Quaternary Ammonium based Eutectic Ionic Liquids (EILs) as absorbent for Sulfur Dioxide (SO\textsubscript{2})

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Abstract. Sulfur dioxide (SO\textsubscript{2}) is a corrosive acid gas which pose severe threat to the environment and human health. Therefore, its removal from air is necessary to protect human health and environmental quality. Existing SO\textsubscript{2} removal technologies involves using lime or limestone in wet scrubbers. Recently, the application of eutectic ionic liquids (EILs) were extensively employed to capture SO\textsubscript{2} gases. The main objective of this study is to determine the SO\textsubscript{2} absorption capacities of quaternary ammonium based EILs. Quaternary ammonium-based EIL, choline chloride which is known to display many advantages in absorbing acidic gas, were selected as the hydrogen bond acceptor (HBA) and three different types of hydrogen bond donor (HBD) were investigated; glycerol, ethylene glycol, and urea. The absorption experiments were conducted in a laboratory scale reactor. SO\textsubscript{2} gas stream was passed continuously through the reactor to get contact with the EIL surface and be absorbed, and the absorption was monitored using sodium hydroxide (NaOH) solution with pH 10. The results show that SO\textsubscript{2} was absorbed by choline chloride (ChCl) based EILs within 120 min of contact time. The absorption capacity of ChCl with glycerol was 0.54 mg/g, 0.54 mg/g and 0.53 mg/g for 1:2, 1:3 and 1:4, respectively. The results also show that the SO\textsubscript{2} absorption capacity increases as the ChCl:Gly molar ratio increases. The extent of absorption was also greatly affected by the composition of the EILs. ChCl with ethylene glycol gave the highest absorption capacity of 0.57 mg/g of the SO\textsubscript{2} was absorbed compared to ChCl with glycerol as well as with urea. The use of EILs as an absorbent are a promising method for SO\textsubscript{2} capture.

1. Introduction

Air pollution is the main reason of greenhouse effects where it emits harmful gases to the atmosphere. One of the major sources of air pollutant is the acidic gas, sulphur dioxide (SO\textsubscript{2}) which are very harmful to environment and human health. It is one of the dangerous acidic gas whereby in current era, the emission concentration in a normal environment is about 4.8 ppm per day. SO\textsubscript{2} can be categorized as clastogenic and genotoxic agent. One of the biggest challenges for a sustainable environment is in managing the acidic gases that are easily emitted into the environment. Many alternatives and methods have been extensively employed but this problem still exist. The technologies in capturing SO\textsubscript{2} have attracted increasing interests among industries. The current and most used method globally to regulate the emission of SO\textsubscript{2} is the flue gas desulfurization (FGD) process using lime or limestone in wet scrubbers [1-3]. This process exploits the natural alkalinity of seawater to absorb acidic gases before passing to a water treatment plant [4]. The absorbed SO\textsubscript{2} is oxidized to sulphate and to saturate the seawater with oxygen. However, there are by-products such as heavy metals and chlorides present in the water which is then discharged to the sea. Despite there are...
many enhancements made in FGD, limitations include high operation cost, low desulfurization efficiency, complexity in SO₂ recovery have encouraged the continuous development of alternative methods to be explored [5].

Later, ionic liquids (ILs) was introduced and developed as a suitable alternative for absorbing SO₂ due to their good adsorption capacities [6-9]. There are four types of common ILs for binding SO₂ including hydroxyl ammonium based ILs, quaternary ammonium based ILs, guanidinium based ILs and imidazolium based ILs [10-12]. The SO₂ absorption capacity of ILs are later enhanced with the introduction of immobilization and polymer technology [13]. However, factors including complex preparation and purification process, high expenses, high toxicity and low biodegradability have hindered the wide application of ILs as practical absorbents [14].

