 1%) can cause drastic changes in viscosity (on the order of 100 cP)²¹.

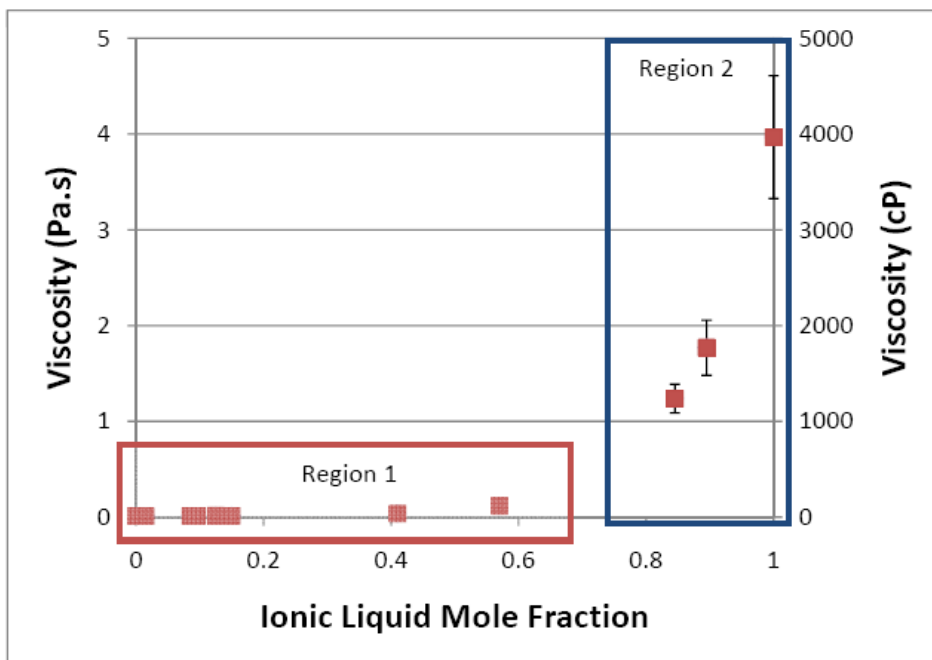


Figure 8: Viscosity of TPSA as a function of ionic liquid mole fraction, 25°C (Reprint)²¹

TPSA has a modest reversal temperature of 64 °C, an absorption capacity which is higher than the ILs in literature, and a tunable viscosity based on its extent of conversion, with a viscosity of 1050 cP at 40 °C. Also, there is a significant gap between its reversal temperature (64 °C) and its evaporation temperature (180 °C), making TPSA a thermally stable CO₂ capture solvent. Therefore it is chosen as the model silylated amine candidate for the studies in this project²¹.

1.4 Research Objectives

This study is aimed at providing a fundamental understanding of how reversible ionic liquids can be used in a real flue gas stream to reversibly capture CO₂ in the presence of SO₂. DOE reports indicate the presence of 45 ppmv of SO₂ in flue gas streams after removing 90% of SO₂ using wet or dry flue gas desulfurization systems⁴. This leads to concerns of SO₂ reacted stable products accumulating in the recycled solvent. The reaction taking place between the silylated amines and the SO₂ is essentially unknown. Prior studies in our group focused on reactions of pure CO₂ with silylated amines. In this study, we focus on reaction of TPSA with pure SO₂. Isolating a specific gas for reacting with the model silylated amine solvent, Tripropylsilylamine (TPSA), allows analyses of the effects of that gas on the solvent. We then move on to the reaction of TPSA with mixed gases consisting of CO₂/SO₂/N₂ to simulate realistic flue gas compositions.

CHAPTER 2

EXPERIMENTAL

The following experiments were performed with the model silylated amine, Tripropylsilylamine (TPSA). TPSA is in the molecular form initially (TPSA_{ML}). Upon absorption of SO₂, CO₂, or a mixture of SO₂/CO₂/ N₂ in different proportions, TPSA switches from its molecular form to its ionic form (TPSA_{IL}). Ionic liquids formed upon absorption of CO₂ and SO₂ will be referred to as TPSA_{CO₂IL} and TPSA_{SO₂IL} respectively. With a mixture of SO₂ and CO₂, the ionic liquid formed will be referred to as TPSA_{CO₂SO₂IL}.

Starting Materials: Tripropylsilane (Sigma-Aldrich, 99%), Allyl amine (Sigma-Aldrich, 99+%), Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt-DVDS) (Sigma-Aldrich, approximately 2% solution in xylene), Toluene Anhydrous (Sigma-Aldrich, 99.8%), SO₂ (Airgas, 99.98% anhydrous), CO₂ (Airgas, 99.999%), and N₂ (Airgas, 99.98%).

Synthesis of Tripropylsilylamine (TPSA_{ML}) : The synthesis of TPSA_{ML} has been established in the research group previously²¹. Tripropylsilane was reacted with two equivalents of allyl amine in toluene (Figure 9) and heated for 24 hours at 110 °C over reflux in the presence of 0.1 mol% Pt-DVDS (Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene) catalyst²¹. This is a one-step, simple and efficient synthetic scheme. Once TPSA was formed, it was cooled to room temperature and separated from unreacted allyl amine and toluene with a rotary evaporator. The remaining

mixture was distilled to remove Pt-DVDS. The isolated TPSA_ML was thoroughly characterized using ^1H and ^{13}C NMR, FT-IR, and elemental analysis²¹.

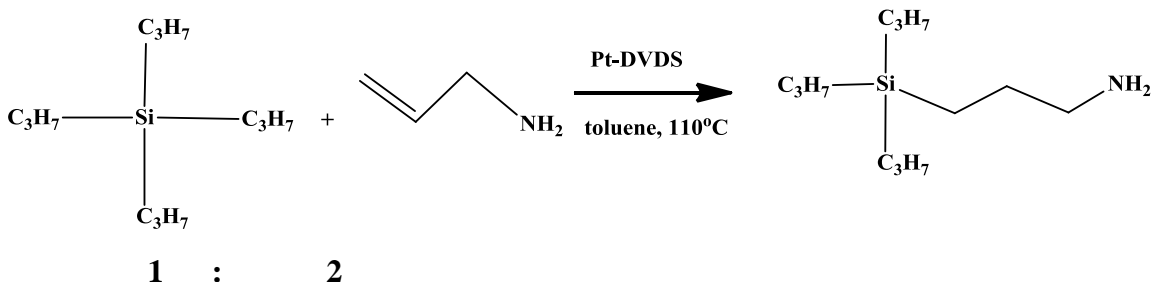


Figure 9: Synthesis of Tripropylsilylamine (TPSA_ML)²¹

2.1 Experiments of Pure SO_2 with TPSA_ML

2.1.1 Formation of TPSA_ SO_2 _IL

TPSA_ SO_2 _IL was formed by bubbling pure SO_2 using a 16 gauge stainless steel needle through approximately 1 mL of TPSA_ML in an airtight 1 or 2 dram vial. The vial was purged with N_2 after securely taping a rubber septum to its mouth; this ensures the removal of any air or moisture in the vial (Figure 10). A long stainless steel vent, with one end inserted through the septum reaching the headspace of the vial, and the other end reaching the back of the fume hood, ensures proper release of SO_2 . The reaction was run at 1 bar for 75 minutes at an overall gas flow rate of 400 ml/min.

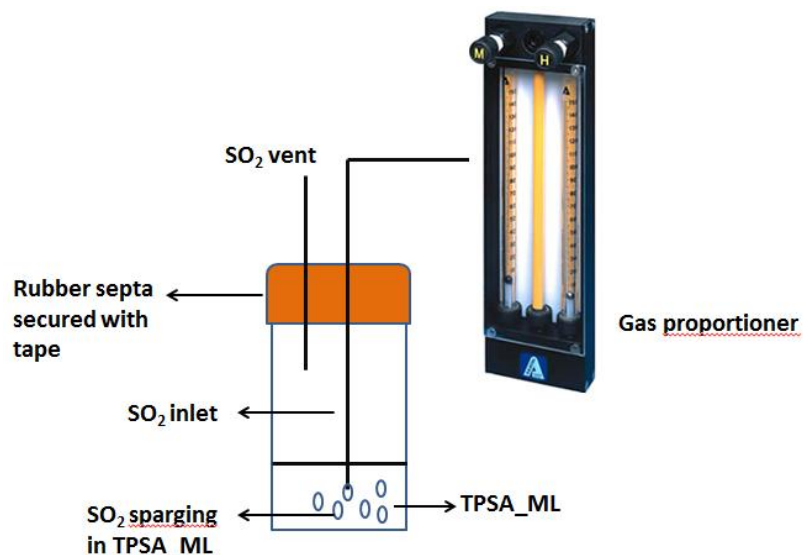


Figure 10: Schematic for TPSA_SO₂_IL formation; not to scale; gas proportioner image credits-Aalborg ²³

2.1.2 Measuring SO₂ Uptake Capacity of TPSA_ML

Gravimetric techniques were employed to determine the overall capture capacity of TPSA molecular liquid. The net weight gain after completion of the reaction of TPSA_ML with pure SO₂ represents combined chemisorption and physisorption of SO₂ by TPSA. The vial and needle weight were measured before and after the reaction to calculate the net weight gain.

2.2 Characterizing TPSA_SO₂_IL Products

TPSA_SO₂_IL was characterized using ¹H and ¹³C NMR, Fourier transform infrared (FT-IR) spectroscopy, Thermogravimetric Analysis, and Elemental Analysis.

2.2.1 FT-IR Measurements

The Fourier transform infrared (FT-IR) absorbance measurements were collected with a Shimadzu IRPrestige21 using a DLaTGS detector, with 32 scans and a resolution of 1 cm^{-1} . About 50 mg of sample was placed on the diamond ATR crystal and the spectrum was taken at room temperature and 1 bar. The bands in the spectra, representing various functional groups, were identified. To identify the band representing physisorbed SO_2 the following were done.

First, a preformed sample of SO_2 absorbed into the conventional ionic liquid [BMIM] $[\text{BF}_4]$, was placed in the sample cell and the IR spectra was taken. [BMIM] $[\text{BF}_4]$ absorbs SO_2 via physisorption alone and thus comparing the spectra of [BMIM] $[\text{BF}_4]$ before and after absorbing SO_2 allows identification of the physisorbed SO_2 peak.

Secondly, we placed a preformed TPSA_ SO_2 _IL in the sample cell and took spectra at 0 minute, 25 minute, and 50 minute, at room temperature and 1 bar atmospheric pressure. The peak that showed significant loss was assumed to be the physisorbed SO_2 peak.

2.2.2 NMR Analysis

Qualitative ^1H and ^{13}C NMR experiments for molecular structural determination were run at room temperature using a Bruker AMX 400 MHz spectrometer. An NMR sample of TPSA_ML was prepared by diluting the sample in deuterated chloroform (CDCl_3). For TPSA_ SO_2 _IL, neat NMRs were run in order to prevent any possibility of reversion of the ionic liquid back to its molecular form. A standard NMR tube was loaded with TPSA molecular liquid, and SO_2 was bubbled into it until complete conversion to

the ionic liquid was observed by gravimetric measurements. A capillary tube containing CDCl_3 , which locks the sample in the NMR, was placed inside the sample.

The conversion of the molecular liquid to the ionic liquid is observed in the ^1H and ^{13}C NMR spectra. Cases of incomplete conversion are evidenced by the presence of both carbon peaks from the molecular and ionic liquids. After the 75 minute reaction, no peaks representing the molecular liquid were present, indicating complete conversion to the ionic liquid.

2.2.3 Desorption Experiments using the Thermogravimetric Analyzer (TGA)

In a TGA Q50 Thermogravimetric Analyzer, approximately 18 mg of the preformed ionic liquid was heated to $500\text{ }^\circ\text{C}$ at a ramp rate of $5\text{ }^\circ\text{C}$ per minute. Multiple events were observed in the sample as the temperature increased. To de-convolute the events, changes in weight with respect to changes in temperature were plotted. Three separate peaks were observed. To analyze the extent of reversal or sample degradation, IR spectra of the sample were taken after each observed event in the TGA and analyzed.

2.2.4 Desorption Experiments in a Vial

Separate events occurred at approximately $75\text{ }^\circ\text{C}$ and $100\text{ }^\circ\text{C}$ in the TGA thermogram of TPSA_SO₂_IL. To identify products forming when TPSA_SO₂_IL was heated in TGA at these temperatures, both IR and NMR techniques were employed and the experiment was scaled up.

A vial containing preformed TPSA_SO₂_IL was placed in a sandbath maintained at the desired temperature ($75\text{ }^\circ\text{C}$). A rubber septum was taped to its mouth and a vent

was inserted through the septum. The experiment was run for 16 hours. Sampling was done frequently for the first six hours and then less frequently during the remaining ten hours. A second vial containing preformed TPSA_SO₂_IL was heated and sparged with N₂, which is considered a more rigorous desorption technique. IR and NMR techniques were employed to analyze samples from both experiments.

2.2.5 Elemental Analysis

Elemental micro-analyses of both TPSA_ML and TPSA_SO₂_IL, by combustion using automatic analyzers, were conducted by Atlantic Microlab, Inc. located in Norcross, GA. The molecular liquid samples were stored under argon and mailed to the lab. The ionic liquids were delivered in person and run within 12 hours. The atoms tested for are carbon (C), hydrogen (H), sulfur (S), and nitrogen (N). The elemental analysis of oxygen was expressed to be inaccurate (by employees at Atlantic Microlab, Inc.) relative to the other 3 compounds, and was therefore not requested. The compositions were reported in terms of weight percents.

2.3 TPSA_ML Reactions with Dilute SO₂ Streams

2.3.1 Mixed Gas Compositions

Effects of varying gas compositions on TPSA_ML uptake capacities were also analyzed. The use of a model B gas proportioner meter from Aalborg was implemented, which gave us the flexibility of mixing three gases at any one given time.

The gas proportioner was calibrated using a bubble gas flow meter from Bubble-O-Meter. Gas compositions of 8 vol% SO₂ in N₂, and 4 vol% SO₂ in 15 vol% CO₂ + 81

vol% N₂ were experimented with to study gas uptake capacities in simulated streams. SO₂ concentrations in these mixtures were orders of magnitudes higher than in real streams for analysis purposes.

Compositions of 4 vol% SO₂ in CO₂, 10 vol% SO₂ in CO₂, and 50 vol% SO₂ in CO₂, were employed for a more fundamental understanding of the effects of mixed gas streams on uptake capacities of silylated amines.

TPSA Ionic Liquids with mixed gases were formed in the same manner that TPSA_SO₂_IL was formed; with the gas composition carefully adjusted using the flow meter. The ionic liquids were characterized using FT-IR, elemental analysis, and TGA as explained above. Slight modifications, however, were made to the NMR set-up for mixed gas TPSA ionic liquids as explained below.

2.3.2 NMR of Mixed Gas TPSA Ionic Liquids

It was difficult to take the NMRs of mixed gas TPSA ionic liquids neat due to their relatively higher viscosities compared to TPSA_SO₂_IL and TPSA_CO₂_IL. A neat NMR of mixed gas ionic liquid could not be successfully locked and shimmed in the NMR instrument. Mixed gas ionic liquids were thus pre-formed in a vial, instead of in an NMR tube. They were then diluted with CDCl₃ to minimize viscosity related issues, and then pipetted to the NMR tube from the vial.

To validate this technique, neat NMRs of both neat CO₂ ionic liquid and neat SO₂ ionic liquids were compared with NMRs of pure SO₂ ionic liquid and pure CO₂ ionic liquids diluted with CDCl₃. The resulting ¹H and ¹³C NMRs did not show any significant changes in chemical shifts. To prevent any possibility of degradation or reversal of the

ionic liquid in CDCl_3 , waiting times between adding CDCl_3 to the ionic liquid to when the NMR was taken, were kept at a minimum.

CHAPTER 3

RESULTS & DISCUSSION

Given the potential of silylated amines as CO₂ capture solvents for flue gas, it is important that we investigate not only reactions of pure CO₂ with these solvents, but also move a step further and analyze the effects of other flue gas components, such as SO₂, and N₂, on the reactivity, selectivity, and reversibility of the solvent. The experiments are conducted using TPSA, a compound with demonstrated CO₂ capture capability and reversibility at modest temperatures. TPSA has a relatively low molecular weight (215.45 g/mol), a high CO₂ uptake capacity (2.561 mole CO₂/kg of TPSA_ML), modest reversal temperature (65 °C), and evaporation temperature of 116 °C. Additionally, there are further benefits with being able control the viscosity of TPSA_CO₂_IL based on the extent of conversion to the ionic form (Figure 8).

Our aim is also to identify products of reaction of mixed gas streams with TPSA_ML, with a broader/additional purpose of separating CO₂ and SO₂ from potential mixed gas streams having compositions other than that of flue gas. The following sections present results of the reaction of TPSA_ML with pure SO₂ and with mixed gas streams of CO₂/SO₂/N₂. Gravimetric uptakes, IR and NMR characterization, and thermogravimetric analyses of TPSA_SO₂_IL, TPSA_CO₂_IL, and TPSA_ILs with mixed gas compositions are presented.

