Absorption Capacity of Ammonia into Ionic Liquids for Absorption Refrigeration Applications

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Abstract. In this paper ionic liquids are proposed as a novel absorbent for absorption refrigeration application with ammonia as refrigerant. The main objective of this work is to develop a measurement setup to study the absorption capacity of the ammonia vapour in ionic liquids in a pool type absorber. This investigation is essential in order to identify the most suitable ionic liquid as an absorbent for ammonia refrigerant. The ionic liquids studied in this work are combinations of two different cations ([EtOHmim]+ and [emim]+) and three different anions ([BF4]−, [NTf2]− and [EtSO4]−). The absorption processes are observed within 20 minutes in each experiment at different temperatures and pressures. The detail of the methodology and experimental setup are explained in this paper and measurement results of absorption capacity of ammonia into ionic liquid are discussed. Among all ionic liquids studied in this paper [EtOHmim]+ based ionic liquids shows higher absorption capacity than [emim]+ based ionic liquids, which means that the OH structure in the cation may improve the absorption capacity of ammonia.

1. Introduction
Absorption refrigeration system is a good known technology. The absorption systems, which can utilize renewable energy such as solar and geothermal energy or waste heat sources such as exhausts of diesel engines and industrial plants to produce cold, carries a primary energy saving, and thus emission reduction. In addition, the absorption systems contain non-HFC and thus, environmentally friendly and becomes a competitive alternative to the conventional vapour compression refrigeration systems. Similar to the compression cycle, absorption cycle is based on the cooling and heating process associated with phase changes of evaporation and condensation of refrigerant fluid at different temperatures and pressures. The working fluid consists of refrigerant and absorbent, so that the boiling temperature can be modified by changing the pressure or composition of the mixture.

One of the most common working fluid pair in absorption refrigeration systems is ammonia/water. In this working pair, ammonia works as refrigerant and water as absorbent. The ammonia/water absorption cycle is used mainly for refrigeration purpose, since it can produce cold below 0°C. Being natural fluids, both are emission free and ozone friendly resulting with zero global warming potential (GWP) and ozone depletion potential (ODP). However, the characteristic of water is volatile, thus it is necessary to add an additional component, namely rectifier, to minimize the amount of water entering to the condenser.

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Many researchers have been investigating to find working fluid pairs that can overcome the above limitation. One of the working fluid has been investigated for absorption refrigeration cycle is ammonia/ionic liquid. The use of ionic liquid (IL) as an alternative to water as absorbent in the absorption refrigeration cycle gives some advantages such as elimination of the rectification process in ammonia/water system. The use of IL as absorbent with ammonia as refrigerant in the absorption refrigeration cycle has been discussed by researchers [1–7]. According to them, one of the main advantages in comparison with a conventional ammonia/water absorption refrigeration cycle is that the ammonia/IL absorption refrigeration system may not require the costly rectifier unit needed for traditional ammonia/water system due to there being practically no vapour pressure for the absorbent.

Ionic liquids, or often referred as room temperature ionic liquids (RTIL), have the character of molten salts, which are stable at room temperature [8]. These liquids, which usually consist of organic cation and inorganic anion, have negligible vapour pressure and good thermal stability. In addition, the thermophysical properties of ionic liquids can be adjusted by combining the cation and anion pair. These unique characteristics make ionic liquids to be a potential candidate as a novel absorbent for absorption system eliminating the drawbacks of conventional working fluids.

Absorption refrigeration system has four main components namely absorber, generator, condenser, and evaporator. Among these, absorber is considered to be the most critical part in the system, both in terms of influence on system performance and cost [9]. Absorption system based on ammonia/ionic liquid is desirable for subzero temperature applications. Thus it is essential to investigate the absorption characteristic of the ammonia vapour into ionic liquid absorbent.

The main objective of this research is to develop a measurement set up to study the absorption capacity of the ammonia vapour in ionic liquids in a pool type absorber. This investigation is necessary to find the most suitable ionic liquid as an absorbent for ammonia refrigerant. Furthermore, it is also important to find the most suitable absorber configuration for the proposed ammonia/ionic liquids absorption system.