Recently, deep eutectic solvents (DESs), which are also recognized as eutectic ionic liquids (EILs), have been introduced and developed vastly [15-17]. A eutectic system is a combination of chemical compounds that exhibits a single chemical composition that solidifies at a lower temperature than any other composition. EILs are structurally different from ILs, as EILs have both ionic and non ionic species and linked with a hydrogen bonding network. However, EILs can replace ILs in many applications due to their shared characteristics. EILs are the advanced generation of ILs and their synthesis processes are easy by mixing two or three suitable compounds made up of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) [18-20]. Examples of HBAs are quaternary ammonium salts, quaternary phosphonium salts and inorganic salts [21-22]. Meanwhile, alcohols, organic acids, amides and sugars are examples of HBDs [23-25]. Compared with traditional ionic liquids, EILs have a few remarkable features including relatively simple and eco-friendly synthetic procedures, low economical cost and higher efficiency which have made them become suitable for large-scale production [26]. Today, EILs have been applied in isolation process, organic synthesis and electrochemistry [27-28]. According to Abbott et al [17], the design and application of EILs is still in its early stage and more researches are needed to be carried out. Nevertheless, the main objective of this research is to determine the SO₂ absorption capacities of different types of EILs and it is believed that EILs will be able to capture the SO₂ efficiently.

2. Materials and Methodology

2.1 Materials

The Sulfur dioxide gas for the absorption study was obtained from Linde Gas Malaysia. The concentration of the SO₂ gas is 5.62 ppm with nitrogen as the carrier gas. The chemicals for synthesis of quaternary ammonium based EILs are tabulated in Table 1 below.

| Materials        | Purity      | Supplier       |
|------------------|-------------|----------------|
| Choline chloride | (>99%)      | Sigma Aldrich  |
| Urea             | (99.4%)     | Fisher Scientific |
| glycerol         | (99.5%)     | Fisher Scientific |
| ethylene glycol  | (>99%)      | Merck.         |

2.2 Synthesis of Eutectic-based Ionic Liquid

Several EILs were synthesized by using the quaternary ammonium-based salt as the hydrogen bond acceptor (HBA). Choline chloride (ChCl) is the HBA which were paired with a few hydrogen bond donors (HBD) such as glycerol (Gly), ethylene glycol (E-gly), and urea prepared in different molar ratios of HBA:HBD as in Table 3 below. All the mixtures of HBA and HBD were heated at 80°C, until the salts fully dissolved (1h). The mixtures were then cooled down to room temperature before further use.
2.3 1H NMR Characterization for EILs

1H NMR analysis was conducted to determine the chemical properties and mechanism of EILs performances. For H NMR, 20 mg EIL was dissolved in about 600 µL to 1000 µL of deuterated solvent (DMSO). The dissolved EIL was transferred directly to a NMR tube. The samples were analysed using Bruker 500 MHz Ascend spectrometer by using TMS as an internal reference.

2.4 Absorption of SO2

A laboratory scale reactor as in Figure 2 below was fabricated for the SO2 absorption process. The SO2 gas stream was flowed continuously into EIL at 20 mL/min. The absorption of SO2 was carried out at room temperature in 20ml of EIL. 200ml of NaOH solution at pH 10 was used as a scrubber. The liquid chemistry change was analysed using pH as an indicator continuously for every 5 mins until pH 6-8. Table 2 summarizes the operating conditions for SO2 absorption in NaOH solution. The absorption capacity (mg/g), of the EILs to absorb SO2 was determined as in equation (1):

\[
\text{SO}_2 \text{ Absorption Capacity (mg/g)} = \frac{\text{mass of SO}_2 \text{ absorbed (mg)}}{\text{EIL (g)}}
\]

(1)

![Figure 2. Schematic diagram of the laboratory scale reactor](image)

| Condition                          | Value      |
|-----------------------------------|------------|
| Flow Rate                         | 20 mL/min  |
| Volume of NaOH                    | 200 mL     |
| Initial pH of NaOH solution       | 10         |
| Time interval                     | 5 min      |
| Volume of EIL                     | 20 mL      |

Table 2. Operating conditions for SO2 absorption in NaOH solution
3. Results and Discussion

3.1 Synthesis of Eutectic-based Ionic Liquid (EILs)
EILs were synthesized by mixing choline chloride (ChCl) as HBA with glycerol (Gly), urea or ethylene glycol (E.Gly) as HBD. Their compatibility study results are displayed in Table 3. Unsuccessful combinations of the EILs resulted in a white highly viscous liquid or a liquid with suspended particles.