3.1 TPSA_ML Reactions with Dilute SO₂ Streams

3.1.1 Formation of Ionic Liquid

By analogy with the procedure for CO₂ capture, pure SO₂ is sparged through 1 mL of TPSA_ML in a 1 dram vial for 75 minutes at a flow rate of 400 mL min⁻¹, pressure of 1 bar, and at room temperature. Within the initial 30 seconds of the reaction, the sample turns pale yellow and the vial feels warm upon touch indicating that an exothermic reaction is occurring. After the first 5 minutes, the vial is no longer warm upon touch and the sample is bright yellow and clear. In 75 minutes, the sample changes to an amber color and is opaque. The viscosity of the sample increases from a liquid to a gel-like consistency. Despite the applied flow rate of SO₂ being constant over time, the size of the bubbles in solution increases and the observed rate of bubble formation decreases, signifying increased sample viscosity. Overall, color and consistency changes of the sample indicate that TPSA_ML has reacted with SO₂.

3.1.2 Gravimetric Uptake of SO₂ by TPSA_ML

The net weight gain after 75 minutes is determined by weighing the vial and the needle through which SO₂ is bubbled, before and after the reaction. Table 3 presents molar uptake ratios of absorbed SO₂ to TPSA_ML at 200 mL min⁻¹ and at 400 mL min⁻¹. The uptake capacity at 400 mL min⁻¹ is 6.3% higher than that at 200 mL min⁻¹, indicating that the reaction of pure SO₂ with TPSA_ML is mass transfer limited, since we observe further increase in uptake, despite the 200 mL min⁻¹ system having an excess of SO₂. Also, due to the high viscosity of the sample we were unable to measure it using a Rheosys Merlin II rotational viscometer.

Table 3: Molar uptake capacity of SO₂ by TPSA_ML at 20 °C, 1 bar, and 75 minutes

Flow Rate (mL min ⁻¹)	Mole SO ₂ /kg TPSA ML	Mole SO ₂ /Mole TPSA ML
200	6.402 +/- 0.041	1.378 +/- 0.00694
400	6.814 +/- 0.068	1.465 +/- 0.01467

Figure 11 shows results from a preliminary experiment done at 212 mL min⁻¹ with the same experimental set-up as discussed above, to measure the molar ratio of the absorbed SO₂ to TPSA_ML, as a function of the absorption time. The amount of SO₂ absorbed increases rapidly with time up until about 50 minutes and then gradually begins to plateau, suggesting that the solvent is reaching its saturation capacity.

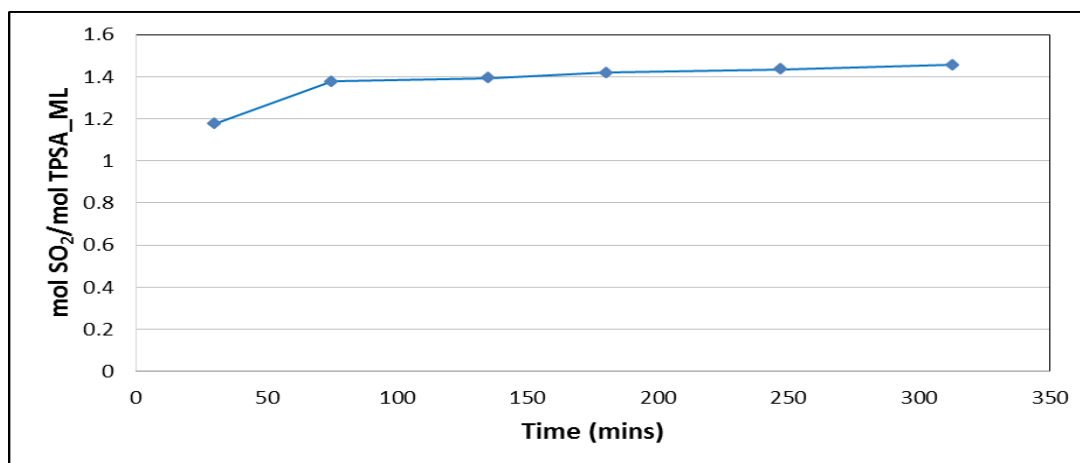


Figure 11: Molar ratio of SO₂:TPSA_ML as a function of time. Condition: 20 °C, 1 bar, 212 mL.min⁻¹

We next determine the maximum SO₂ absorption capacity of TPSA_ML. SO₂ was sparged through 1 mL of TPSA in a 1 dram vial for 6 hours at a rate of 200 mL.min⁻¹ using a diffuser tube. A similar preliminary experiment was performed using a stainless steel needle for sparging at an unknown SO₂ flow rate. The net weight gains after 6 hours in both cases were noted and the molar ratio of SO₂ to TPSA_ML were calculated. The average molar uptake capacity is 1.59205 with a standard deviation of 0.00134. Therefore regardless of the flow rate of SO₂ and the means of sparging used, the SO₂ uptake after 6 hours is constant, indicating that a saturation limit has been reached. Absorption capacities of TPSA_ML for pure SO₂ are higher than those of most conventional ILs, such as [BMIM] [BTA], [TMG] [BF₄], [BMIM] [BF₄], and [BMIM] [Tf₂N] with SO₂ to IL molar ratios of 1.33, 1.27, 1.5, and 0.916, respectively^{16,17}.

While reactions for longer durations give the maximum uptake, uptakes achieved after 75 minutes of SO₂ sparging at 200 mL min⁻¹, 1.378 mol SO₂ to TPSA_ML, was deemed sufficient for examining the products formed from the reaction. Based on stoichiometry alone, the expected molar ratio of absorbed SO₂ to TPSA_ML is 0.5. Therefore at 75 minutes, we expect the molecular liquid to completely react to form TPSA_IL. We propose the following scheme for the reaction between TPSA_ML and SO₂.

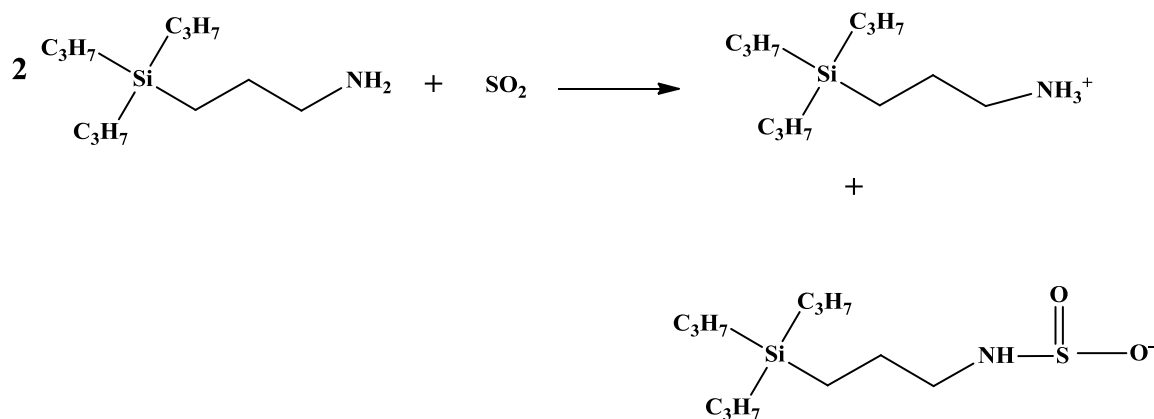
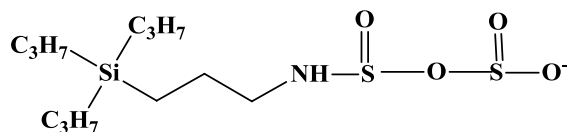
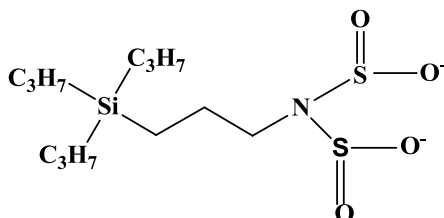


Figure 12: Proposed reaction between TPSA_ML and SO₂

This reaction scheme is analogous to the established reaction of CO₂ with silylated amines (Figure 7). The neutral TPSA_ML reacts with SO₂ to form a cation with an ammonium (NH₃⁺) species and an anion with a sulfamate (NHSO₃⁻) species. We propose that the increased uptakes observed experimentally from gravimetric measurements, 1.378 at 200 mL.min⁻¹ and 1.465 at 400 mL.min⁻¹, are due to physisorption of SO₂ by TPSA_IL, and/or additional reactions occurring between SO₂ and TPSA. The side products we propose are shown in Figure 13. The two possible side products have very similar functional groups that are rearranged differently and they could potentially double the SO₂ uptake capacities.



1.0 mol SO₂/mol TPSA_ML



1.0 mol SO₂/mol TPSA_ML

Figure 13: Possible side products from reaction of TPSA_ML with pure SO₂

We characterize the samples before and after exposing to SO₂ by FTIR and NMR. The detection of side products can be difficult because in an NMR we observe an averaging of signals due to high viscosities and hydrogen bonding within the molecules. Also, an IR spectrum gives a series of bands which make a definitive structural elucidation difficult.

3.1.3 IR Analysis of TPSA_SO₂_IL

IR spectra of TPSA_SO₂_IL samples from triplicate experiments were seen to overlap well validating repeatability. Figure 14 presents the IR spectra of both TPSA_ML and TPSA_SO₂_IL.

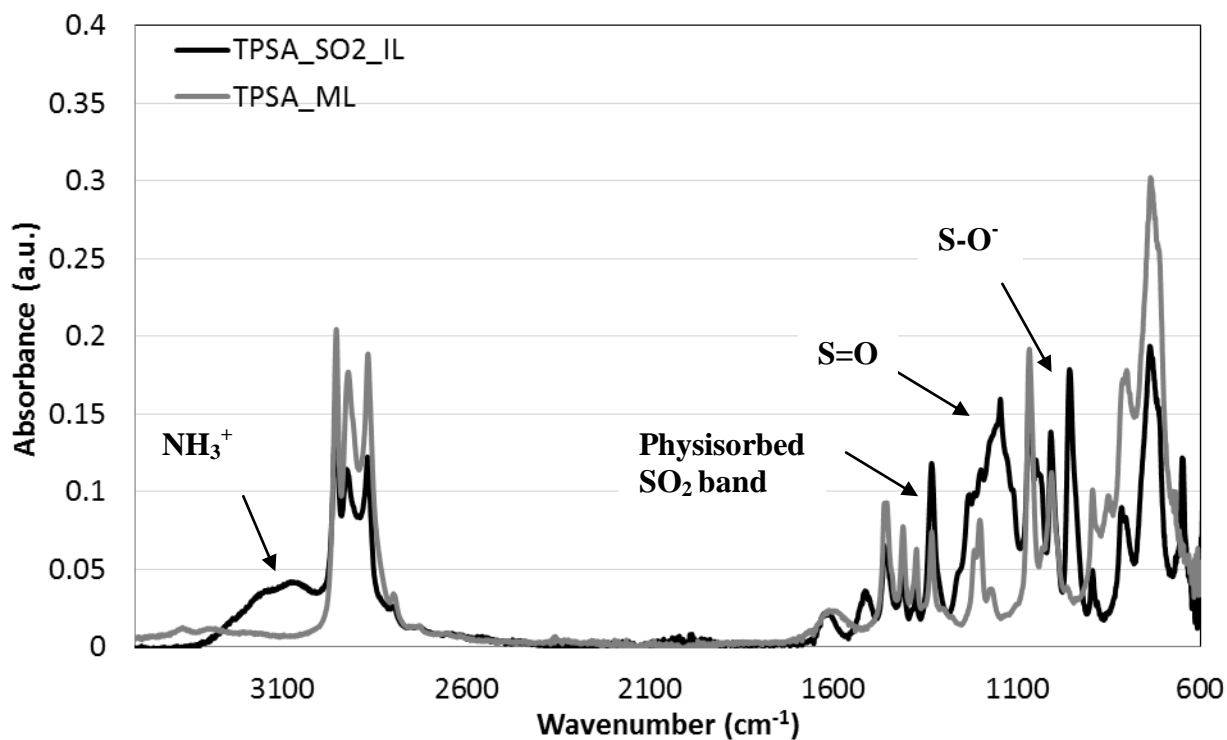


Figure 14: IR spectra of TPSA_ML and TPSA_SO₂_IL, at 20 °C, 1 bar, 75 minute

New absorption bands form, when SO₂ reacts with TPSA_ML. These bands and their respective frequencies were identified and correspond to the types of chemical bonds that they represent (Table 4). Figure 15 presents the bands identified in the fingerprint region of the TPSA_SO₂_IL spectra.

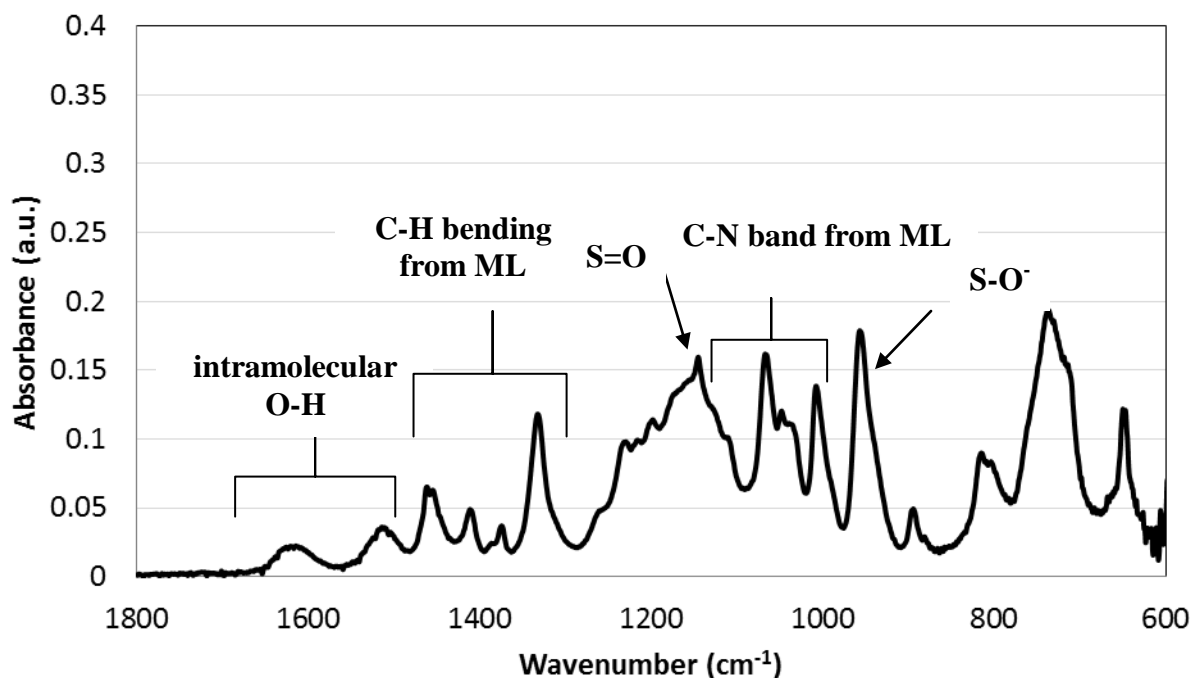


Figure 15: Fingerprint region of IR of TPSA_SO₂_IL at 20 °C, 1 bar

Table 4: Characteristic IR bands for TPSA_SO₂_IL

Group	Absorption (cm ⁻¹)	Intensity	Reference
C-N stretch in amines	1058	narrow, strong	Wu <i>et al.</i> ^{3,24}
S=O	1080-1270	broad, strong	Wu <i>et al.</i> ^{3,24}
S-O ⁻	1013-1049	narrow, strong	Wu <i>et al.</i> ^{3,24}
N-H bending	1566-1700	broad, weak	Wu <i>et al.</i> ^{3,24}
Intermolecular O-H interaction	1475-1562	broad, weak	Wu <i>et al.</i> ^{3,24}
NH ₃ ⁺	2600-3200	Strong	Heldebrant <i>et al.</i> ¹⁸
C-H bending from ML	1279-1479	Moderate	characteristic band ²⁴

The IR spectrum of TPSA_SO₂_IL clearly shows: strong S=O bond (1080-1270 cm⁻¹), strong S-O⁻ bond (1013-1049 cm⁻¹), strong N-H bond in NH₃⁺ (2600-3200 cm⁻¹), weak O---H band from intramolecular attraction between the NH and SOO groups in the anion (1475-1562 cm⁻¹), weak N-H bending from the anion (1566-1700 cm⁻¹), and C-H bond from the -CH₂ and -C₃H₇ groups (1279-1479 cm⁻¹) (Figure 15). Compared to the spectrum of TPSA_SO₂_IL, TPSA_ML shows a band for the amine (-NH₂) functional group which overlaps with the NH₃⁺ group of the IL.

Also, the physisorbed SO₂ peak for TPSA_SO₂_IL overlaps with the C-H stretches of the TPSA_ML, in the 1275-1364 cm⁻¹ range. The IR peak corresponding to physisorbed SO₂ peak was nonetheless positively confirmed by placing pre-formed TPSA_SO₂_IL at room temperature on the diamond IR cell, covering the sample with an inverted vial, capturing IR spectra of the sample over a period of 50 minutes (Figure 16) and monitoring changes in the peaks. Since physisorbed SO₂ can easily be released at room temperature, the peak which shows significant decrease in intensity corresponds to the physisorbed SO₂ peak.