2. Materials and Experimental Setup

2.1. Materials
The anhydrous ammonia (purity 99.98% by mass, CAS no. 7664-41-7) is obtained from Carburos Mëtalicos and is used directly without any further purification. Commercial ionic liquids, 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO₄], assay ≥95%, MW=236.29, CAS no. 342573-75-5) is obtained from Aldrich Chemistry, whereas 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄], assay ≥98%, MW=197.97, CAS no. 143314-16-3), 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([emim][NTf₂], assay 99%, MW=391.31, CAS no. 174899-82-2), 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([EtOHmim][BF₄], assay ≥98%, MW=213.97, CAS no. 374564-83-7) and 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoro-methylsulfonfyl)imide ([EtOHmim][NTf₂], assay 99%, MW=2407.31, CAS no. 374564-83-7) are obtained from Iolitec. Chemical structure of cations and anions of ionic liquids used in this study are shown in figure 1. Ionic liquids are dried in a vessel under vacuum and simultaneously stirred and heated for at least 48 hours to reduce their water contents before used. The water content of ionic liquids after drying process is determined using Karl Fisher coulometer (Mettler Toledo model C20). The results show that the water content for all ionic liquids is below 200 ppm (by mass).

2.2. Experimental Setup and Procedures
In this study, static pool type absorber is selected to examine the absorption rate of ammonia refrigerant into ionic liquid absorbent as this configuration is suitable for the measurement of absorption capacity in liquid static conditions [10]. In addition, this configuration is suitable to handle high viscosity fluids such as ionic liquids.
Figure 1. Chemical structures of studied ionic liquids

The main components of the experimental set-up for absorption measurement are liquid cell, mass flow controller, temperature and pressure sensor, data logger, thermal bath, magnetic stirrer, ammonia tank and vacuum pump.

The liquid cell is a cylinder and is made up of stainless steel to avoid corrosion problems due to ammonia contact. It has inner volume of 14 ml, outside diameter of 30 mm and wall thickness of 2 mm. The liquid cell has a temperature sensor (PT-100) and pressure sensor (Wika S-20 pressure transducer). The temperature and the pressure sensors are connected to the data logger (DataTaker DT80) to record the temperature and pressure in a certain interval of time. The cell is immersed in a thermal bath to maintain the temperature, and is placed over a magnetic stirrer to agitate the liquid absorbent inside the cell in order to ensure that the ionic liquid/ammonia solution is in homogenous condition and the liquid surface is less than equilibrium condition so that the absorption process can occur until the solution reaches the equilibrium condition with the refrigerant vapor. The detailed schematic diagram of the measurement setup is shown in figure 2.

The main ammonia line is connected to the ammonia tank which has a valve and a pressure regulator. A mass flow controller (Alicat gas flow controller, model MCS-500SCCM-D) is installed in the ammonia line close to the cell to record ammonia mass flow. Another valve and a pressure regulator are installed in the setup to control the pressure and to start and terminate the measurement. In addition, the ammonia line has a connection to the vacuum pump to remove non-absorbable gas inside the system.

An amount of about 5 ml of ionic liquid is taken using a syringe and weighted on a digital mass balance Mettler AE 260 DeltaRange (±0.1 mg), and then is injected carefully into the cell via injection line.

After the liquid is inserted into the cell, all the lines are connected properly. Before starting the measurement, it is important to remove the non-absorbable gas trapped both in the line and the cell. To remove the non-absorbable gas, vacuum is applied to the whole gas pipeline and the cell, in order to remove the air inside them. The vacuum pressure is monitored with the digital Pirani gauge meter, until that segment reaches vacuum (c.a. 0.01 bar). After removing the non-absorbable all valves are closed. The temperature and pressure sensors are connected to the data logger. The cell is then immersed into the thermal bath placed over the magnetic stirrer.
The final step before starting the measurement is to set the ammonia pressure regulator to the desired pressure. The first step to set the ammonia pressure is to ensure that the ammonia tank valve and the pressure regulator are closed, and then to reduce the pressure by opening the release valve. The second step is to open the ammonia tank valve and then carefully open the pressure regulator until reach the desired pressure.