| HBA             | HBD            | EILs               | Synthesis Characterization |
|-----------------|----------------|--------------------|----------------------------|
| Choline chloride| Glycerol       | ChCl : Gly (1:1)   | 1:1 No                     |
|                 |                | ChCl : Gly (1:2)   | 1:2 Yes                    |
|                 |                | ChCl : Gly (1:3)   | 1:3 Yes                    |
|                 |                | ChCl : Gly (1:4)   | 1:4 Yes                    |
|                 |                | ChCl : Gly (2:1)   | 2:1 No                     |
| Choline chloride| Ethylene Glycol| ChCl : E.Gly (1:1) | 1:1 No                     |
|                 |                | ChCl : E.Gly (1:2) | 1:2 Yes                    |
|                 |                | ChCl : E.Gly (1:3) | 1:3 No                     |
|                 |                | ChCl : E.Gly (2:1) | 2:1 No                     |
| Choline chloride| Urea           | ChCl : Urea (1:1)  | 1:1 No                     |
|                 |                | ChCl : Urea (1:2)  | 1:2 Yes                    |
|                 |                | ChCl : Urea (1:3)  | 1:3 No                     |
|                 |                | ChCl : Urea (2:1)  | 2:1 No                     |

3.2 $^1$H NMR for choline chloride based EIL
$^1$H NMR spectroscopy is one of the best tools to check the structural similarities and difference between the synthesized EILs. The structure of choline chloride based EILs was characterized by $^1$H NMR spectra. There are 5 peaks observed in the $^1$H NMR spectrum in DMSO solvent for ChCl : Gly based EILs. The lowest chemical shift ($\delta=3.139$) of ChCl:Gly (1:1), ($\delta=3.131$) of ChCl:Gly (1:2) and ($\delta=3.128$) of ChCl:Gly (1:3), ($\delta=3.265$) of ChCl:E.Gly and ChCl:Urea of ($\delta=3.197$) indicates the presence of $\text{N-(CH}_3\text{)}$ from choline chloride with relative integration of 9 indicating 9 hydrogen present. A multiplet peaks at ($\delta=3.256$-$3.371$) in ratio 1:1, ($\delta=3.258$-$3.375$) in ratio 1:2 and ($\delta=3.256$-$3.373$) in ratio 1:3 belongs to CH$_2$-OH of glycerol which are symmetry to each other. Another multiplet at ($\delta=3.392$-$3.442$) for 1:1 ratio, ($\delta=3.393$-$3.433$) for 1:2 ratio and ($\delta=3.394$-$3.432$) for 1:3 ratio indicates the presence of (2H, CH$_2$-OH) from choline chloride while (1H, CH=OH) for ratio 1:1, (2H, CH$_2$-OH) from choline chloride while (2H, CH=OH) from glycerol for ratio 1:2 as well as 1:3. A multiplet peak at ($\delta=3.815$) for 1:1 ratio, ($\delta=3.820$) for 1:2 ratio and ($\delta=3.425$) for 1:3 ratio belongs to CH$_2$ bonded to the nitrogen in the choline chloride. The chemical shift ($\delta=6.095$) in ChCl:urea for ratio 1:2 belongs to the (NH$_2$)$_2$ bond with 8 hydrogen present.

Based on the NMR results, it can be seen that OH functional groups as well as hydrogen number increased when double the molar ratio especially for glycerol of ChCl:Gly (1:2). While for ChCl:Gly (1:3), there is no increase for OH functional groups as well as hydrogen number and remain same as in ratio 1:2. This indicates that there are no changes in the hydrogen bond. There are 3 factors for the resonance positions of most protons which are electronegative elements, pi-bonded electrons in the molecule and hydrogen bonding. Comparing all the EILs, the chemical shift of $-\text{CH}_2$ and $-\text{CH}_2$-OH which was deshielded is due to the presence of the OH functional group. Hydrogen bonding lengthens the O-H bond and reduces the valence electron density around the proton. The NMR peak shows
resolution started from 3.00 ppm above because atom C is attached to an electronegative atom which is atom N.

The spectra of EILs samples revealed that the characteristic signal of both ChCl and HBDS protons were downfield shifted when compared to the pure ChCl salt and HBD. Downfield chemical shifts were indicative of the formation of ion-hydrogen-bond-donor supramolecular complexes that characterize EILs [29-30]. These results confirm the structure of the EILs synthesized.

| Compounds                      | Chemical shift (δ, ppm) | Relative integration (%) | No. of H | Type of proton          |
|--------------------------------|-------------------------|--------------------------|----------|-------------------------|
| Chemical shift for ChCl:Gly (1:2) spectra | 3.131                    | 9.00                     | (9H)     | N-(CH₃)₃                |
|                                | 3.258-3.375             | 8.20                     | (4H,4H)  | CH₂-OH                  |
|                                | 3.42                    | 4.01                     | (2H)     | N-CH₂ (ChCl)            |
| Chemical shift for ChCl:Gly (1:3) spectra | 3.404                    | (2H)                     |          | -CH-OH (glycerol)       |
|                                | 3.815                    | 2.00                     | (2H)     | -CH₂-OH (ChCl)          |
| Chemical shift for ChCl:Gly (1:4) spectra | 3.139                    | 9.00                     | (9H)     | N-(CH₃)₃                |
|                                | 3.256-3.371             | 7.69                     | (4H,4H)  | CH₂-OH                  |
|                                | 3.415                    | 3.87                     | (2H)     | N-CH₂ (ChCl)            |
| Chemical shift for ChCl:E.Gly (1:2) spectra | 3.404                    | (2H)                     |          | -CH-OH (ethylene glycol) |
|                                | 3.821                    | 2.00                     | (2H)     | -CH₂-OH (ChCl)          |
| Chemical shift for ChCl:Urea (1:2) spectra | 3.265                    | 9.00                     | (9H)     | N-(CH₃)₃                |
|                                | 4.038                    | 2.01                     | (2H)     | CH₂-OH                  |
|                                | 3.621                    | 8.22                     | (4H, 4H) | -CH₂-OH (ethylene glycol) |
|                                | 3.554                    | 2.01                     | (2H)     | N-CH₂                   |
| Chemical shift for ChCl:Urea (1:2) spectra | 3.197                    | 9.00                     | (9H)     | N-(CH₃)₃                |
|                                | 3.505                    | 2.01                     | (2H)     | CH₂-OH                  |
|                                | 4.424                    | 2.23                     | (1H, 1H) | N-OH                    |
|                                | 6.095                    | 8.01                     | (4H, 4H) | CO-(NH₂)₂               |
3.3 Effect of pH of NaOH

Figure 3. pH profiles of NaOH\(_{aq}\) during absorption process in the presence of EILs.

Figure 3 shows the maximum recovery of SO\(_2\) obtained, when the gas was passed into the NaOH solution directly. The initial pH of NaOH was maintained at pH 10 for all systems. Based on the results from figure 1, it can be observed that the EILs successfully absorbed the SO\(_2\) because there was a slight decrease in pH of NaOH noted with time. The pH of NaOH decreases slightly when it is flowed through the EILs solution because the SO\(_2\) was absorbed by the EIL and there was minimal flow into the NaOH solution. For the blank run, all SO\(_2\) was taken up by the NaOH solution, thus the pH decreases rapidly as function of time. The remaining gas that could not be absorbed by EILs was passed into the stream which enters the NaOH solution represented as a scrubber to neutralize the acid gasses prior to disposal.

Based on the results obtained, the trend of the decrease in pH vs time from highest to the lowest pH were ChCl: E.Gly (1:2), ChCl:Urea (1:2), ChCl:Gly (1:2), followed by ChCl:Gly (1:3), ChCl:Gly (1:4). All the EILs are considered as good absorbers because the pH mostly stabilizes between pH 6-8. The pH value of the absorption solution drops from pH 10 to around 6 to 8, because of the faster consumption of OH\(^{-}\) in the absorption solution. This indicates that the alkaline solution become neutral and easy for disposal of the NaOH solution. Generally, if the pH drops lower than 6, it indicates that the EILs did not absorbed the SO\(_2\) gas very well whereas al SO\(_2\) has been absorbed by the NaOH solution. In addition, if the pH value of the absorption solution decreases slowly from pH 6 to 3, it indicates that the solution has converted into buffer solution [31]. Hence, the pH value of the absorption solution should be above 6 in this process in order to make it an effective absorption.