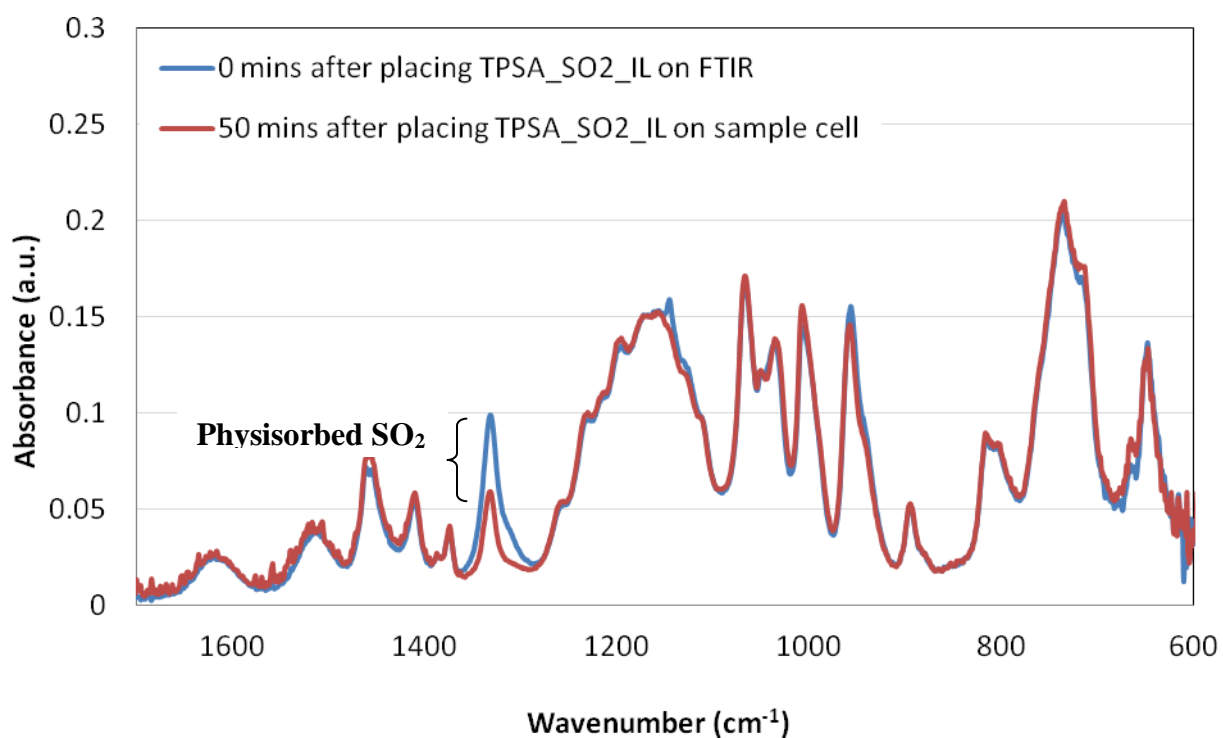
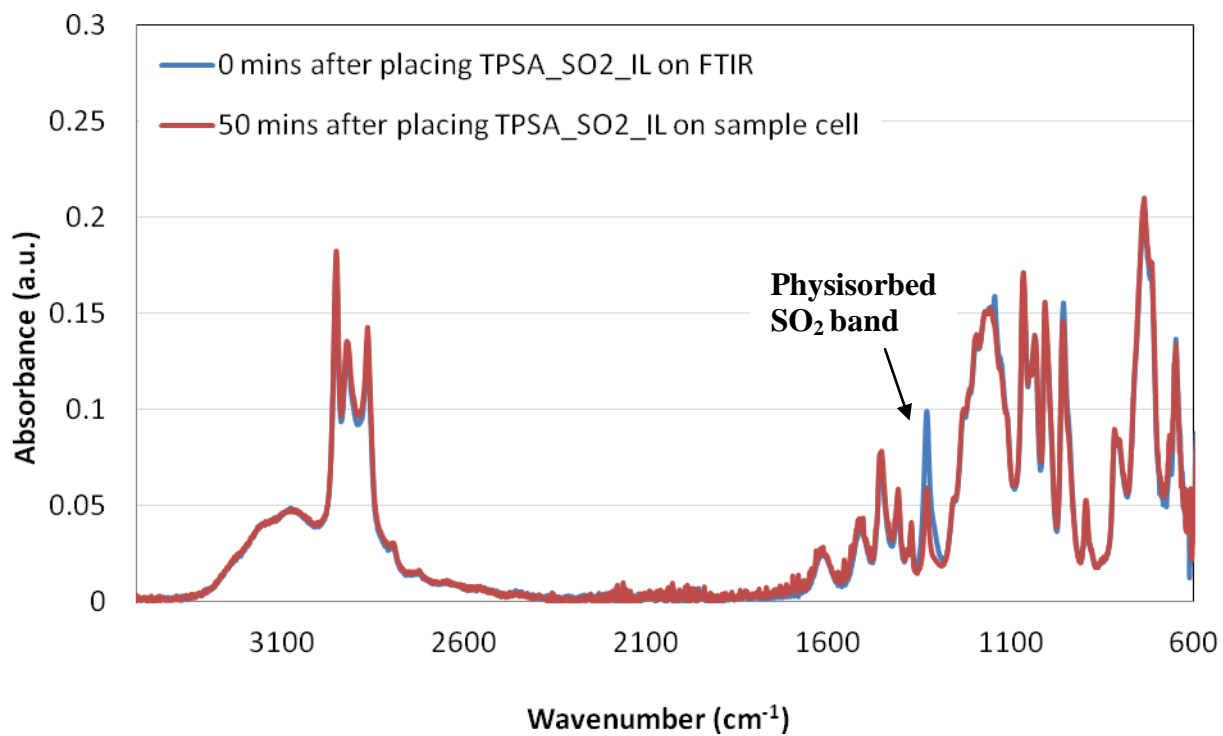


Figure 16: IR spectra of TPSA_SO₂_IL showing changes in peaks, to monitor the physisorbed SO₂ peak

Additionally, SO₂ was absorbed into a conventional ionic liquid [BMIM][BF₄] for 75 minutes at room temperature and the IR spectra before and after exposure to SO₂ were compared. [BMIM][BF₄] is known to absorb SO₂ by physisorption alone and thus any changes observed in the peaks were expected to be due to physisorption. Changes in peaks were again monitored (Figure 17). A medium intensity, narrow peak forms in the 1300-1370 cm⁻¹ range. The shape of the peak is very similar to the physisorbed SO₂ peak in TPSA_SO₂_IL. It also falls within the same range. The experiment with the conventional IL therefore further confirms the location of the physisorbed SO₂ band.

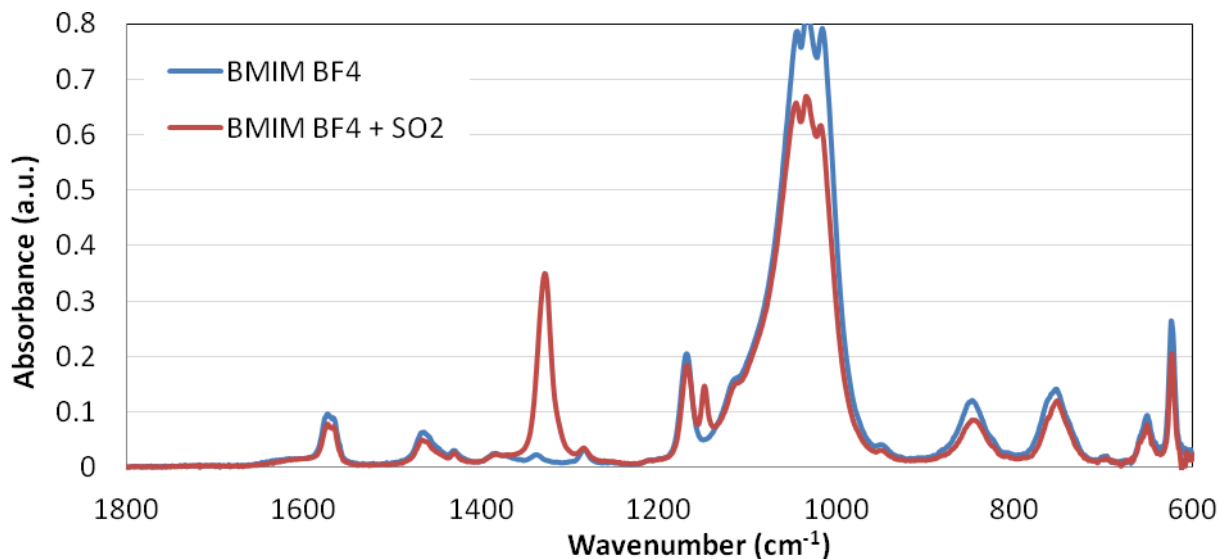


Figure 17: IR spectra of [BMIM] [BF₄] and SO₂ absorbed [BMIM] [BF₄]

3.1.4 NMR Analysis of TPSA_SO₂_IL

¹³C NMR spectra of TPSA_SO₂_IL and TPSA_ML are presented in Figure 18 and Figure 19. Details of the assignments of the resonances of TPSA_ML (Figure 18) and TPSA_SO₂_IL are presented (Figure 19). Besides the reference peaks from CDCl₃ at 77.68-77.31 ppm, nine distinct peaks are visible. The peaks at 9.83 and 10.30 ppm correspond to carbons that are α to the Si atoms in the cation and anion of the IL, respectively. Similarly, the peaks at 22.25 and 25.20 ppm correspond to the carbons β to the N atom in the cation and anion of the IL, respectively. The carbon atoms that are α to the N atoms in the cation and the anion, show up at 43.40 and 51.48 ppm, respectively. The C atoms of the propyl groups of both the cation and the anion are also shown in Figure 12 as three distinct peaks with the highest intensities (15.30, 15.35, 17.62, 17.64, 18.69, 18.77 ppm).

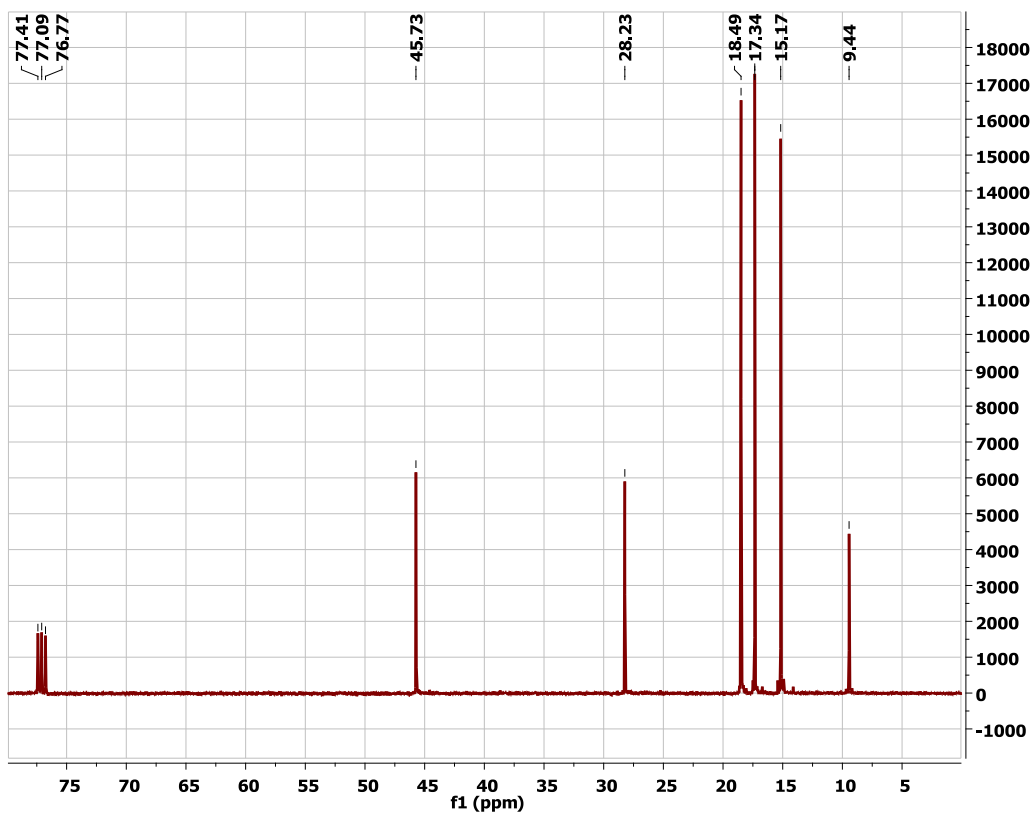
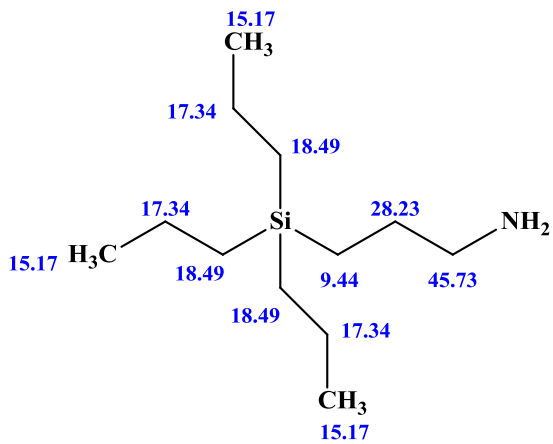
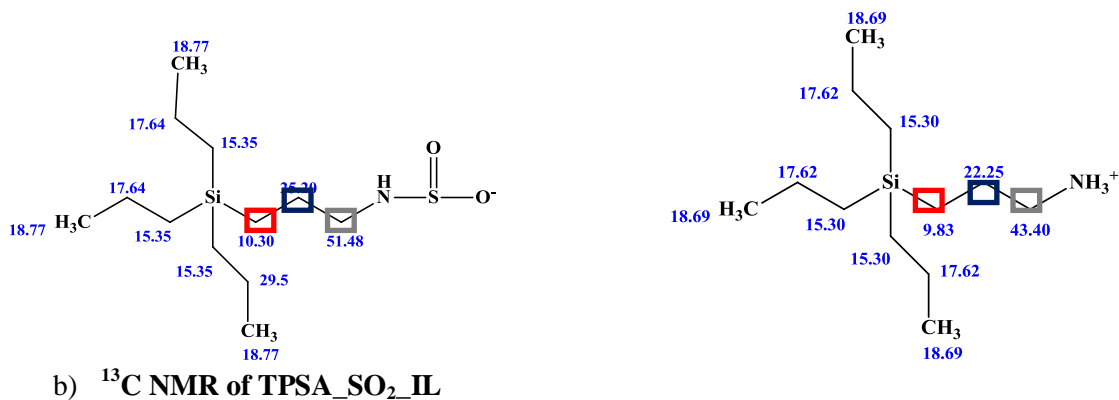


Figure 18: ^{13}C NMR spectra of TPSA_ML

a) **TPSA_SO₂_IL** products with the chemical shift values from the ¹³C NMR spectra in below



b) ¹³C NMR of TPSA_SO₂_IL

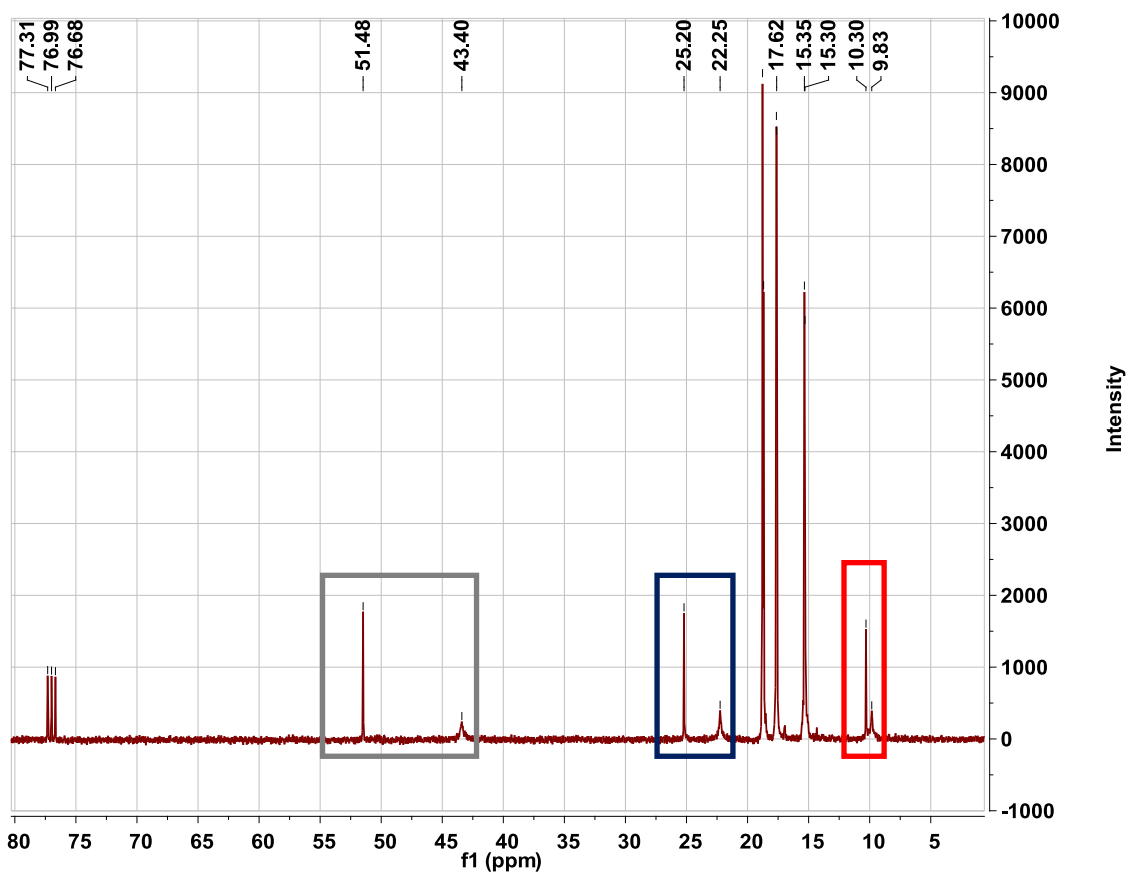


Figure 19: ¹³C NMR spectra of TPSA_SO₂_IL

The ^1H NMR spectra of the TPSA_ML, and the SO_2 treated IL are presented in Figure 20 and Figure 21. The observed ^1H NMR shifts (δ , ppm) and the corresponding splitting pattern (singlet = s, doublet = d, triplet = t, quartet = q, pentet = p, and multiplet = m; broad peaks are denoted with 'br') and integration values for the TPSA molecular liquids and TPSA_ SO_2 _IL are given:

TPSA Molecular Liquid: 2.60 (t,2); 1.38 (p,2); 1.26 (m, 6); 1.07 (s, 2.01); 0.87 (t, 9.28);0.47 (m,7.90)

TPSA_ SO_2 Ionic Liquid: 7.37 (br,34.82); 3.91 (tr,1); 2.90 (tr, 30.27);1.66 (br, 26.27);1.29(m,149.45);0.92 (tr,234.20);0.49 (m,188.62)

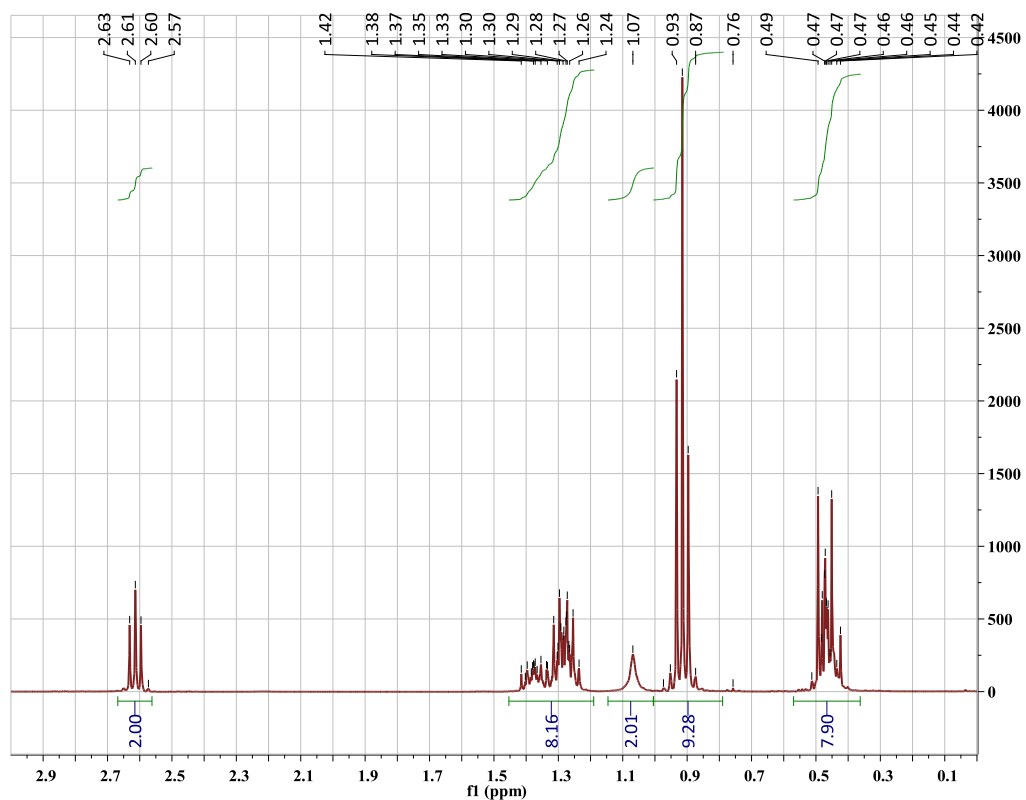


Figure 20: ^1H NMR of TPSA_ML

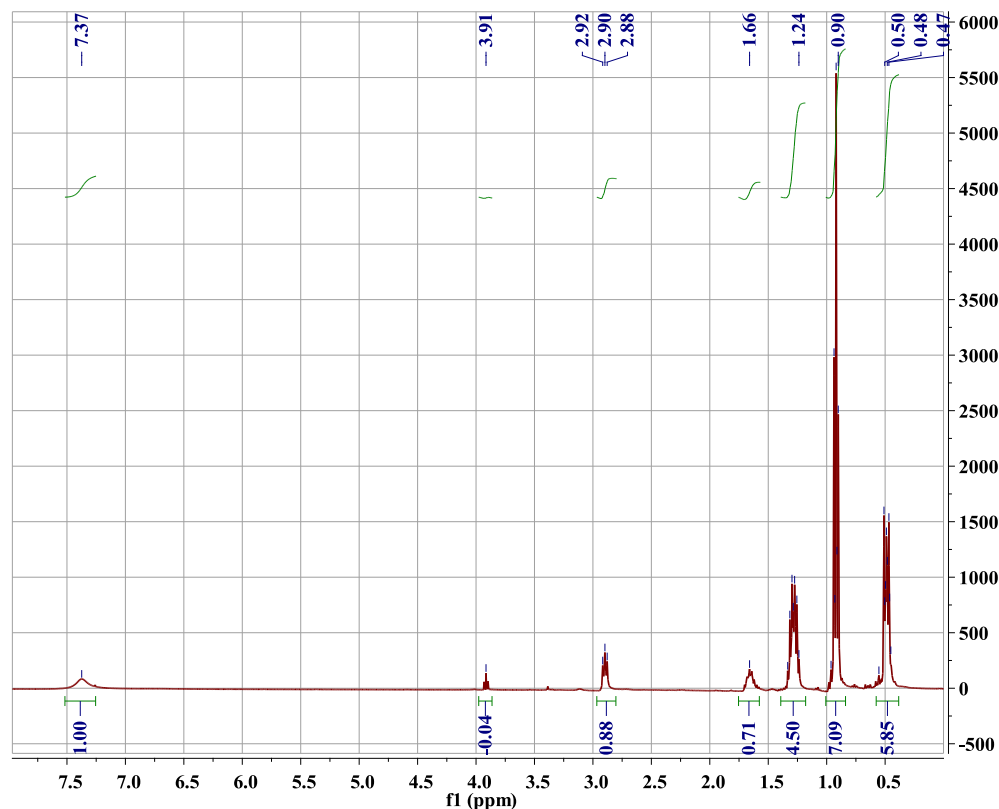
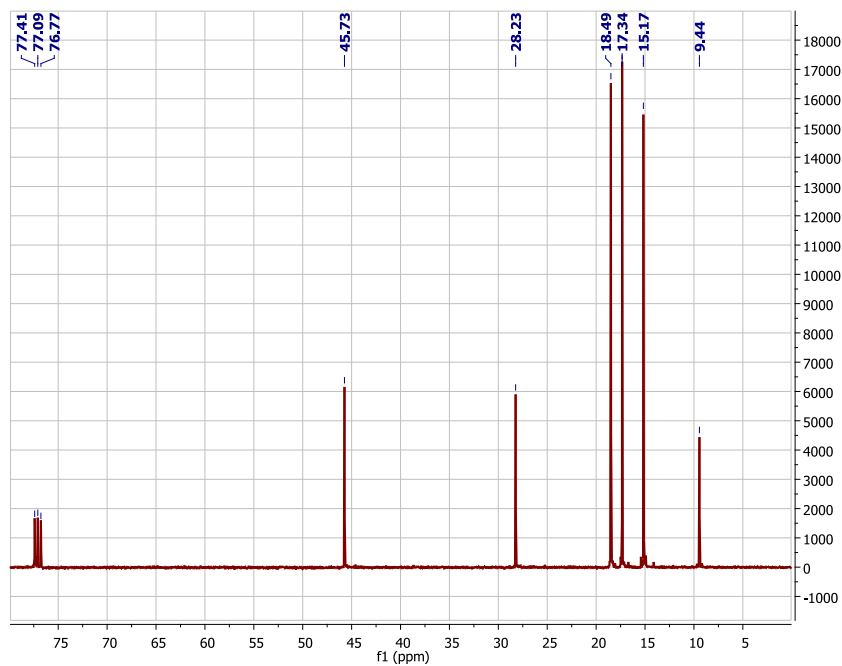


Figure 21: ^1H NMR of TPSA_SO₂_IL

Comparing the NMRs of TPSA_ML and TPSA_SO₂_IL (Figure 22), shows that the peak at 45.78 ppm in TPSA_ML splits to 43.30 and 51.48 ppm. Similarly, the peak at 9.47 ppm splits to 9.83 and 10.30 ppm; the peak at 28.27 splits to 22.25 and 25.20 ppm. Since each of these peaks in the TPSA_ML split into two peaks in the TPSA_SO₂_IL, (Figure 19), NMR results are consistent with the formation of our proposed counter ions. Because of the similarity in structures among the anions, while the IR and NMR spectra support the formation of our proposed IL, they do not rule out the possibility of the side products forming.

a. TPSA_ML



b. TPSA_SO₂_IL

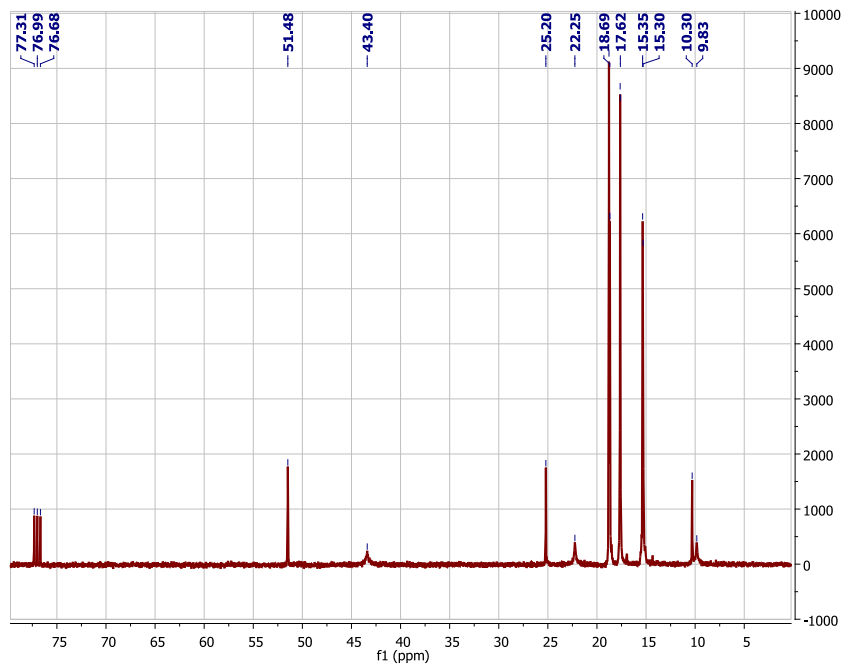


Figure 22: ^{13}C NMR spectra of (a) TPSA_ML and (b) TPSA_SO₂_IL in CDCl_3

Prior studies of TPSA_ML with pure CO₂ gave uptake capacities of 0.64 mole CO₂/mole TPSA_ML, compared to uptakes of 1.378 with pure SO₂ for 75 minute reactions at a total flow rate of 200 mL.min⁻¹. Assuming that no side products are forming, and given that the stoichiometric ratio of both CO₂ and SO₂ to TPSA_ML is 0.5, the increased experimental uptake is then due to physisorption of the gas by the IL. We can then assume that interactions between the gas and the IL are dominated by non-specific forces. The gas molecule (CO₂ or SO₂) with the smaller solubility parameter, δ , will be more soluble in the IL.

$$\text{Solubility parameter } (\delta) = (\Delta U^{\text{vap}}/V)^{0.5}$$

where, ΔU^{vap} -heat of vaporization, V – molar volume

If one assumes that the heats of vaporization are similar, SO₂ has the larger molar volume (since the sulfur atom in SO₂ is larger than the carbon atom in CO₂) and hence the smaller solubility parameter, leading to greater solubility in TPSA_ML, compared to CO₂. Anthony et al. had compared the solubility of CO₂ in two conventional ILs using the solubility parameter concept as well.¹²

SO₂ has a net dipole moment which allows it to engage in dipole-dipole interactions with the amine. In contrast, CO₂, which is linear with no net dipole moment, interacts with the amine via Vander Waals forces alone. Therefore, the bonding between SO₂ and the amine is stronger, giving rise to higher uptake capacities.

For TPSA_ML, the actual values of the elements C, H, and N, are consistent with the theoretical prediction. For TPSA_SO₂_IL, the actual values of C, H, N, and S are

consistent with a 1:1 TPSA_ML: SO₂ molar ratio. This is not supported by what we observe gravimetrically (1.45 mole SO₂ per mole TPSA_ML at 400 mL/min⁻¹). We had earlier seen that physisorbed SO₂ gets released from TPSA_IL, over time, at room temperatures. This may have led to the actual molar ratio of TPSA_ML to CO₂ being lower than the approximate 1.45 uptake ratio obtained with the gravimetric approach

TPSA Molecular Liquid: Expected: C(66.90), H(13.57), N(6.50)

Actual: C(66.74), H(13.64), N(6.35)

TPSA_SO₂ Ionic Liquid: Expected: C (51.38), H (10.195), N (4.86), S (11.795)

Actual: C (51.56), H (10.46), N (5.01), S (11.47)

3.2 Reaction of Mixed Gas Streams with TPSA_ML

Table 5 summarizes the reaction of mixed gas stream with TPSA_ML and the objective of these studies. Gas compositions of 8 volume% SO₂ in N₂, and CO₂/SO₂/N₂ (15/4/81 volume %) were tested to get a more realistic picture of reactions occurring between TPSA_ML and flue gas components. SO₂ concentrations in these mixtures were orders of magnitudes higher than in real flue gas streams for analysis/detection purposes.

Compositions of 4 vol% SO₂ in CO₂, and 50 vol% SO₂ in CO₂, were employed for a more fundamental understanding of the effects of mixed gas streams on uptake capacities of silylated amines, from a chemistry stand point.

In the following sections we present IR, NMR, and gravimetric uptake results, based on which we identify expected products formed from reaction of TPSA_ML with the gas streams in Table 5.

Table 5: Composition of mixed gases for reaction with TPSA_ML

Volume Percent SO ₂	Volume Percent CO ₂	Volume Percent N ₂	Objective of Study
8	0	92	Comparing with published literature for traditional and task specific ILs in N ₂ rich stream
4	96	0	Analyzing TPSA_ML absorption capacities and reactions in CO ₂ rich stream
50	50	0	Selectivity of TPSA_ML for CO ₂ and SO ₂ with reaction time
4	15	81	Effect of SO ₂ on TPSA_ML in a stream containing typical flue gas proportions of CO ₂ and N ₂

3.2.1 Investigating Effects of SO₂ Lean Streams with N₂ on TPSA_ML

Herein we present uptake capacities of TPSA_ML from the reaction of TPSA_ML with SO₂ in N₂ rich streams. We compare SO₂ absorption capacities of TPSA_ML with the absorption capacities of traditional and task-specific ILs in N₂ rich streams simulating flue gas conditions (N₂/SO₂-92/8). N₂ is an inert gas and we expect it to be unreactive with the solvent. However, since SO₂ concentration in the gas stream is dilute, 8 vol%, we expect that it will take longer for the molar ratio of SO₂ to TPSA_ML to reach approximately 1.465 mol SO₂/mol TPSA_ML, with analogous conditions in terms of total flow rate, temperature, and pressure. Based on Henry's law, the physisorption by TPSA_ML may be proportional to a 0.08 bar partial pressure of SO₂ and 0.92 bar partial pressure of N₂. Furthermore, N₂ is usually used as a sparging gas to

reverse absorption of SO₂ in TPSA_ML and release the gas from conventional and task specific ILs (with or without heat and under vacuum) as shown by Heldebrant¹⁸, Riisager^{16,17} and others. These factors are believed to contribute to the lower absorption capacities of SO₂ in TPSA_ML in a N₂ rich stream (Table 6); with pure SO₂, the molar ratio of SO₂ to TPSA_ML is 44 % higher than with the 8 vol% SO₂ in N₂ mixture.

Table 6: Molar ratio of SO₂ to TPSA_ML at 20 °C, 1 bar, 400 mL.min⁻¹, for 75 minutes

Gas Stream	Mole SO ₂ /kg TPSA ML	Mole SO ₂ /Mole TPSA ML
Pure SO ₂	6.814 +/- 0.041	1.465 +/- 0.00694
8 vol% SO ₂ in N ₂	4.697 +/- 0.073	1.012 0+/- 0.01570

The bar chart of molar ratio of SO₂ to TPSA_ML (Figure 23) shows that experimentally, with pure SO₂ and in dilute SO₂ streams, the molar ratios are higher than the theoretical chemisorbed molar ratio of 0.5. The increased uptakes are attributed to physisorption of SO₂ by TPSA, and/or additional side product formation.

¹³C NMR is consistent with the formation of the cation and the anion of TPSA_SO₂_IL (Figure 24); the peaks in the mixed gas IL NMR clearly align with the peaks in the TPSA_SO₂_IL. No additional peaks are detected. It should be noted here that ¹³C NMR was conducted for qualitative structural determination purposes, and not as a quantitative approach. Intensities of peaks vary with sample viscosity and concentration, which were not maintained in the samples. Therefore, instead of analyzing the intensities of the peaks, only the chemical shifts of the peaks are analyzed.

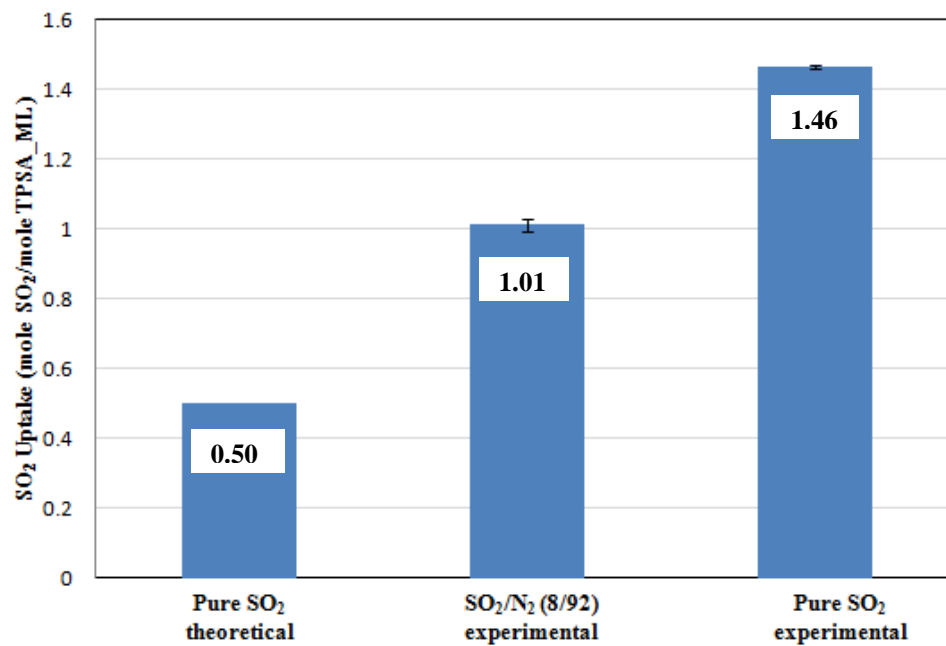
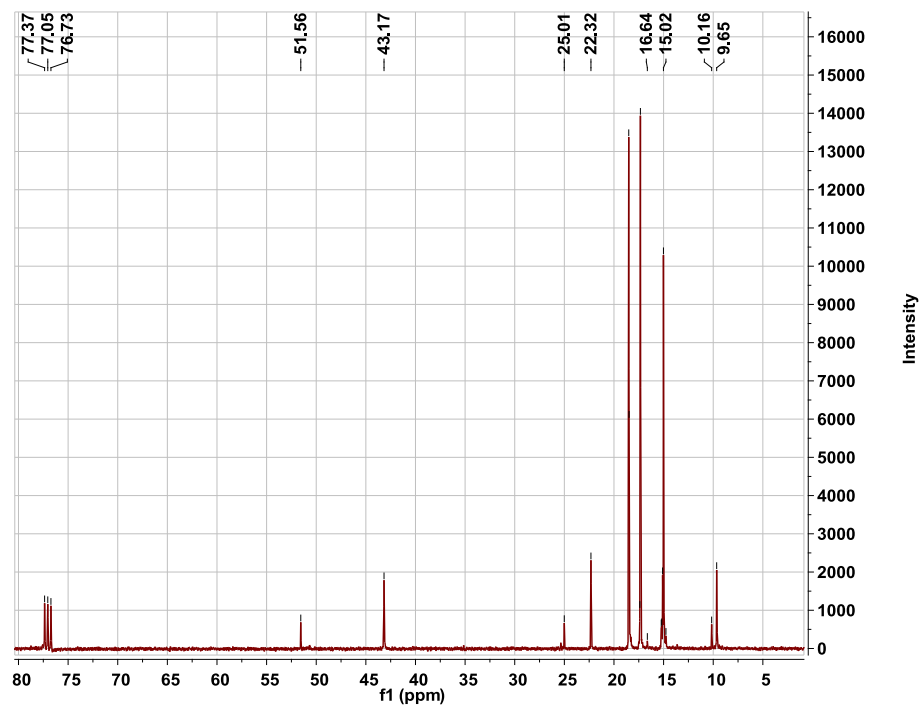


Figure 23: SO₂ uptake capacity of TPSA_ML in pure and SO₂/N₂ (8/92) gas streams

a) TPSA_8 vol%SO₂_IL



b) TPSA_SO₂_IL

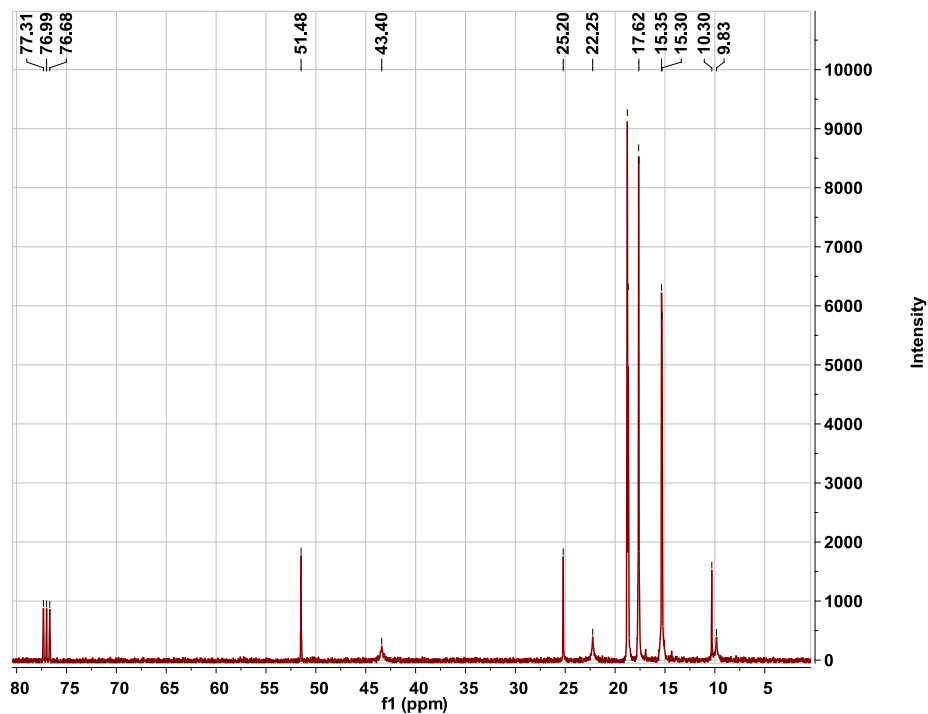


Figure 24: ¹³C NMR spectra of ILs with 8 vol% SO₂ (top) and with pure SO₂ (bottom)

IR spectra (Figure 25) show a decrease in intensity of the physisorbed SO_2 peak, due to a combination of factors: the reversal effect of N_2 on the IL, but more importantly due to a thermodynamic equilibrium being reached for the physisorption of SO_2 and N_2 by the IL, in the proportions of their concentrations in the gas mixture. There is no evidence of any significant chemical reversal in both IR and NMR and no signs of additional products forming.

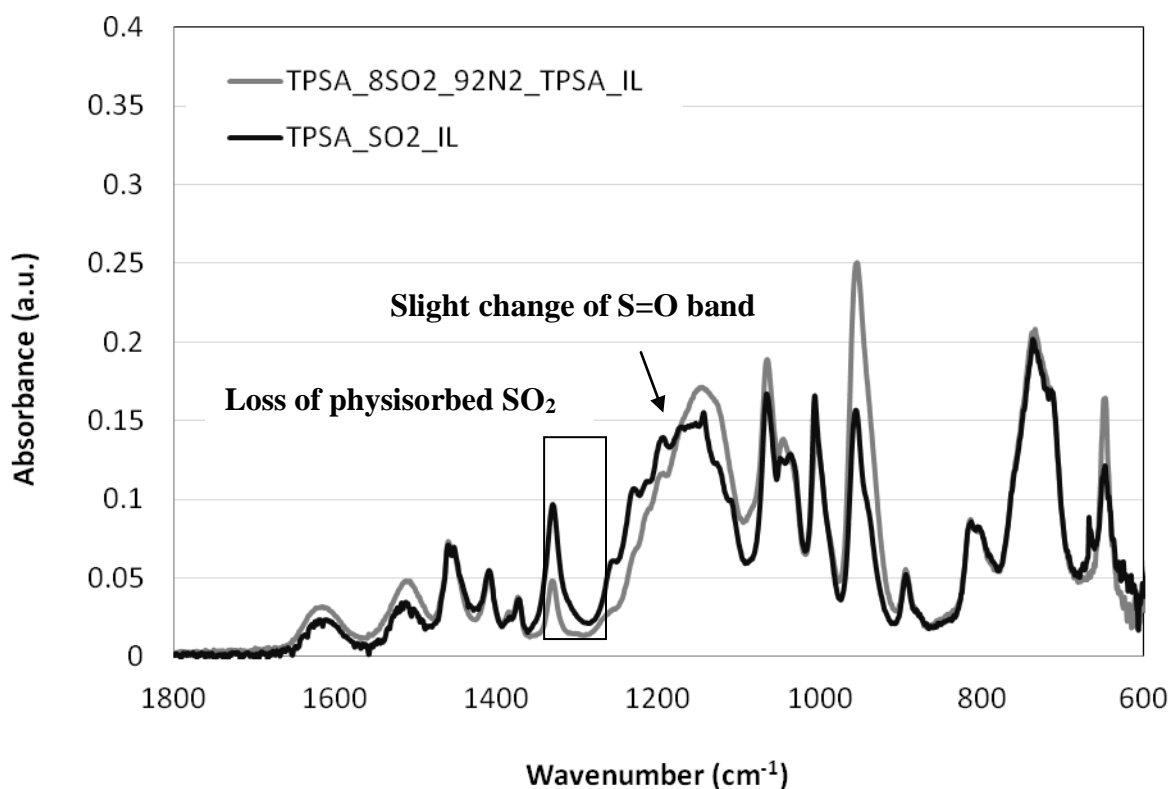


Figure 25: Fingerprint region of IR spectra of TPSA_IL with pure SO_2 and 8 vol% SO_2

Table 7 shows a comparison of the SO_2 absorption capacities of both task-specific (TMG Lactate) and conventional ILs ([TMG] $[\text{BF}_4]$ and [BMIM] $[\text{BF}_4]$) in dilute SO_2

streams (8-10 vol% in N₂) The uptake capacities of conventional ILs at 20 °C and 1 bar are significantly lower than those of task-specific ILs which absorb SO₂ via physi- and chemi-sorption. TMG lactate has the highest absorption capacity, with 6 moles of SO₂ captures per kg of the IL. Wu *et al.* designed this IL as a potential solvent for desulfurization in flue gas streams³. TPSA also demonstrates a significant uptake of SO₂ in diluted streams consisting N₂, with an uptake capacity of 4.697 mole SO₂ per kg IL. Therefore, in terms of SO₂ uptake capacities, TPSA_ML has capacities close to that of task specific ILs such as [TMG] [Lactate] and much higher than that of conventional ILs such as [BMIM] [BF₄].

Table 7: Comparison of SO₂ uptake capacities in N₂ rich streams at 20 °C, 1 bar pressure of SO₂ and N₂

Solvent	Volume % SO ₂ in N ₂	Mole SO ₂ /kg IL	Mole SO ₂ /Mole IL	Reference
TPSA	8	4.697	1.012 (per mol ML)	Gravimetrically
[TMG] [Lactate]	8	6.0	0.978	Wu et al. ³
[BMIM] [BF ₄]	10	0.022	0.005	Huang et al. ^{16,17}
[TMG] [BF ₄]	10	0.339	0.064	Huang et al. ^{16,17}

3.2.2 Investigating Reaction of TPSA_ML with SO₂/CO₂ – 50/50 and SO₂/CO₂-4/96 mixtures

Herein we present results from the reaction of 4 vol% SO₂ in CO₂ with TPSA_ML and the reaction of 50 vol% SO₂ in CO₂ with TPSA_ML. We choose a SO₂/CO₂ ratio of 4/96 in an attempt to simulate flue gas conditions by incorporating two of its component gases, CO₂ which is one of its major components (15.8 vol%) and SO₂

which is present in the ppm levels. We acknowledge that the SO₂ concentration is orders of magnitude higher than that in real streams and this was selected to maintain sufficient analytical accuracy.

We also analyze the affinity of TPSA_ML toward CO₂ and SO₂ with exposure of TPSA_ML to an equimolar, 50/50 - CO₂/SO₂ gas mixture. In the earlier sections we have shown that TPSA_ML reacts with both CO₂ and SO₂. The gas mixture is sparged through TPSA_ML at 400 mL min⁻¹, room temperature, and 1 bar total pressure. The gas uptake by TPSA is measured with gravimetric techniques. The 50/50-CO₂/SO₂ reaction was performed for durations of 1 minute and 75 minutes. The IR and NMR of the resulting ILs are compared.

Figure 26 shows that the mass uptake of TPSA_ML with pure CO₂ (0.1127 kg CO₂/kg of TPSA_ML) is lower than the mass uptake with pure SO₂ (0.409 kg SO₂/kg of TPSA_ML), with the SO₂/CO₂ (4/96) mixture (0.21163 kg/kg of TPSA_ML), and with the SO₂/CO₂ (50/50) mixture (0.3271 kg/kg of TPSA_ML). We see that as the proportion of SO₂ in the gas mixture increases from a 4 vol% to a 100 vol%, so does the overall uptake capacity of TPSA_ML.

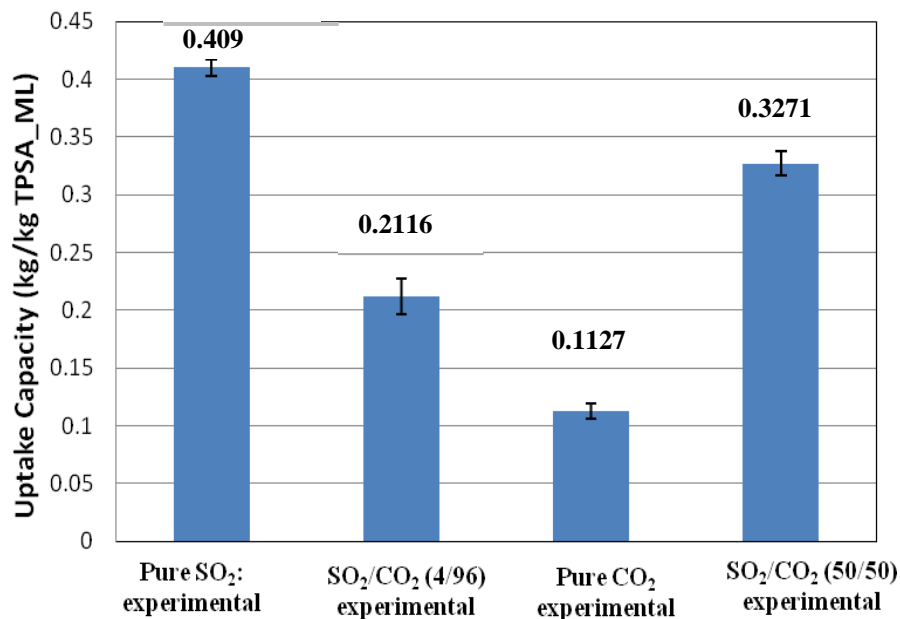
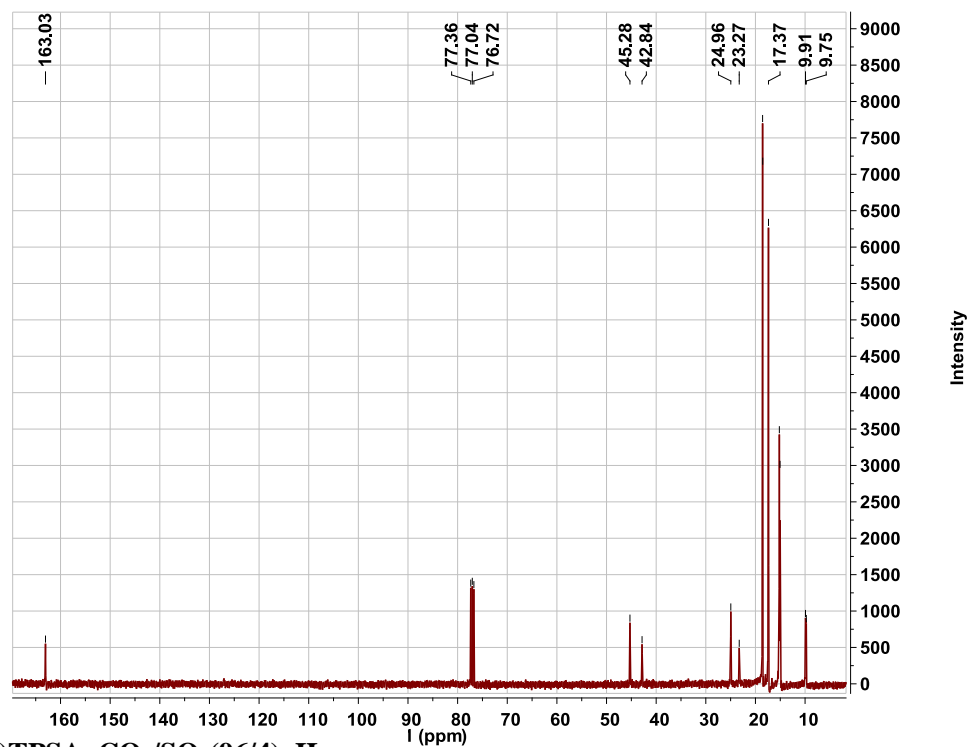