To start the measurement, the valve (V3) is opened. The pressure and the temperature are recorded every two seconds until these parameters become invariant and then the measurements and experiment are stopped.

2.3. Data Reduction

Two parameters, mass absorption rate and mass absorption flux, are used to analyse the absorption capacity of ammonia into ionic liquids. The following equations are used for processing and analysing the data obtained from the measurements.

2.3.1. Mass Absorption Capacity. Mass absorption rate can be defined as the total mass of refrigerant absorbed into the absorbent in a unit of time. This mass absorption rate can be used to determine the total mass absorbed into ionic liquids and ammonia mass concentration in the solution. In a formula, it can be calculated as follows

\[ m_{NH_3} = \int \dot{m}_{NH_3} \, dt \]

where \( \dot{m}_{NH_3} \) represents the ammonia mass flow rate (g/s), \( m_{NH_3} \) is the total mass of the solution (g), and \( t \) is the time (s).

In addition, ammonia mass concentration in the solution can be expressed as follows

\[ X_{NH_3} (\%) = \frac{m_{NH_3}}{m_{NH_3} + m_{IL}} \times 100 \]

where \( X_{NH_3} \) is the ammonia mass concentration in the solution (%) and \( m_{IL} \) is the mass of ionic liquid in the solution.
2.3.2. Mass Flux. Mass flux which is defined as the mass absorption rate per unit area can be calculated using a formula as follows

\[ m_f = \frac{\dot{m}_{\text{NH}_3}}{A} \]  
(3)

where \( m_f \) is mass flux (g/s cm\(^2\)) and \( A \) is interface area (cm\(^2\)).

3. Results and Discussion

The absorption capacity of ammonia into five ionic liquids in a static pool type absorbent is studied in this work. Pool type absorber is chosen due to its ability to measure the absorption capacity of absorbent having low solubility with the refrigerant by small quantity of absorbent [10]. The ionic liquids studied in this work are combinations of two different cations ([EtOHmim]+ and [emim]+) and three different anions ([BF\(_4\)]\(^-\), [NTf\(_2\)]\(^-\) and [EtSO\(_4\)]\(^-\)). The absorption processes are observed within 20 minutes in each experiment at different temperatures and pressures.

3.1. Effect of temperature and pressure

It is known that the ammonia solubility in ionic liquids decreases when the temperature is increased and the ammonia solubility in ionic liquid increases when the system pressure is increased [1-3]. However, it is interesting to understand the behaviour of ammonia absorption into ionic liquids at different temperatures and pressures. Due to limited space, not all ionic liquids studied in this work will be presented and discussed in this subsection.

![Figure 3. Temperature difference profile (a) and NH\(_3\) mass concentration profile (b) of [emim][BF\(_4\)] at different temperatures and pressures](image)

The effect of initial temperature to the absorption process of ammonia into [emim][BF\(_4\)] is shown in figure 3. When the initial temperature is increased, the absorption rate decreases and thus decreasing the heat releases to the ambient, resulting the decrease of temperature different (\( \Delta T \)) (see figure 3(a)). From figure 3(b) it can be confirmed that the ammonia absorption capacity in ionic liquid decreases when the initial temperature is increased. For instance, the ammonia concentration at pressure of 5 bar decrease from 11.67% at initial temperature of 30\(^\circ\)C to 8.75% at initial temperature of 40\(^\circ\)C. Similarly, at pressure of 4 bar the ammonia concentration slightly decreases from 8.56% at initial temperature of 30\(^\circ\)C to 7.54% at initial temperature of 40\(^\circ\)C.