Below is the chemical equation of NaOH and SO\(_2\) gas when reacted to each other that lead to the formation of sodium sulfite:

\[
\text{SO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \tag{2}
\]

3.4 Efficiency of EILs in SO\(_2\) absorption

Due to the non-toxic, cheap and biodegradable characteristics of choline chloride, five quaternary ammonium salts based EILs were synthesized. The hydrogen bond donors were selected from low molecular weight organic compounds such as glycerol, urea and ethylene glycol. Based on the findings as in Table 5, it reflects that the solubility of SO\(_2\) in these EILs was good. The organic compounds were the dominant factor affecting the SO\(_2\) absorption amount. Among the five EILs, ChCl:E.Gly (1:2) gave the highest SO\(_2\) solubility with 0.57 mg SO\(_2\)/g EIL. The second highest absorption capacity was displayed by ChCl:Urea with 0.55 mg SO\(_2\)/g EIL. This finding was supported
by Sun et al [32] who had carried out a study on the capacities of ChCl with ethylene glycol (EG) at molar ratio 1:2 and urea at 1:2. The amount of SO$_2$ absorbed by ChCl-EG (1:2) and ChCl-urea (1:2) were the two highest with 0.7 g SO$_2$/ g eutectic and 0.88 g SO$_2$/ g eutectic at 293 K and 1 atm. According to Abott et al [17], choline chloride based EILs has excellent SO$_2$ absorption ability and they could be used as a benchmark in comparison.

| No | EILs          | Molar Ratio | SO$_2$ Absorption Capacity (mg SO$_2$/ g EIL) after 120 minutes |
|----|---------------|-------------|----------------------------------------------------------------|
| 1. | ChCl :Gly    | 1:2         | 0.54                                                            |
|    |               | 1:3         | 0.54                                                            |
|    |               | 1:4         | 0.53                                                            |
| 2. | ChCl : E.Gly | 1:2         | 0.57                                                            |
| 3. | ChCl : Urea  | 1:2         | 0.55                                                            |

In addition, the results from ChCl:Gly based EILs showed that the absorption capacity decreases as the molar ratio increases. ChCl:Gly (1:2) and ChCl:Gly (1:3) has an absorption capacity of 0.54 mg SO$_2$/g EIL, followed by ChCl:Gly (1:4) with 0.53 mg SO$_2$/g EIL of absorption capacity. The amount of SO$_2$ captured was significantly controlled by the composition of ChCl:Gly. The increase in ChCl:Gly molar ratio diminishes its SO$_2$ capturing ability. This was due to the change transfer interaction between acidic SO$_2$ and nucleophile Cl$^-$ of ChCl. Hence, the SO$_2$ capturing capacity is high as the concentration of glycerol in the EILs is the lowest.

Therefore, the SO$_2$ capturing capacities of ChCl:E.Gly eutectic were higher than ChCl:Urea as well as ChCl:Gly EILs. This was due to the structural difference between ethylene glycol (E.Gly), Urea and Glycerol in which the alcohol group in E.Gly could capture more SO$_2$ [14]. Higher molecular weight of organic compound also resulted in lower SO$_2$ capturing capacity of the EIL. Furthermore, incremental molar ratio of the EILs in the same group would decrease the SO$_2$ absorption capacity.

4. Conclusion
In conclusion, five quaternary ammonium based EILs were successfully synthesized. The NMR spectra confirmed the structure of the synthesized EILs. When there is an increase in the duration for SO$_2$ absorption in EIL, there was a significant decrease in pH. This indicates that the SO$_2$ that was not absorbed by the EIL has reacted with NaOH. The results demonstrates that ChCl:E.Gly (1:2) displayed the highest absorption capacity of 0.57 mg SO$_2$/g EIL among all the other investigated EILs. ChCl:Urea had an absorption capacity of 0.55 mg SO$_2$/g EIL followed by ChCl:Gly (1:2) and (1:3) with an absorption capacity of 0.54 mg SO$_2$/g EIL and finally ChCl:Gly (1:4) with an absorption capacity of 0.53 mg SO$_2$/g EIL. ChCl:E.Gly exhibits highest absorption capacity because of the structural difference between ethylene glycol (E.Gly), Urea and Glycerol in which the alcohol group in E.Gly could capture more SO$_2$. The high efficiency, low energy consumption and ease of operation make the present EILs to be promising absorbents for SO$_2$. Therefore, this research is driven by the desire to develop technologies that surpass current options in terms of performance, costs, operability, and by-product properties. New issues, such as concern over global climate changes and the health effects of toxic air emissions are also helping to shape and prioritize in the development of the research.

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