Figure 26: Comparison of gas uptake in kg/kg TPSA_ML for pure SO₂, pure CO₂, SO₂/CO₂ (4/96), and SO₂/CO₂ (50/50) at 20 °C, 1 bar, for 75 minutes

¹³C NMR spectra of TPSA_SO₂/CO₂ (4/96) _IL corresponds to the presence of TPSA_CO₂_IL products alone. Figure 27 presents the spectra of TPSA_CO₂_IL and TPSA_SO₂/CO₂ (4/96) _IL for comparison. The appearance of the quaternary carbon at approximately 162 ppm is consistent with the formation of the carbamate (COO⁻) ion in TPSA_CO₂_IL. The chemical shifts of the peaks in both spectra are within experimental errors given that TPSA_CO₂_IL was run neat and TPSA_SO₂/CO₂ (4/96) _IL was diluted with CDCl₃ to cut down viscosity for better shimming for NMR.

a) TPSA_CO₂_IL



b) TPSA_CO₂/SO₂(96/4)_IL

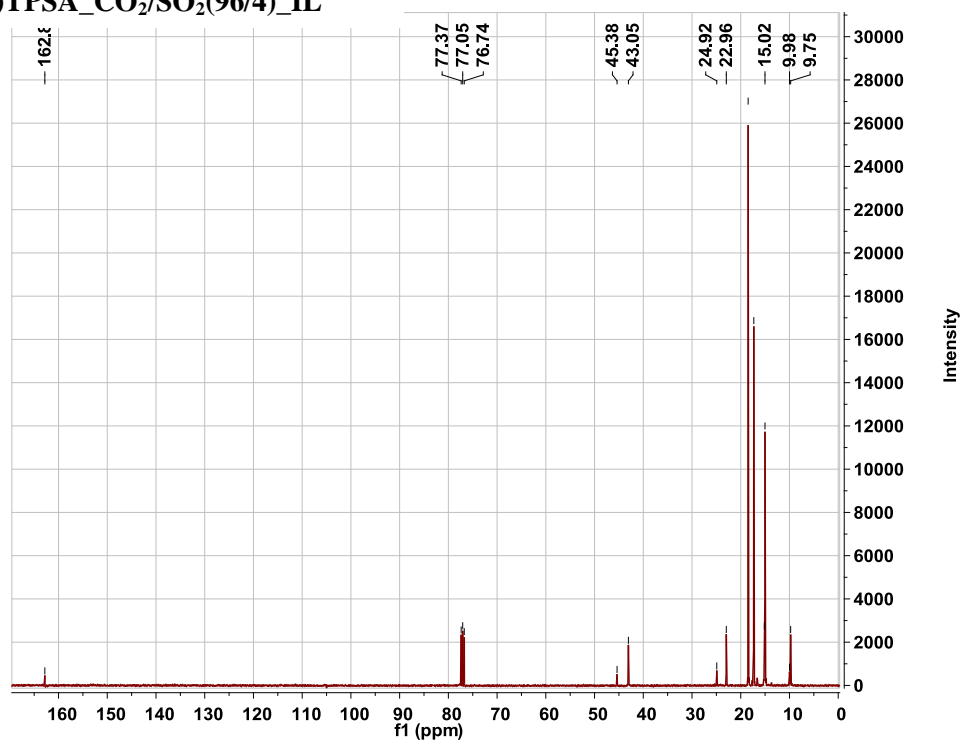


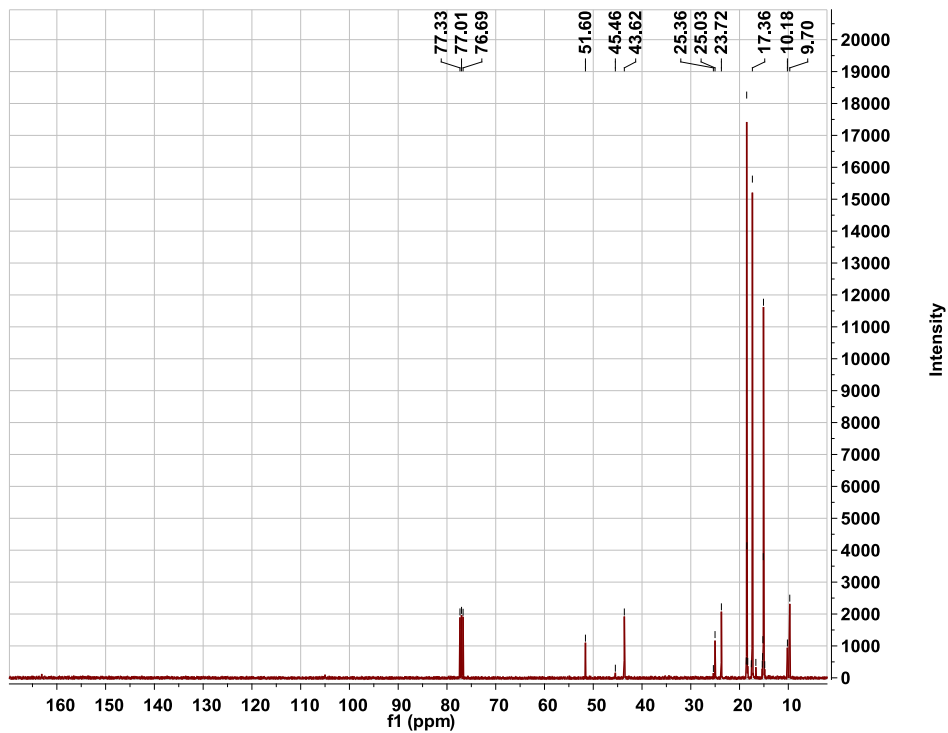
Figure 27: ¹³C NMR of a) TPSA_CO₂_IL and b) TPSA_CO₂/SO₂(96/4)_IL

Figure 28 compares the ^{13}C NMR of TPSA_(CO₂/SO₂-50/50)_IL at 1 minute (b) and 75 minutes (c). At 1 minute, the NMR clearly shows additional peaks corresponding to both TPSA_CO₂_IL and TPSA_SO₂_IL forming. At 75 minutes, the NMR peaks (c) coincide with the peaks for TPSA_SO₂_IL (a), indicating the presence of sulfur containing products exclusively.

For the 50/50 SO₂/CO₂ mixture, IR spectra at both 1 minute and at 75 minute overlap with the IR spectra for TPSA_SO₂_IL, strongly indicating the presence of sulfur containing products at both times (Figure 29). Therefore, at shorter times we see indication of both products forming, at longer times, the sulfur containing ionic liquid products are exclusively detected in both IR and NMR.

There are several possible explanations for this. Firstly, TPSA_CO₂_IL may be more easily reversed than TPSA_SO₂_IL over time in an SO₂ rich environment, driving the reaction equilibrium towards SO₂ ionic liquid products. Secondly, silylated amines may have a higher preference for SO₂ than for CO₂. SO₂ is a bent molecule and it has dipole-dipole interactions, which induces polarity within the molecule. In contrast, CO₂ is a linear, neutral molecule. SO₂ has higher polarizability than CO₂. Therefore, a higher polarity and polarizability of the SO₂ molecule, makes it more reactive with TPSA_ML in an equimolar CO₂/SO₂ mixed gas stream (in other words, TPSA_ML has a higher affinity for SO₂ relative to CO₂ in a mixed gas stream).

a) 1 minute reaction time



b) 75 minute reaction time

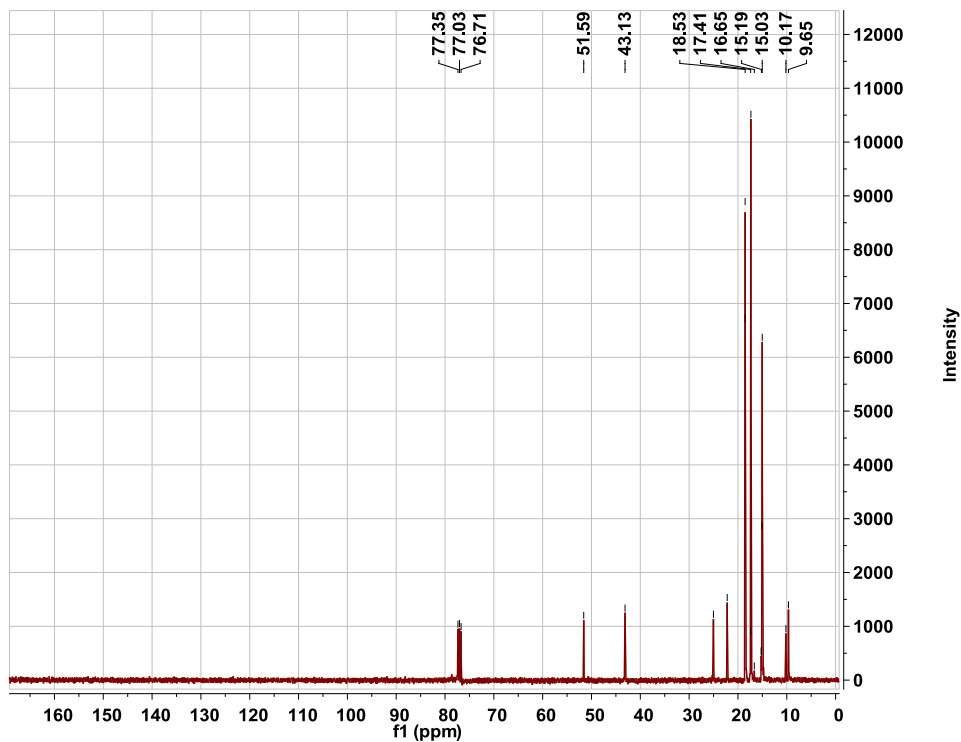


Figure 28: ¹³C NMR of TPSA_CO₂/SO₂(50/50)_IL at a) 1 minute and b) 75 minute reaction times

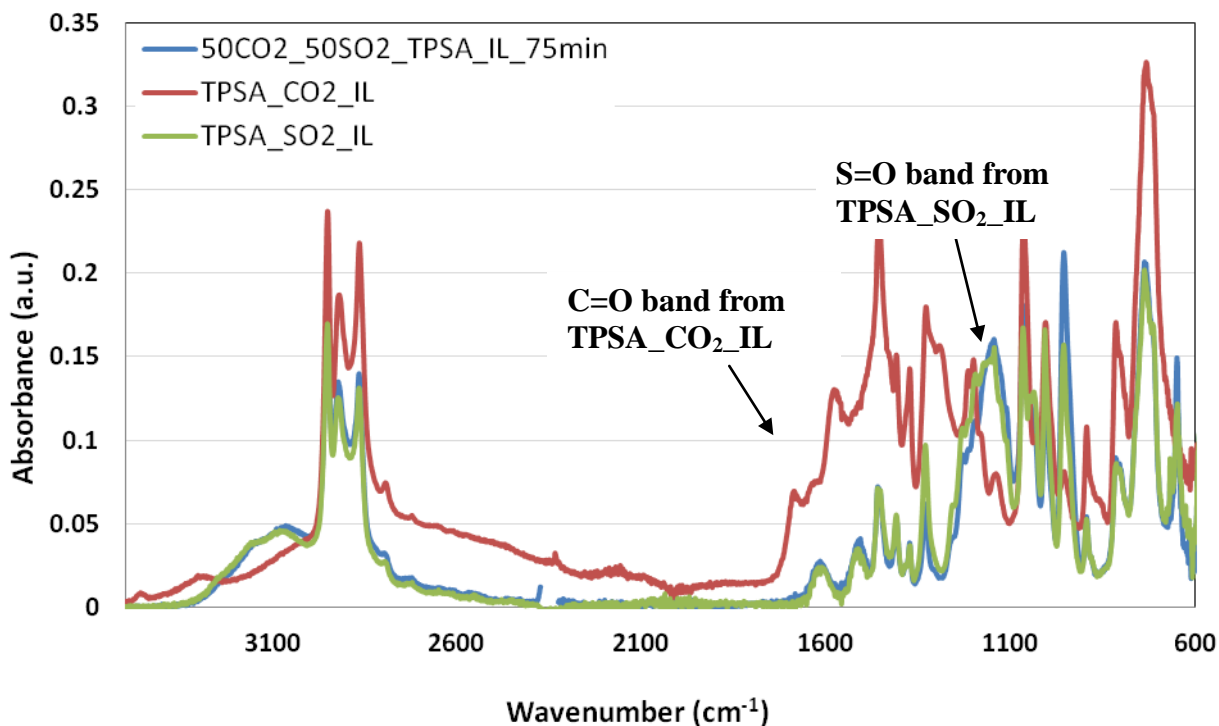


Figure 29: IR spectra TPSA_CO₂/SO₂ (50/50) _IL for 75 minute reaction at 20 °C, 1 bar total pressure

Figure 30 presents the IR spectra of TPSA_ML, TPSA_SO₂_IL, TPSA_CO₂_IL, and TPSA_SO₂/CO₂ (4/96) _IL. Within the 1200-1800 cm⁻¹ region in the IR spectra, the peaks of the TPSA_SO₂_CO₂_IL mirrors those from TPSA_CO₂_IL, and both spectra clearly show a physisorbed CO₂ peak in the 2200-2400 cm⁻¹ region and a carbamate (COO⁻) peak in the 1600 cm⁻¹ region. There are also additional peaks in the 907-970 cm⁻¹ region corresponding to the S-O⁻ bond and a slight indication of the S=O bond in the 1080-1270 cm⁻¹ with a weaker intensity than that observed in the TPSA_SO₂_IL spectra. The physisorbed SO₂ peak is absent in the mixed gas IL sample.

FT-IR which is a more sensitive instrument than an NMR thus detects the presence of sulfur containing compounds in the mixed gas sample. However, NMR does

not detect the presence of TPSA_SO₂_IL forming, and thus we can safely assume that the concentrations of sulfur containing compounds forming are low in the sample when a gas mixture of 4/96 SO₂/CO₂ is used.

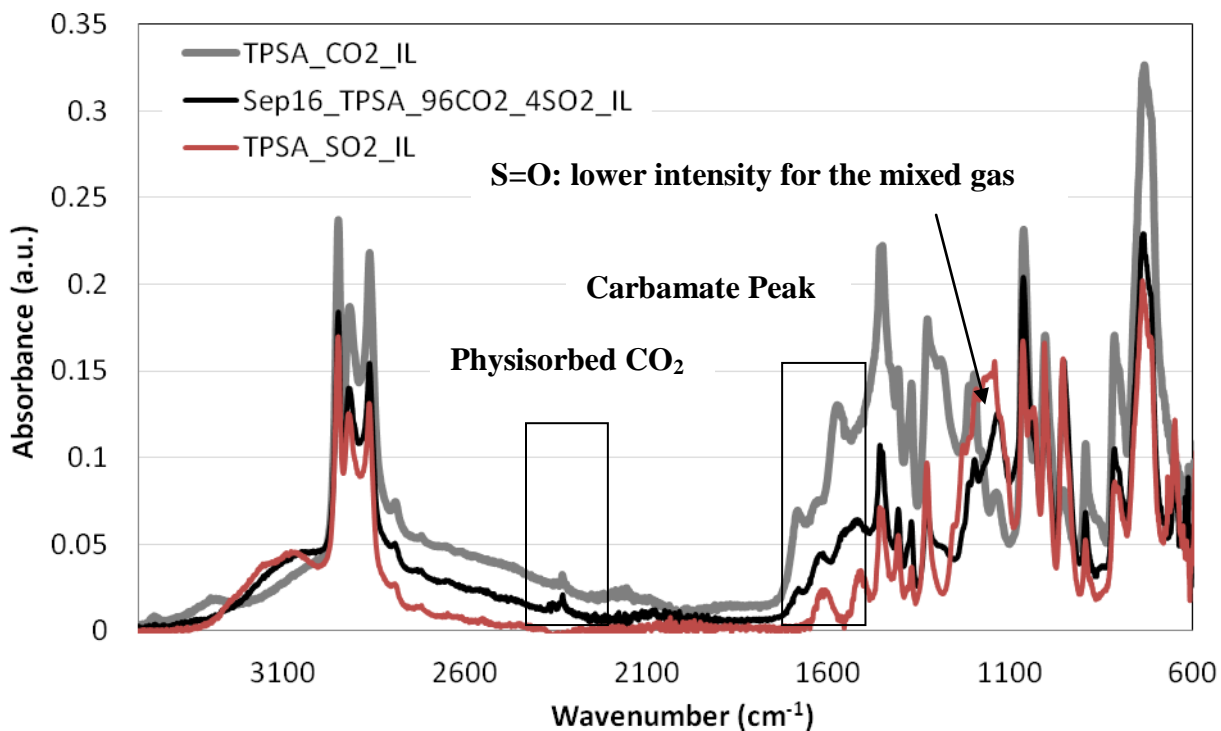


Figure 30: IR spectra of TPSA_CO₂/ SO₂ (96/4) _IL at 20 °C, 1 bar overall pressure

With gravimetric techniques alone, the TPSA uptake capacity calculated for the 96/4 mixed gas stream is 0.21163 kg per kg TPSA_ML. With a pure CO₂ stream, TPSA uptake capacity is 0.1127 kg CO₂ per kg TPSA_ML for a 75 minute reaction at a CO₂ flow rate of 200 mL. min⁻¹. The increased uptake of 0.10893 kg per kg TPSA_ML in the mixed gas stream may be due to 0.10893 kg of SO₂ per kg TPSA_ML (0.3663 mole SO₂ per mole TPSA_ML) being absorbed.

Assuming that uptake occurs at a 4:96 SO₂:CO₂ molar ratio, the expected experimental uptake of the gases by TPSA_ML is 0.139 kg (CO₂/SO₂) per kg TPSA_ML. The actual experimental uptake is however 0.21163 kg/kg TPSA_ML. The gas uptake by TPSA_ML therefore does not occur in the 4:96 SO₂:CO₂ ratio.

The question we approach next is if 4 volume % SO₂ in a gas stream effects reversal of TPSA ionic liquid. To answer this, we isolate and compare thermogravimetric results from TPSA_SO₂_IL, TPSA_CO₂_IL, and TPSA_CO₂/SO₂(96/4)_IL, including studying the effects of SO₂ and CO₂ on the reversal of TPSA ionic liquid.

3.3 Thermogravimetric Analysis (TGA) of TPSA Ionic Liquids

TGA enables monitoring changes in sample weight with regards to changes in temperature. Herein we present weight change plots of IL samples, TPSA_SO₂_IL, TPSA_CO₂_IL, and TPSA_CO₂/SO₂(96/4)IL, upon heating the samples from 0 °C to temperatures of 400 °C /500 °C at a ramp rate of 5 °C per minute. The samples were heated in an open pan, with N₂ flowing in the headspace a rate of 60 mL.min⁻¹. Derivative weight loss curves are also extracted to identify temperatures at which weight losses are most significant and where possible phenomena are occurring.

3.3.1 Investigating Reversibility of TPSA_SO₂_IL

The TPSA_SO₂_IL thermogram (Figure 31) shows that only 7% of the sample remains in the pan after heating the IL to 500 °C, which indicates that the majority of the sample in the pan reverses at high temperatures with a small portion of the sample

forming a stable product with a very low vapor pressure even at temperatures as high as 500 °C.

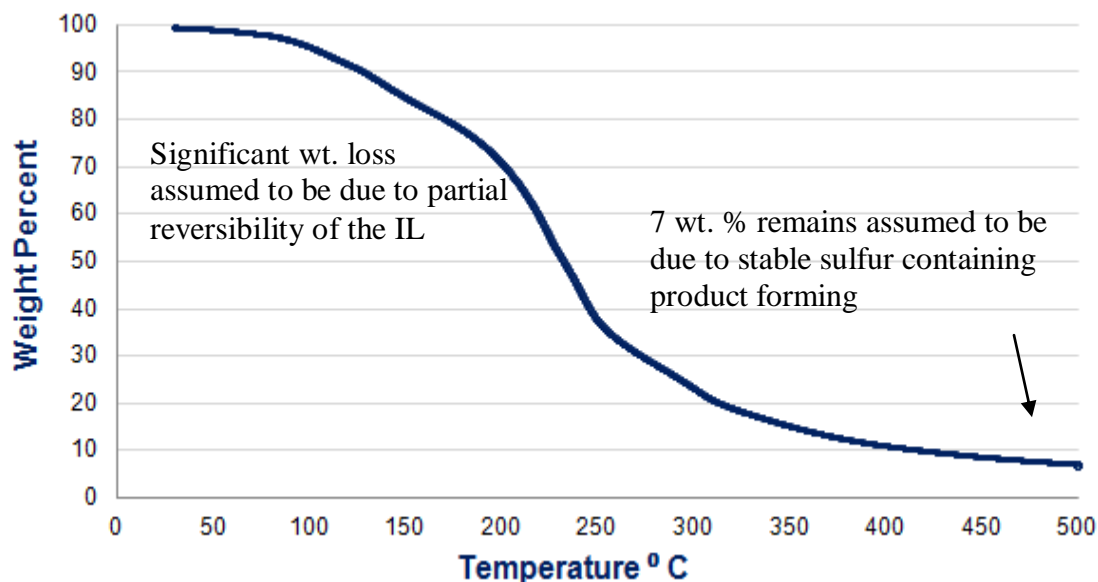


Figure 31: Weight loss curve of TPSA_SO₂_IL: heated to 500 °C at 5 °C/min

Therefore, TPSA_SO₂_IL is partially reversing upon heating to 500 °C.

Furthermore, additional products may be forming upon heating, products that have low vapor pressures even at high temperatures. This is supported by observations made of a deep brown, rubbery material remaining in the pan after heating.

To further interpret the phenomena, the sample was heated isothermally to temperatures at which significant weight losses were observed. TPSA_SO₂_IL was thus heated in the TGA at 75 °C for 45 minutes. A second TPSA_SO₂_IL sample was also heated at 75 °C for 16 hours.

IR spectra of the samples after 45 minutes and 16 hours of heating at 75 °C in the TGA are shown in Figure 32. In red is the TPSA_SO₂_IL before heating the sample in TGA, in green is the IR spectra of the sample when it was heated to 75 °C for 45 minutes, in blue is the IR spectrum when the sample was held at 75 °C for 16 hours. There is not much change upon heating the sample from 45 minutes to 16 hours. We see that the physisorbed SO₂ peak and the S-O⁻ band has significantly decreased in intensity. Also, the S=O bond peak shows a significant change in shape.

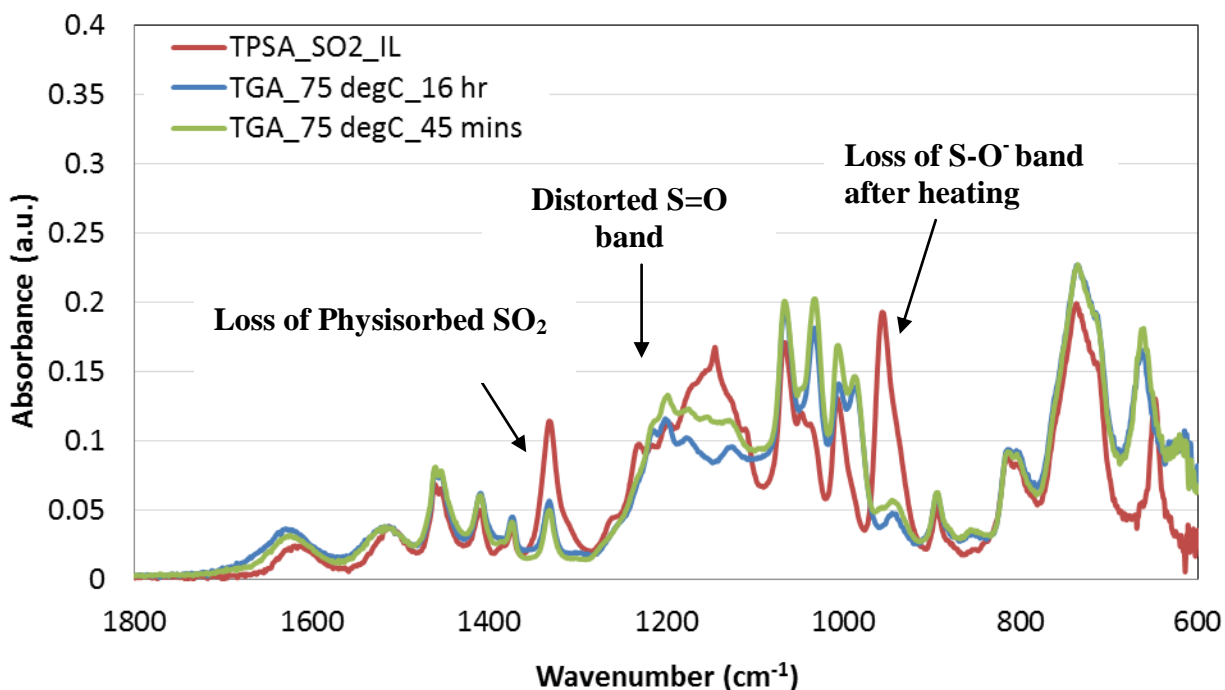


Figure 32: IR spectra of TPSA_SO₂_IL TGA samples upon heating at 75 °C for 45 minutes and for 16 hours

Both ^{13}C NMR and IR spectra analyses of TPSA_{SO₂}_IL are required to understand if additional products are forming upon heating the IL at 75 °C. Therefore, 1-2 ml of the pre-formed ionic liquid is heated to 75 °C in a 1 dram vial and maintained isothermal at 75 °C for 16 hours. Sampling was performed frequently for the first several hours and then again at the end of 16 hours. The samples were analyzed via IR and NMR. The experiment was repeated by sparging it with N₂ in addition to heating it to 75 °C in an attempt to enhance reversal. The IR and ^{13}C NMRs of samples from both experiments were compared. The IR spectra of the heated samples looked similar to the spectra in Figure 32.

Interestingly, NMRs of the two samples differ. ^{13}C NMR of the sparged sample shows the presence of only carbon atoms corresponding to the ammonium component of TPSA_{SO₂}_ILs. ^{13}C NMR of the sample that was heated without sparging does not show much change; all the peaks from TPSA_{SO₂}_IL are still present after 16 hours of heating. Therefore, there is no evidence of additional products forming in either case. However, we see here that N₂ sparging with heating does remove the sulfur containing component of the IL, which is consistent with what we see from the IR of the TGA experiment (Figure 32).

For both cases, the consistency and color of the samples change to a thick, rubbery coffee brown material. This suggests that despite IR and NMR results being consistent with partial reversibility, TPSA_{SO₂}_IL is not a completely reversible compound.

Even though sparging with N₂ is a more rigorous form of reversal (as shown by Heldebrant and others^{3,18}) it is clear from our NMR, IR and TGA results that pure TPSA_SO₂_IL does not chemically reverse back to its molecular form at 75 °C. The data also shows that both at room temperature and at higher temperatures, physisorbed SO₂ does get released. Further studies at higher temperatures are required to better understand the phenomenon.

3.3.2 Prior Results of Reversal of TPSA_CO₂_IL

Two separate events are observed (Figure 33) in the TPSA_CO₂_IL derivative weight plot; the first at ~100 °C (weight loss of 0.9175%) representing loss of both chemisorbed and physisorbed CO₂, and the 2nd peak representing solvent evaporation at ~180 °C (weight loss of 7.181%). (Quarterly report)

The reversal temperature of TPSA_CO₂_IL was confirmed by members of our group. TPSA_CO₂_IL was heated in a vial at ~95 °C for 75 minutes. Based on refractive index and ¹³C NMR data it was confirmed that the IL had reversed back to its molecular form. Solvent recyclability was successfully demonstrated for 5 consecutive cycles.

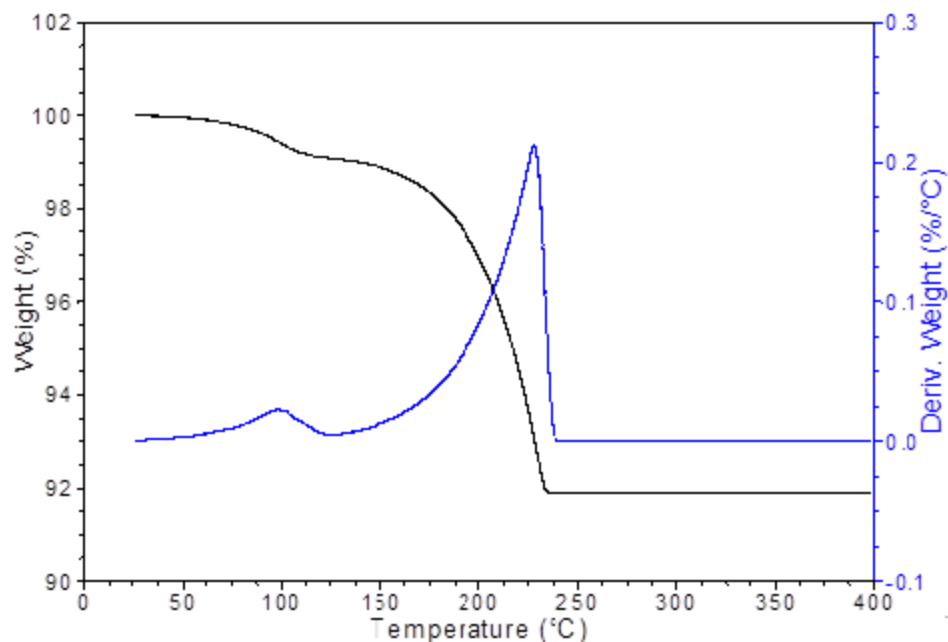


Figure 33: TGA plot of TPSA_CO₂_IL upon heating to 400 °C at a ramp rate of 5 °C/ min²¹

Earlier isothermal TGA experiments with TPSA_CO₂_IL have shown a continual decrease in weight when the sample is heated at either 65 °C or 95 °C, the rate of decrease increases with increasing temperature. Figure 34 shows the normalized weight loss plot of TPSA CO₂ ionic liquid at the two temperatures. The vertical red line in the graph denotes the expected weight loss due to CO₂ removal. At both the temperatures, we can see CO₂ removal as well as solvent loss due to evaporation. At 65°C, the reversion is slower while at 95°C, CO₂ removal is much faster.

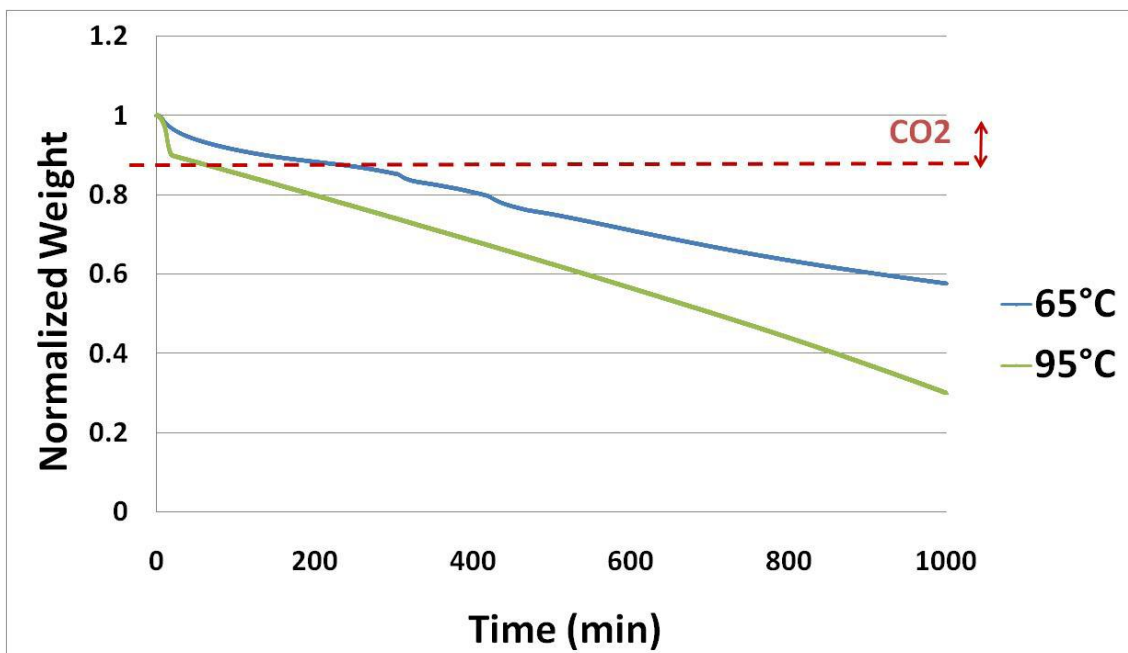


Figure 34: Isothermal TGA analysis at 65°C and 95°C for TPSA_CO₂_II. The red line presents the expected CO₂ loss based on gravimetric calculations (*Quarterly Report, 9 Reprint*)²¹

3.3.3 Investigating Reversibility of TPSA_CO₂/SO₂ (96/4) _IL from TGA

The TPSA-IL with the CO₂ rich mixed gas was heated isothermally at 95 °C; in just 150 mins, there was weight loss of ~ 62% (Figure 35). We predict that this corresponds to the reversal of CO₂ and trace amounts of SO₂ from the IL, and the evaporation of some of the ML. About 40% of the sample remains in the pan, which we predict is the TPSA_ML. Further tests with IR and NMR are needed to confirm our hypothesis that TPSA_mixed gas IL is reversible.

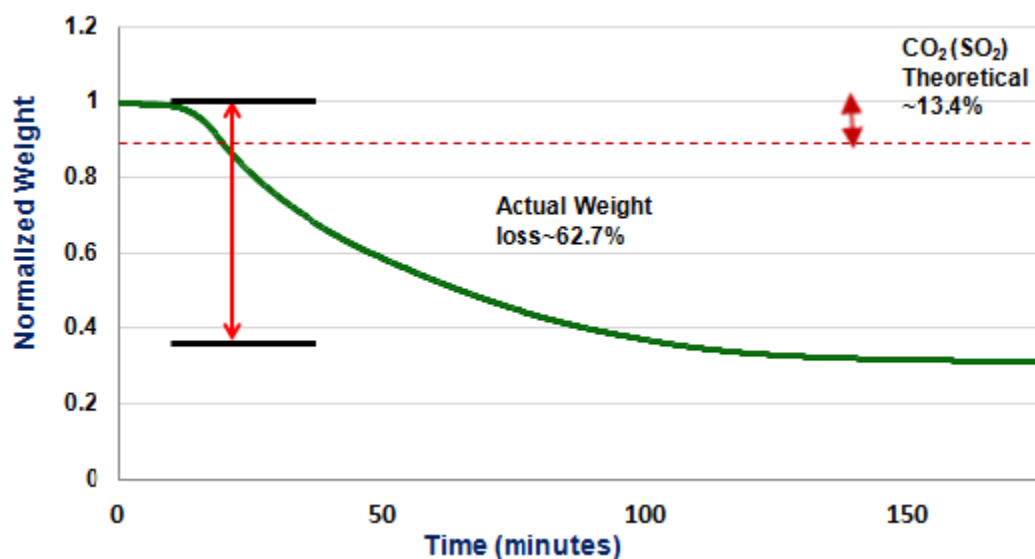


Figure 35: TGA plot of TPSA_CO₂/SO₂ (96/4) _IL upon heating to 400 °C at a ramp rate of 5 °C/min

3.4 Investigating Reactivity and Capacity of TPSA_ML upon reacting with SO₂/CO₂/N₂ (4/15/81) gas mixture

TPSA_ML was sparged with a gas mixture consisting of SO₂/CO₂/N₂ (4/15/81) for 75 minutes at an overall flow rate of 400 mL.min⁻¹, 20 °C, and 1 bar total pressure. The mass uptake ratio was 0.2069 kg gas per kg TPSA_ML. From IR, we see that the main product is TPSA_CO₂_IL (Figure 36). Future experiments could involve studying reversibility of ILs formed from mixed gas streams consisting of SO₂/CO₂/N₂ in the 4/15/81 proportion or having SO₂ at much lower concentrations to simulate flue gas compositions.

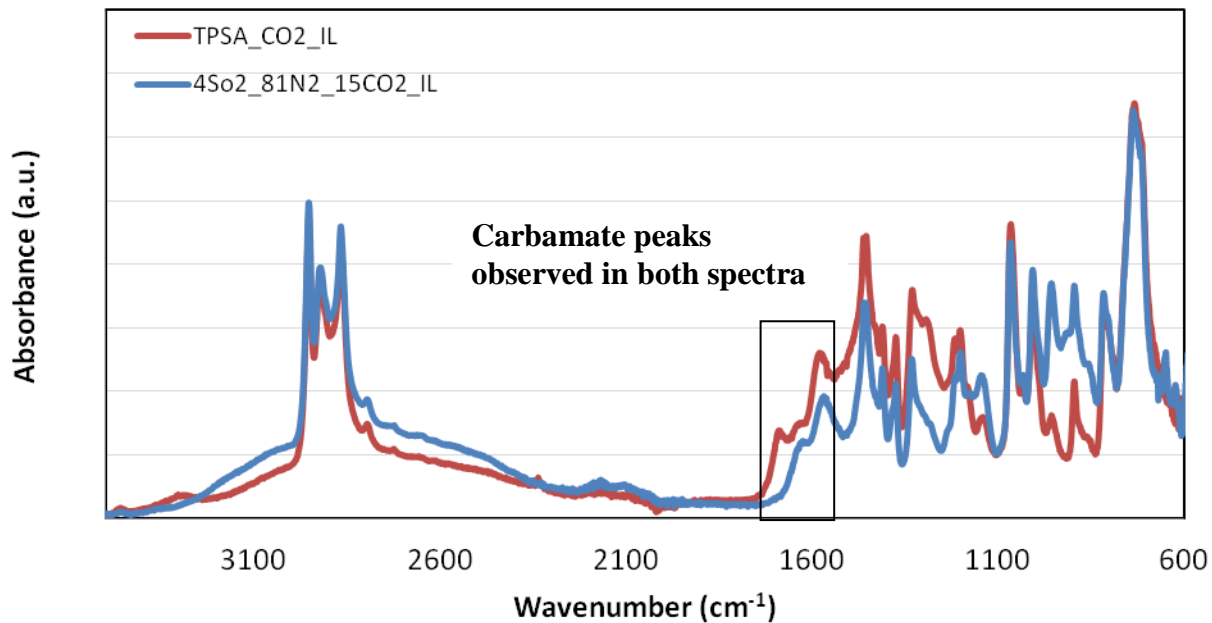
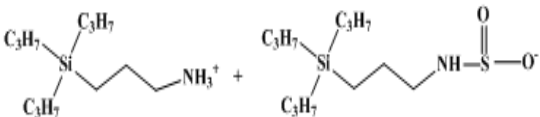
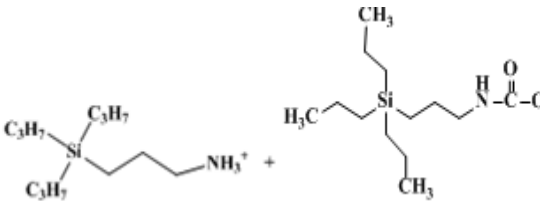


Figure 36: IR spectra of TPSA_SO₂/CO₂/N₂ (4/15/81)_IL at 20 °C, 1 bar

Following is a summary of the products formed from the reaction of TPSA_ML with various gas mixtures, assuming side product formation is negligible.

Table 8: Summary of products formed from reaction with TPSA_ML

Vol % SO ₂ in gas stream	Vol % CO ₂ in gas stream	Vol % N ₂ in gas stream	Products Formed
8	0	92	
50	50	-	<i>both reactions at 75 minutes</i>
4	96	-	
4	15	81	<i>both reactions at 75 minutes</i>
50	50	-	<i>Both TPSA_CO₂_IL and TPSA_SO₂_IL forms for a 1 minute reaction</i>

During our experiments we observed that the reaction of pure SO₂ with TPSA_ML, pure CO₂ with TPSA_ML, and of mixed gas streams (CO₂/SO₂/N₂) with TPSA_ML, occur within a few seconds. Changes in sample color, and sample viscosity are the most obvious indicators of the reactions. This is further confirmed by IR and NMR spectra of samples taken after 1-5 minutes of reaction time, which show the presence of new peaks, and the absence of the molecular liquid peaks (there were no changes in peak position or peak chemical shifts in IR and NMR of samples taken within

short times and at longer times; IR spectra of samples overlapped well, except that the physisorbed SO₂ IR peak continues to increase in intensity over the duration of the experiment).

The reaction of pure SO₂ with TPSA_ML is mass transfer limited. For the same 75 minute reaction time, increasing the flow rate of SO₂ from 200 mL.min⁻¹ to 400 mL.min⁻¹, was observed to increase the SO₂ absorption capacity of TPSA_ML. This shows that despite there being excess of SO₂ in the vial for the reaction at 200 mL.min⁻¹, the SO₂ uptake is still limited. The absorption time is thus dictated initially by the mass transfer of SO₂ through the ionic liquid into the bulk molecular liquid and then by the diffusion of SO₂ into the bulk ionic liquid. Assuming the limiting thickness of the IL layer to be 1.8 μm²¹, the time taken for SO₂ to diffuse through the layer (~981 seconds) is orders of magnitude longer than that for CO₂ (> 1 second). Therefore, even though SO₂ is more reactive than CO₂, the viscosity of the resulting IL is much higher for SO₂ than for the CO₂ containing IL.

The viscosity of the TPSA_SO₂_IL sample was orders of magnitude higher than that of the pure CO₂ containing ILs and could not be successfully measured using a Rheosys Merlin II rotational viscometer. When the rotational speed/shear rate of the instrument was increased, the viscosity of the sample was seen to increase as well, which indicates that the SO₂ containing IL is not a Newtonian fluid.

Mass transfer of SO₂ in the IL can be increased by heating the sample, sparging SO₂ through the sample using a fritted diffuser tube instead of a stainless steel needle, mixing the sample, or diluting the IL with water. Increasing the temperature of the IL to

even modest temperatures of 40 °C can reverse TPSA_CO₂_IL samples. For TPSA_SO₂_IL, partial reversal (of physisorbed SO₂) at 75 °C is observed. Concurrent experiments with diffuser tubes for reactions of TPSA_ML with pure CO₂, done by other group members in our lab, have demonstrated higher CO₂ absorption capacities versus when a needle is used for sparging. This is a viable path forward for future experiments for forming ILs. The sample is stirred frequently, every five minute or so, to increase contact among reactants and enhance reaction. Adding diluents is another way of cutting down sample viscosity and increasing mass transfer of the gas in the sample. Before doing this however, we would need to understand reactions of TPSA_ML with flue gas components in the presence of water. IR and NMR techniques can be used to identify the reaction products.

TGA and vial desorption of TPSA_SO₂_IL upon heating have shown that SO₂ reacts irreversibly with TPSA_ML. Concerns with accumulation of irreversible products in the flue gas stream arise. Preliminary TGA results of TPSA_ (96/4) CO₂/SO₂_IL show that 4 vol% of SO₂ in a CO₂ rich stream, may allow reversal upon heating to 95 °C. This will need to be further confirmed via IR and NMR experiments.

In a real flue gas stream, SO₂ concentration is orders or magnitude lower, and thus we expect it to not affect regeneration of the IL. The irreversible sulfur containing IL will be allowed to build up over several cycles before the temperature is raised high enough (above 100 °C) to reverse the SO₂ containing IL. This may lead to solvent loss via evaporation, since TPSA_ML has an evaporation temperature of 116 °C and additional regeneration energy requirements.

Following is a hypothetical estimation of the build-up of irreversible sulfur compounds in three power companies and one steel company with installed flue gas desulfurization (FGD) technologies from Mitsubishi Heavy Industries Ltd.²⁵ If the plant were to be retrofitted with our model silylated amine, TPSA, 1.4 tonnes to 12.5 tonnes of irreversible sulfur compounds would be forming every 24 hours, assuming that the FGD plant is functioning all year round.

Table 9: Hypothetical worst case scenario estimation of TPSA_SO₂_IL build-up

FGD Customer	TPSA_SO₂_IL_products (tonnes/year)	tonnes/day
Georgia Power Company (Plant Scherer#1, U.S)	3036	8.32
Kobe Steel Limited	515	1.41
Kashima Power Co.	4580	12.55
Tata Power Company Limited	2121	5.81

Sample worst case scenario calculation with FGD installed in Southern Company- Georgia Power Company (Plant Scherer#1, U.S)

Plant Capacity – 923 MW, Coal fired boiler, Flue Gas Desulfurization (FGD) Capacity – 3,959,000 Nm³/hr, SO₂ content from FGD outlet – 17 mg/Nm³-d²⁵

$$\text{SO}_2 \text{ Entering CO}_2 \text{ Absorber: } 17 \frac{\text{mg}}{\text{Nm}^3\text{-d}} \times 3,959,000 \frac{\text{Nm}^3\text{-d}}{\text{hr}} = 6.7 \times 10^7 \frac{\text{mg}}{\text{hr}}$$

$$\sim 5.89 \times 10^8 \frac{\text{gram}}{\text{year}}$$

Experimentally, 1 mole of TPSA_ML absorbs 1.5 moles of SO₂

$$\text{TPSA_ML required} - 6.13 \times 10^6 \frac{\text{moles}}{\text{year}}$$

Stoichiometrically, TPSA_SO₂_IL produced – $6.13 \times 10^6 \frac{\text{moles}}{\text{year}}$

~ $3036 \frac{\text{tonnes}}{\text{year}}$ or ~ $8.32 \frac{\text{tonnes}}{\text{day}}$

Therefore after several cycles of CO₂ absorption and regeneration, a slip stream may be required to add more of the CO₂ capture solvent for the entire process to be functioning as a continuous system.

CHAPTER 4

CONCLUSIONS

We present here studies identifying products formed upon reaction of SO₂ with the silylated amine, Tripropylsilylamine (TPSA). Silylated amines have been designed and structurally modified by the Eckert Liotta group for potential use as solvents for CO₂ capture from flue gas. IR and NMR analysis are consistent with the formation of ionic liquids with an ammonium group in the cation and a sulfamate group in the anion, when TPSA_ML reacts with pure SO₂. TPSA_SO₂_IL does not completely reverse back to the TPSA_ML when heated to temperatures as high as 500 °C in the TGA. We also show that TPSA_ML selectively reacts with SO₂ in an equimolar mixture of SO₂ and CO₂. However, with simulated flue gas mixtures— (96/4) CO₂/SO₂, and (15/81/4) CO₂/N₂/SO₂, which are SO₂ lean gas mixtures, only TPSA_CO₂_IL products dominate. The concentrations of SO₂ in the gas mixtures are orders of magnitude higher than that in a realistic scenario for analysis purposes. Future experiments will include observing reactions of silylated amines with gas mixtures consisting of much lower concentrations of SO₂; we expect that the concentrations of TPSA_SO₂_IL in these mixtures will be insignificant. TGA studies of ionic liquids formed from the mixed gas composition of 96/4 CO₂/SO₂ were conducted, which gave insight to possible TPSA_96/4 CO₂/SO₂_IL reversal temperature in the 86-163 °C range.

CHAPTER 5

RECOMMENDATIONS

The reaction of TPSA_ML with pure SO₂ or with mixed gas streams are mass transfer limited. Triplicate runs for each experiment were done to validate repeatability. During the experiments, the samples were mixed frequently to minimize mass transfer limitations. For reactions with mixed gases, the consistency of the sample was very thick upon conversion of TPSA_ML to TPSA_IL, and the IL tended to stick to the sparging needle in lumps. To prevent clumping, the samples were thus stirred gently. Using a diffuser tube for all experiments in the future, instead of a stainless steel needle, would allow better dispersion of the gases, and hence increase mass transfer of the gas in the IL. Other members in the group have done reactions of pure CO₂ with TPSA at room temperature. They observed that for a 1 minute reaction, TPSA absorbed thrice as much CO₂ when a tube was used for sparging versus a needle. For 75 minute reactions, the CO₂ uptake capacities were 10% higher with a diffuser tube than with a needle (Quarterly Report, 11)²¹.

To simulate flue gas conditions, the reactions can be done at 40 °C, at the real operating conditions of flue gas streams. SO₂ concentrations that are much lower than the 4 vol% used in our current experiments, should be pursued to get a more realistic picture.

With thermogravimetric analysis, reversibility should be investigated for TPSA_SO2_IL at temperatures well above 75 °C. For TPSA_CO₂/SO₂ (96/4) _IL samples, we were able to show that there is a ~62 % weight loss, upon heating the sample

isothermally at 95 °C. To understand the events taking place both at 95 °C and at higher temperatures, IR and NMR analysis of the samples are required. It should be noted here that the weight of the samples added to the pan needs to be normalized for these heating experiments to be consistent. Therefore, if a larger mass than that used for past experiments (~50 mg) is required for analysis purposes, a ramp experiment (5 °C/min to 500 °C) should first be run with the larger mass. Then, based on the temperatures at which events are seen to occur, isothermal experiments can be run for desired duration of times (e.g. 75 minutes), and the IR and NMR of the samples taken to test reversibility and to identify the phenomena occurring.

Earlier TGA experiments with the Trihexylpropylamine ionic liquid, THSA_CO₂_IL, have shown events (CO₂ release and solvent evaporation) occurring that are less overlapped, in other words, they are occurring at temperatures relatively well apart compared to that of TPSA_CO₂_IL. Preliminary TGA ramp up experiments were done using THSA IL pre-formed from a 96/4 (CO₂/SO₂) gas mixture. The events observed in the derivative plot of THSA_96/4 (CO₂/SO₂)_IL show less overlap than that in TPSA_96/4 (CO₂/SO₂)_IL. There are events occurring in the 37-106 °C, 136-282 °C, and 303-387 °C, corresponding to weight losses of 5.9%, 82.6% and 8.0% respectively. This observation needs to be confirmed and the sample remaining after heating needs to be identified using IR and NMR.

For the reaction of TPSA with mixed gas streams, to cut down viscosity of the IL formed, diluents such as water may be added to the system. It would then be necessary to analyze reactivity, selectivity and reversibility of TPSA molecular liquid in the presence of water. Furthermore, kinetic degradation analysis of the CO₂ capture solvents in the

presence of CO₂, SO₂, H₂O, and NO₂^{10, 11, 26}, which are all flue gas components, may be pursued. A residual gas analyzer could be implemented here to monitor changes in proportions of gases during the experiment.

Furthermore, solubility studies based on Henry's law can be used to determine how much SO₂ is being absorbed by RevILs via physisorption alone. This would allow us to determine if additional side products are forming or if the increased uptake by TPSA_ML is due to physisorption alone.

Finally, we need to investigate if pre-formed TPSA_CO₂_IL can further absorb SO₂ at room temperature and 1 bar total pressure to simulate situations in flue gas streams

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