Figure 4 shows the effect of pressure to the absorption process of ammonia into [EtOHmim][NTf\(_2\)]. This figure confirms that the ammonia absorption capacity in ionic liquid increases when the system pressure is increased. As shown in figure 4(a), the ammonia mass flow rate increases when the system pressure is increased. The ammonia concentration at pressure of 5 bar decreases from 11.19% to 9.72% at pressure of 40\(^\circ\)C and decreases to 7.58% at pressure of 3 bar (see figure 4(b)).
3.2. Temperature and mass concentration profile

Figure 5(a) shows the temperature profile during absorption process at initial temperature of 30°C and pressure of 3 bar. It can be seen that the pool type absorber with small volume can give relatively significant in temperature change considering that ionic liquid has relatively low solubility in ammonia. It also can be seen that the temperature increase significantly in the beginning of the measurement as in this time the absorption capacity is in its highest rate, and the heat is released to the system. The temperature then decreases as the absorption rate decrease until the solution reach equilibrium. For all ionic liquid studied, the temperature increases in the beginning of absorption process which indicates that the absorption processes for all studied ionic liquids are exothermic process.

The temperature increase of ionic liquids with [EtOHmim]+ cation is higher as compared to those ionic liquids with [emim]+ cation which means that ionic liquids with [EtOHmim]+ cation release more heat as compared to other ionic liquids. The temperature difference between peak temperature and initial temperature ($\Delta T$) of [EtOHmim][BF$_4$] and [EtOHmim][NTf$_2$] at initial temperature of 30°C and pressure of 3 bar lays about 8.6°C and 8.2°C, respectively whereas temperature differences of [emim]+ based ionic liquids just lay around 3–4°C which are less than half of the temperature difference of [EtOHmim]+ based ionic liquids.

In terms of same cation, it can be clearly seen from figure 3 that ionic liquids having [BF$_4$] anion give higher temperature difference as compared to other anion. For instance, [EtOHmim][BF$_4$] shows higher temperature difference than [EtOHmim][NTf$_2$] and [emim][BF$_4$] has higher temperature difference.
difference than [emim][NTf₂] and [emim][EtSO₄]. In addition, for same cation ionic liquid with [NTf₂] anion has higher temperature difference than that of [EtSO₄] anion. However, although for same cation [BF₄] has higher temperature difference than other anions, these differences are much lower as compared to those given by different cations. In a simple way, it can be said that different cations can give more influence in temperature differences as compared to different anions.

Figure 5(b) shows the ammonia mass concentration profile during the absorption process. This figure shows that similarly with the trends of temperature differences, at the end of each measurement for operation condition at temperature of 30ºC and pressure of 3 bar the [EtOHmim] based ionic liquids can absorb more ammonia as compared to [emim]⁺ based ionic liquids. In addition, [EtOHmim][BF₄] has the highest ammonia concentration and [emim][NTf₂] has the lowest ammonia concentration as compared to the other ionic liquids. At the end of measurement, the ammonia mass concentration in [EtOHmim][BF₄] and [EtOHmim][NTf₂] is 11.94% and 7.58%, respectively. For [emim] based ionic liquids, the ammonia mass concentration at the end of measurements follows the trend [BF₄] >[EtSO₄] >[NTf₂]. The ammonia mass concentrations for these three ionic liquids are 5.23%, 5.11%, and 3.50%, respectively.

Although [EtOHmim]⁺ based ionic liquids absorbs more ammonia, it is interesting to see that in the beginning of the process [emim][BF₄] absorbs slightly faster than [EtOHmim][NTf₂]. This trend occurs until the process takes place for around 70 s. After 70 s, the ammonia concentration of [emim][BF₄] remains lower than [EtOHmim][NTf₂] as [emim][BF₄] absorbs less ammonia. On the other hand, faster absorption of ammonia in the beginning of the process is shown by [emim][BF₄] in comparison with [emim][EtSO₄] and [emim][NTf₂] in comparison with [emim][EtSO₄].

3.3. Mass Absorption Flux

Mass absorption flux is calculated using eq. (2) and mass absorption rate is recorded directly from gas mass flow controller using data logger. When the absorption process is started, the ionic liquid is in its highest purity and thus absorbs ammonia quickly. As the absorption process continues, the absorption rate decreases until the solution reaches equilibrium condition. This process can be confirmed in figure 6(a) which shows mass absorption flux of ammonia into ionic liquids at operation condition of 30ºC and 3 bar, was very high in the beginning of the process and then decreases until the solution reach equilibrium. The initial mass flux for all ionic liquids in this operation condition lays between $4 \times 10^{-4}$ g/cm² s and $14 \times 10^{-4}$ g/cm² s.

![Mass Absorption Flux](image)

**Figure 6.** Ammonia mass flux at temperature of 30ºC and at pressure of (a) 3 bar and (b) 5 bar

Mass absorption flux at temperature of 30ºC and pressure of 5 bar is shown in figure 6(b). From this figure it can be seen that the mass absorption flux was much higher in the beginning of the process as compared with those at pressure of 3 bar. The initial mass absorption flux for all ionic liquids in this operation condition lays between $11 \times 10^{-4}$ g/cm² s and $15 \times 10^{-4}$ g/cm² s. However, different with those at pressure condition of 3 bar, the mass absorption flux at pressure condition of 5 bar remains high.
until the absorption process takes place for around 2 minutes and after the mass absorption flux decreases sharply.

From figure 6 it is also interesting to note that although the absorption process may take place for more than an hour [2] the mass absorption flux of both 3 bar and 5 bar pressure conditions remains similar after 5 minutes.

4. Conclusions
The absorption capacity of ammonia into five ionic liquids is measured using static pool type absorber at different temperatures and pressures. The measurement confirms that pool type absorber is able to measure the absorption capacity of absorbent having low solubility with the refrigerant by relatively small quantity of absorbent. It is also confirmed that the ammonia solubility in ionic liquids decrease when the temperature is increased and the ammonia solubility in ionic liquid increases when the system pressure is increased.

Among all ionic liquids presented in this paper [EtOHmim][BF₄] based ionic liquids shows higher absorption capacity than [emim][BF₄] based ionic liquids, which means that the OH structure in the cation may improve the absorption capacity of ammonia. In addition [BF₄]⁻ anion shows slightly higher absorption capacity than other anions with same cation. However, in the beginning of the process [emim][BF₄] based ionic liquids show higher absorption capacity than [EtOHmim][BF₄] based ionic liquids. Although [EtOHmim][BF₄] shows high absorption capacity, it is necessary to study its other properties (e.g. viscosity) to have deeper understanding about its feasibility to be a suitable absorbent for ammonia refrigerant.

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References
[1] Yokozeki A and Shiflett M B 2007 Applied Energy 84 pp 1258–1273
[2] Yokozeki A and Shiflett M B 2007 Ind. Eng. Chem. Res. 46 pp 1605–1610
[3] Li G, Zhou Q, Zhang X, Wang L, Zhang S, Lia J 2010 Fluid Phase Equilibria 297(1) pp 34–39
[4] Ruiz E, Ferro V R, de Riva J, Moreno D, Palomar J 2014 Applied Energy 123 pp 281–291
[5] Bedia J, Palomar J, Gonzalez-Miquel M, Rodriguez F, Rodriguez J J 2012 Separation and Purification Technology 95 pp 188–195
[6] Palomar J, Gonzalez-Miquel M, Bedia J, Rodriguez F, Rodriguez J J 2011 Separation and Purification Technology 82 pp 43–52
[7] Kotenko O, Moser H and Rieberer R 2011 Proc. Int. Sorption Heat Pump Conf. 7 pp 89-796
[8] Kim Y J, Kim S, Joshi Y K, Fedorov A G and Paul A, Kohl P A 2012 Energy 44 pp 1005-1016
[9] Killion J D and Garimella S 2001 Int. J. Refrig. 24 pp 755-797
[10] Ariyadi H M, Maiya P M, Valles M, Salavera D and Coronas A 2015 Proc. 28th Int. Conf. on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems