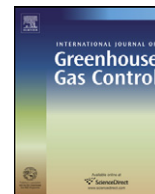




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## Ionic liquids for post-combustion CO<sub>2</sub> absorption

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### ABSTRACT

The present work is a study to evaluate ionic liquids as a potential solvent for post-combustion CO<sub>2</sub> capture. In order to enhance the absorption performance of a CO<sub>2</sub> capture unit, different ionic liquids have been designed and tested. The main goal was to get a comparison between a reference liquid and selected ionic liquids. As the reference, a solution of 30 w% monoethanolamine (MEA) and water was used. A large range of different pure and diluted ionic liquids was tested with a special screening process to gain general information about the CO<sub>2</sub> absorption performance. Based on these results, a 60 w% ionic liquid solution in water was selected and the vapour–liquid equilibrium was measured experimentally between 40 °C and 110 °C. From these curves the enthalpy of absorption for capturing CO<sub>2</sub> into the ionic liquid was determined. With these important parameters one is able to calculate the total energy demand for stripping of CO<sub>2</sub> from the loaded solvent for comparison of the ionic liquid based solvent with the reference MEA solvent. The energy demand of this 60 w% ionic liquid is slightly lower than that of the reference solution, resulting in possible energy savings between 12 and 16%.

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### 1. Introduction

Since it is highly evident that the anthropogenic greenhouse effect is caused by mankind (IPCC, 2007), strong actions need to be taken to find solutions to combat or slow global warming. Today, most scientists are confident that carbon dioxide mitigation by carbon capture and storage (CCS) is a feasible option to significantly reduce the level of carbon dioxide emissions. One of the most promising processes is post-combustion (IPCC, 2005), the capturing of CO<sub>2</sub> after the combustion process. One advantage of this process is the potential for retrofit to existing power plants without changing the existing processes (Figuerola et al., 2008). This circumstance will result in high availability, flexibility and reliability of the power plant operation which will prevail CCS in the beginning (Kather, 2008). CO<sub>2</sub> scrubbing or absorption is the most predominantly proposed post-combustion capture (PCC) process, since it is the most developed process of all CCS options that has been used for decades for applications, such as in the chemical industry. In most CO<sub>2</sub> scrubbing applications, CO<sub>2</sub> is captured from the process stream by absorption into a solvent and subsequently released from the solvent by stripping by changing the temperature. By condensing the water out of the flue gas,

highly concentrated CO<sub>2</sub> can be gained and stored underground after compression. By determination of the total costs of capture, transport and storage it is evident, that the capturing of CO<sub>2</sub> is the most cost intensive stage (Conturie, 2006; IPCC, 2005). Hence significant scientific effort has been directed to find more effective process technologies by the identification or development of new solvents. Increasing the performance is directly linked with lowering operating costs, which opens an enormous saving potential. In the past, much research has been completed in the development of new amines or blend of amines, but also ammonia, amino acids and potassium carbonate. More recently ionic liquids have started to be considered as potential candidates.

Ionic liquids (ILs) are very promising for capturing CO<sub>2</sub> because they have some potential advantages in comparison to other solvents such as monoethanolamine (MEA) based solutions. Ionic liquids are salts with a melting temperature below the boiling point of water (Wasserscheid and Welton, 2008). Most ionic liquids have an organic cation and an inorganic anion. Pure ionic liquids contain only ions and no solvent (e.g. water) is necessary. A major advantage of ILs is that the properties can be selected on the basis of the choice of either anion, cation or other substituents. This flexibility leads to innumerable different structures and variation possibilities. Anderson et al. (2007) suggest that there are about 10<sup>18</sup> possible structures for room temperature ionic liquids. Another big advantage of ILs is their negligible vapour pressure (high “green” potential), hence no contamination of the gas stream

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### Nomenclature

$\Delta H_{\text{Abs}}$	enthalpy of absorption [kJ/mol]
$k$	equilibrium constant
$p_{\text{tot}}$	total pressure [kPa]
$p_i$	partial pressure of substance $i$ [kPa]
$\Delta p_T$	pressure decrease at temperature $T$ [mbar]
$\Delta p$	pressure difference $ \Delta p_{25} - \Delta p_{80} $ [mbar]
$R$	universal gas constant [J/(mol K)]
$T$	temperature [K]
$t_T$	time until equilibrium was reached at temperature $T$ [s]
w%	weight percent [%]
$y_i$	molar fraction of substance $i$ [mol $_i$ /mol $_{\text{total}}$ ]
$\alpha$	CO $_2$ solvent loading [mol $_{\text{CO}_2}$ /mol $_{\text{solvent}}$ ]

### Abbreviations

Abs	absorption
atm	atmospheric
FI	flow meter
g	gaseous
IL	ionic liquid
IR	infrared
l	liquid
MEA	monoethanolamine
PI	pressure gauge
tot	total
VLE	vapour–liquid equilibrium

and negligible losses of ILs due to evaporation would be expected. Despite the relatively short research time on ionic liquids, the application for CO $_2$  absorption was already discussed in the past. Bates et al. (2002) is talking about particular significance of ionic liquids as novel CO $_2$  absorption solvents. Maginn (2004) claims that ILs have the potential to overcome many of the problems associated with current CO $_2$  capture solvents and processes. Anthony et al. (2004) showed that ionic liquids can be used for gas separations, specially capturing CO $_2$  from a N $_2$  or CH $_4$  mixture. In terms of physical solubility, it has been shown that CO $_2$  has the highest gas solubility combined with a good selectivity of all measured gases in ILs (Anderson et al., 2007). The recovering of the dissolved CO $_2$  from the ionic liquid can, as with other solvent based processes, be achieved by increasing the temperature thereby reducing the CO $_2$  solubility and/or reversing the absorption reaction. Anthony et al. (2004) compared the ionic liquids [bmim][PF $_6$ ] and [bmim][BF $_4$ ] with a 30 w% MEA solution as a CO $_2$  capture solvent. For these specific ILs the energy demand was estimated to be too high because the ionic liquids used were not task specific for CO $_2$  capture. However Anthony et al. (2004) and Zhang et al. (2006) believe that a task specific IL can be competitive with a 30 w% MEA solution for capturing CO $_2$ . Compared to conventional ILs, where the absorption of CO $_2$  is mainly based on physical dissolution, task specific ILs have the potential to capture larger amounts of CO $_2$  using chemical interactions between CO $_2$  and reactive groups. It would appear that the CO $_2$  capture performance is mainly influenced by the IL's anion (Anthony et al., 2005; Cadena et al., 2004).

For the current investigation, the CO $_2$  absorption behaviour of several new task specific ionic liquids and blends of ionic liquids was tested. During initial screening tests, the absorption performance could be determined using a small amount of ionic liquid.

Based on the results of these experiments, the vapour–liquid equilibrium (VLE) curves for one ionic liquid were determined experimentally over a temperature range of 40–110 °C. Together with the enthalpy of absorption, which can be deduced from the vapour–liquid equilibrium curves, the determination of the energy demand for the stripping process is possible. The VLE curve and the enthalpy of absorption  $\Delta H_{\text{Abs}}$  specify the ability to capture CO $_2$  and are the underlying basis in the design of every absorption/desorption column. The energy demand for stripping is basically the energy input to the desorber to release the chemical bonded CO $_2$  and hence to regenerate the absorption solvent. The determination of this energy demand is an important parameter for estimating the costs of operating the post-combustion capture process and with that a measure of the performance and viability of the absorption solvent. The obtained results for the selected ionic liquid were compared with a reference absorption process using a 30 w% MEA solution as the solvent. For this reference process, the selected temperature for absorption and desorption were 40 °C and 110 °C, respectively.

## 2. Experimental methods

The experimental section is split into two major sections, namely the screening of various ionic liquids, followed by the characterization of various selected ones and the vapour–liquid equilibrium measurements of an ionic liquid shown the most promise for CO $_2$  capture.

### 2.1. Screening

Due to the wide range of possible ionic liquid structures, a simple screening process was developed to very quickly predict the CO $_2$  absorption performance. Shown in Fig. 1 is the apparatus used to measure CO $_2$  absorption rates for ionic liquids.

The apparatus consists of a 20 ml glass flask, vacuum-tight seal Rotilabo<sup>®</sup>-Aluminum lid that includes a septum. The gas tightness of the glass flask was validated for selected samples using an adjusted vacuum that was maintained over a 24 h period. To ensure pure CO $_2$  in the glass flask during the experiment, the flask including a stir bar was flushed with CO $_2$  prior sealing for about

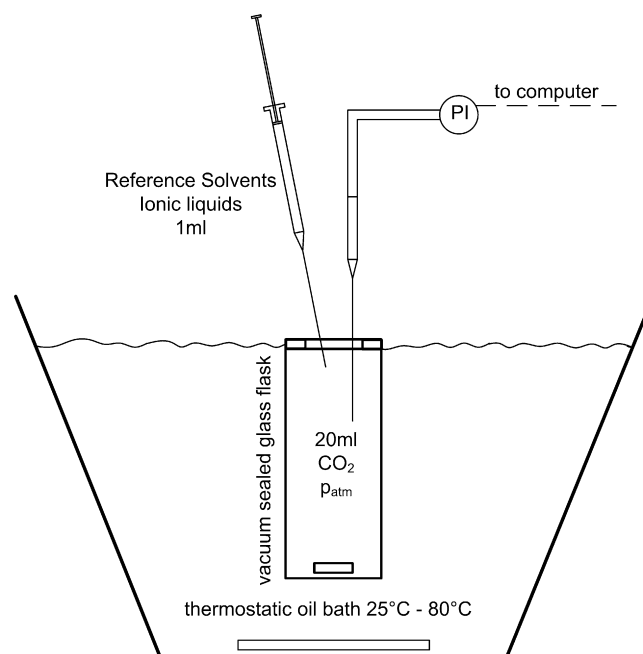


Fig. 1. Screening apparatus for ionic liquids.

10 min. After sealing a needlepoint was used as an outlet and pure CO<sub>2</sub> was injected for about 15 min. The flow rate of CO<sub>2</sub> was fairly high, hence it can be assumed that all the air was replaced by CO<sub>2</sub> after flushing. Before stopping the CO<sub>2</sub> gas flow, the needlepoint was removed to ensure over pressure in the glass flask. The vacuum sealed glass flask was then thermostatted at either 25 °C or 80 °C in a bath agitated by a magnetic stirrer. To measure the pressure in the system, a pressure gauge (PCE-P15) was connected with a needlepoint to the glass flask. The actual pressure in the glass flask was logged once every second. After thermal stabilization the over pressure was released with a needlepoint. Thus the actual pressure of CO<sub>2</sub> in the system before injecting a liquid sample, was always equal to the atmospheric pressure. The over pressure in the glass flask prior to depressurizing to atmospheric pressure ensures that no other gases enter the system. To measure the CO<sub>2</sub> capture performance, 1 ml of a liquid sample was injected with a 1 ml calibrated syringe into the glass flask. It was important to leave the syringe in the septum during the experiment to avoid a pressure drop. The amount of the solvent sample was constant 1 ml for all the tested liquids. To perform a mass balance the syringe was weighted before and after the liquid injection. If the injected liquid was able to absorb CO<sub>2</sub>, the pressure in the glass flask would be observed to decrease after injection. The experiment was stopped after achieving a constant pressure for about 20 min. In the case of a leakage a constant pressure was not realized and the experiment was repeated.

## 2.2. Vapour–liquid equilibrium measurements

For measurement of the vapour–liquid equilibrium between CO<sub>2</sub> and the absorption solvent, an apparatus shown in Fig. 2 was used.

This apparatus is based on the work of Austgen et al. (1991) and Ma'mun et al. (2005, 2007) and was designed for experiments at atmospheric pressure. Hence temperatures up to around 90 °C are possible for a 30 w% MEA solution to obtain useful results. When using ionic liquids combined with water, the maximum temperature can be higher, depending on the water content and the boiling point of the new solvent. The apparatus consist of three 250 ml glass vessels, whereas the first one operates as a water saturator to stabilize the gas flow. The second and the third vessel contain about 150–200 ml of preloaded absorption solvent, which means that the solvent is already loaded with CO<sub>2</sub> before starting the experiment. With the preloading of the solvent shorter experiment periods are realized. The flasks were situated in a thermostat box, containing an oil or water bath with an insulated cap. The

temperature of the oil or water bath was measured with a thermocouple and kept constant at a certain temperature  $\pm 0.5$  °C. Before starting the experiment, the glass flasks and the pipes were flushed with pure nitrogen to ensure that no other gases are present in the system. After starting the experiment, the nitrogen was recirculated via the bypass pipe until the adjusted temperature had been reached. The Watson-Marlow-Bredel 101 U/R squeeze pump is able to pump around about 60 ml/min of gas. Through the heating, the absorbed CO<sub>2</sub> is released according the vapour–liquid equilibrium curve for a certain temperature. After the system had stabilized, the gas flow was sent through the IR Analyzer (Hartmann und Braun Uras 10E), where the amount of CO<sub>2</sub> in the gas flow was measured. To ensure correct CO<sub>2</sub> measurements, water was removed from the gas stream with silica gel. The water losses through the drying were counterbalanced in the first vessel where the gas stream was saturated with water again. Due to the higher water vapour partial pressure in the first vessel compared to the second and third vessel, dilution of the solvent might occur during the measurement period. This dilution effect could not be measured continuously during the experiment, however the water content of the CO<sub>2</sub> absorption solvent was determined after every experiment. No dilution of the solvent could be detected with these measurements, which ensures that the solvent concentration in the second and third vessel remained constant during the vapour–liquid equilibrium measurements. Equilibrium and thus the end of the measurement was obtained when the CO<sub>2</sub> analyser showed constant CO<sub>2</sub> values of the gas phase for about 30 min. Then a liquid sample was taken from the third vessel and analysed to determine the actual CO<sub>2</sub> loading in the liquid. For the calculation of one point on the equilibrium curve the total pressure in the system is necessary. This pressure was measured in the third vessel with a PCE-P15 manometer.

The calculation of the CO<sub>2</sub> equilibrium partial pressure over the tested solvents from the experimental data was realized according to Ma'mun et al. (2005) and Jou et al. (1995). The obtained parameters from the experiment are the CO<sub>2</sub> solvent loading, the total pressure in vessel 3 and the CO<sub>2</sub> fraction of the dry and cooled gas stream measured by infrared detection. Assuming that only carbon dioxide, water and nitrogen are present in the system, the total pressure in vessel 3 is the sum of the partial pressure of the specific gases:

$$p_{\text{tot}} = p_{\text{H}_2\text{O}} + p_{\text{CO}_2} + p_{\text{N}_2} \quad (1)$$

The ratio of CO<sub>2</sub> and N<sub>2</sub> can be measured with infrared detection of the dry gas stream. The partial pressure of water over a 30 w% MEA solution was obtained from literature (Flick, 1998; Jou et al., 1995). The partial pressure of water over the ionic liquid solution was determined experimentally. Therefore a glass flask was first cooled down below the freezing point of the solvent and then evacuated from air. After adjusting a certain temperature, the measured pressure over the ionic liquid solution is equal to the partial pressure of water because the vapour pressure of the pure ionic liquid is negligible per definition. The experiment was validated with pure water and compared with the vapour pressure curve from literature (Flick, 1998). The partial pressure of water over the ionic liquid solution was measured between 40 °C and 120 °C. The results were checked with the boiling point of the ionic liquid solution at various pressures and showed a fairly good agreement.

Back calculated to the conditions in vessel 3, the partial pressure of CO<sub>2</sub> can be determined from the known values according to Eq. (2):

$$p_{\text{CO}_2} = (p_{\text{tot}} - p_{\text{H}_2\text{O}}) \cdot y_{\text{CO}_2} \quad (2)$$

The CO<sub>2</sub> solvent loading of the MEA solution was determined with a volumetric method by adding hydrochloric acid (HCl) and

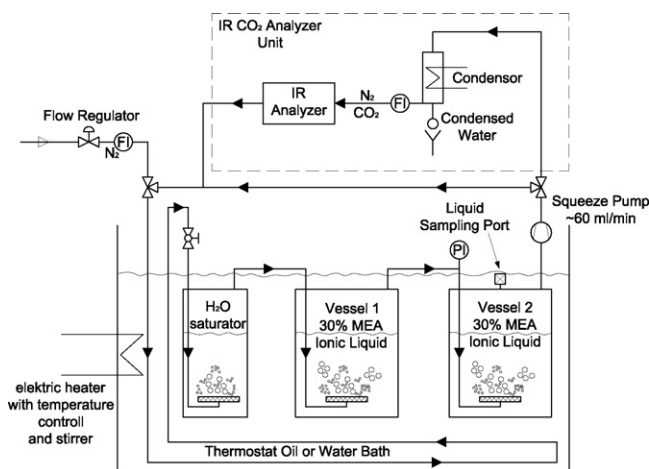


Fig. 2. Vapour–liquid equilibrium apparatus.

**Table 1**Comparison of selected ionic liquids with 30 w% aqueous MEA and K<sub>2</sub>CO<sub>3</sub> solution.

Solvent	Pressure difference between 25 °C and 80 °C	Equilibrium pressure at 25 °C	Equilibrium pressure at 80 °C	Time until equilibrium was reached at 25 °C	Time until equilibrium was reached at 80 °C
1 30 w% MEA in water	238	−676	−438	250	150
2 30 w% K <sub>2</sub> CO <sub>3</sub> in water	302	−645	−343	5000–7000	1800
3 IL 1 pure	323	−446	−122	2500–3700	1600–3800
4 IL 2 pure	324	−419	−96	2000–4000	1000
5 IL 3 pure	364	−490	−126	2400–5000	2000
6 75 w% IL 4 in water	208	−677	−469	1600	1100
7 42 w% IL 5 in water	188	−683	−495	3500	700
8 28 w% IL 6 in water	358	−643	−285	7000	1250
9 43 w% IL 7 in water	240	−610	−370	3400	900
10 48 w% IL 8 in water	211	−691	−480	1600	400

measuring the evolved volume of CO<sub>2</sub>. This method is based on a procedure outlined by the Association of Official Analytical Chemists (Burns, 1995). Due to the properties of the used ionic liquid, the determination of the dissolved CO<sub>2</sub> was possible with standard acid–base titration. This titration was performed with a Metrohm 794 Basic Titrimo.

### 3. Results and analyses

#### 3.1. Screening experiments

In the screening experiments 80 different ionic liquids and blends of ionic liquids were studied. The main goal was to characterize the CO<sub>2</sub> absorption performance of different ionic liquids and to get basic results about the kinetics. The absorption performance is proportional to the reached low-pressure in the glass flask. For a high capture performance more CO<sub>2</sub> is absorbed into the solvent and consequently the pressure in the glass flask decreases to a lower value. Due to the fact that post-combustion CO<sub>2</sub> capture is a reversible process using absorption and desorption, the changing of the CO<sub>2</sub> absorption performance with temperature is also important. Therefore all the screening experiments were performed at 25 °C and 80 °C to get an indication about the impact of temperature on the CO<sub>2</sub> absorption. Another important factor, the absorption kinetics, can also be measured qualitatively with this apparatus. The time until a constant pressure was reached is directly linked with the absorption kinetics. The quicker a constant pressure level is reached the faster is the absorption.

The basis of the screening tests evaluation was:

- equilibrium pressure at 25 °C and 80 °C as a measure of the CO<sub>2</sub> absorption performance;
- difference between the equilibrium pressures at 25 °C and 80 °C to get an indication about the temperature dependence of the CO<sub>2</sub> absorption;
- time until the equilibrium pressure was reached to qualitatively validate the absorption kinetics.

Monoethanolamine (C<sub>2</sub>H<sub>7</sub>NO) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), both as a 30 w% solution in water, were used as the reference solvents because they have been proven in various full scale CO<sub>2</sub> capture units and other gas treating applications. The reason for selecting these solvents for use as references was that MEA has relatively fast CO<sub>2</sub> absorption kinetics, whereas K<sub>2</sub>CO<sub>3</sub> is considered to have too slow kinetics without a promoter. Consequently, the absorption kinetics for an ionic liquid has to be at least faster as K<sub>2</sub>CO<sub>3</sub> for it to be a potential candidate for application in the power generating industry.

Results of the screening tests for several ionic liquids are shown in Table 1.

It is obvious from Table 1 that the absorption kinetics of pure ionic liquids was observed to be much slower than that of MEA. Additionally the reached equilibrium pressure and therefore the amount of absorbed CO<sub>2</sub> was lower than that of both reference solvents. By far the biggest problem of the pure ionic liquids is the high viscosity ranging up to 1000 mPa s at 25 °C, compared to ~2.5 mPa s for 30 w% MEA (Flick, 1998) or ~2.2 mPa s for 30 w% K<sub>2</sub>CO<sub>3</sub> solution (Kohl and Nielsen, 1997). For all screened pure ionic liquids the viscosity was high. Hence, a further use as an absorption solvent is not recommendable. To overcome this problem, water was used to decrease the viscosity. The addition of water to the ionic liquid solution can be directly used as stripping steam in the desorber to enhance the solvent regeneration performance. However, not every ionic liquid is soluble in water, which further decreases the number of possible candidates. The blends of certain ionic liquids with water as an additive (see Table 1 Nos. 6–10) showed better results compared to the pure ILs considering the absorption kinetics and the reached equilibrium pressure. Several of these had comparable CO<sub>2</sub> capture capability with 30 w% MEA solution as suggested by the equilibrium pressure and the pressure difference between 25 °C and 80 °C. All diluted ILs show lower absorption kinetics compared to MEA solution but were faster than the K<sub>2</sub>CO<sub>3</sub> solution. By increasing the temperature the gap of the absorption rate between the ionic liquid and MEA solutions gets smaller. Considering all three important performance indicators, 48 w% IL 8 in water was considered the best performing and was

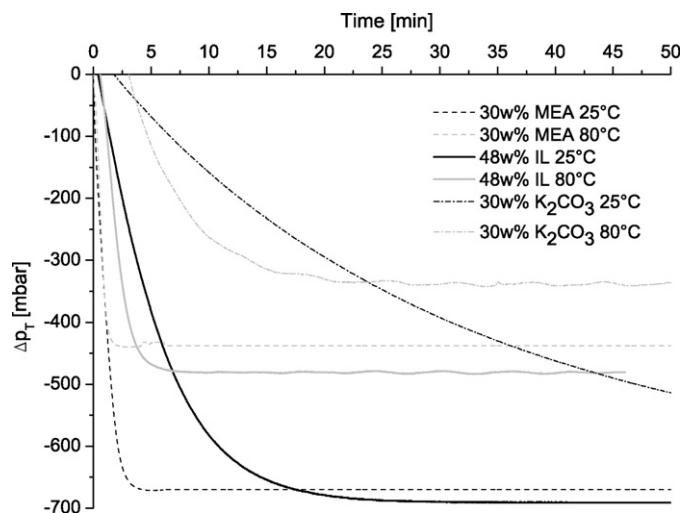


Fig. 3. Screening results of selected ionic liquid and reference solvents.

synthesized for further tests in a larger amount. In Fig. 3 the experimental results for IL 8, MEA and  $K_2CO_3$  solutions are presented as the pressure decrease versus the time.

The time required to achieve the equilibrium pressure was longer for the IL solvent than the MEA solvent. This implies slower  $CO_2$  absorption reaction kinetics. Although the absorption kinetics of the selected ionic liquid blend was slower than that of MEA, it was much faster than the  $K_2CO_3$  solution. The comparative difference with MEA solution decreases with increasing temperature, leading to a relatively small difference at 80 °C. The total amount of absorbed  $CO_2$  by the IL solution was similar to that of the MEA solution, in fact it was slightly higher at 80 °C. From the screening experiments it can be deduced that the ionic liquid blend is comparable to the MEA solution considering only the total absorption of  $CO_2$  and the impact of temperature on the absorption of  $CO_2$ . For the absorption kinetics the ionic liquid blend had still disadvantages when compared to MEA solution.

To increase the proportion of active solvent with consideration of the viscosity, the water content of ionic liquid 8 was decreased to 40%. This 60 w% ionic liquid solution was used for all subsequent measurements and for the calculation of the energy demand for solvent regeneration. The viscosity of the ionic liquid blend, measured using a Brookfield DV-III Ultra Programmabel Rheometer, was  $\sim 60$  mPa s at 25 °C, decreasing to  $\sim 20$  mPa s at 50 °C. In the aqueous ionic liquid solution the concentration of the active solvent was double of the MEA solution. Based on the results of the screening experiments, vapour–liquid equilibrium measurements were necessary to determine the equilibrium curve between  $CO_2$  and the 60 w% ionic liquid blend.

### 3.2. Vapour–liquid equilibrium measurements

A limitation of the experimental setup, shown in Fig. 2, was that the measurement of the vapour–liquid equilibrium was only possible at temperatures below the atmospheric boiling point of the investigated mixtures. To validate the equilibrium apparatus and measurement technique, VLE measurements of the 30 w% MEA solution were compared with data published by Jou et al. (1995). The boiling point of 30 w% MEA at atmospheric conditions is approximately 102 °C (Flick, 1998; Jou et al., 1995). Therefore reference VLE measurements were performed at 60 °C and 80 °C. As the boiling point of the ionic liquid–water solvent was approximately 120 °C, hence the measurements of the equilibrium curves were between 40 °C and 110 °C.

Fig. 4 is a comparison of the experimental results with the data published by Jou et al. (1995) at 60 °C and 80 °C. At both temperatures there is a relatively close correlation, which validates the experimental apparatus.

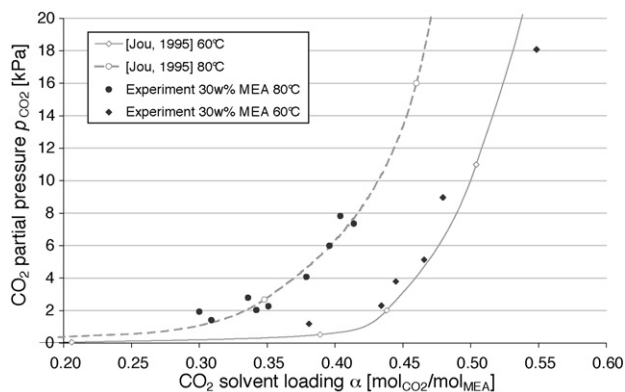


Fig. 4. Comparison of  $CO_2$ –aqueous 30 w% MEA solution equilibrium data at 60 °C and 80 °C.

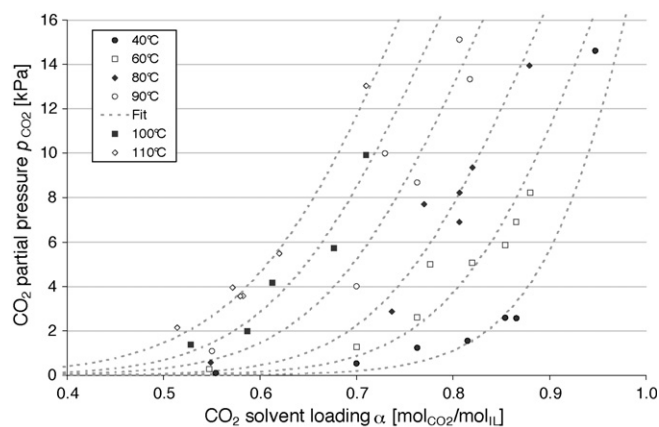


Fig. 5. Vapour–liquid equilibrium curves between 40 °C and 110 °C of the 60 w% ionic liquid solution.

Due to the low partial pressure of  $CO_2$  at lower temperatures, measurements below 40 °C cannot be made accurately using this technique. In the reference process for  $CO_2$  capture the temperature for absorption is typically 40 °C. Therefore this temperature was used as the lowest temperature for the vapour–liquid equilibrium measurement experiments. The experimental results of the vapour–liquid equilibrium measurements for the 60 w% IL solvent between 40 °C and 110 °C are shown in Fig. 5.

The trend of the vapour–liquid equilibrium curves is similar to those of the MEA based system. Hence, the obtained discrete measured points were fitted with exponential functions in order to get the equilibrium curves. These fitted curves show a fairly good correlation with the measured data and also the temperature dependence is conclusive. The trends observed of the equilibrium curves of the selected ionic liquid solvent were similar to that of the reference MEA solution. Notably the solvent loading is much higher than the reference solution, evident from the comparison of the equilibrium curves of MEA in Fig. 4 with those of the ionic liquid presented in Fig. 5 for a certain  $CO_2$  partial pressure and temperature. Based on these measurements, the theoretical energy consumption in the stripper with consideration of the enthalpy of absorption was determined.

### 3.3. Enthalpy of absorption

The enthalpy of absorption is a fundamental value for the estimation of the energy demand for  $CO_2$  capture. It consists of the enthalpy of  $CO_2$  dissolution ( $CO_{2,g} - CO_{2,l}$ ) and the reaction between the dissolved  $CO_2$  and the absorption solvent (chemical binding). Both contributions are exothermic and the heat of absorption is released in the absorber. Neglecting the temperature dependency the same amount of energy has to be supplied to the stripper in order to release the  $CO_2$  from the loaded absorption solvent. Regeneration of the loaded solvent is the major energy requirement of the  $CO_2$  capture process, thus the enthalpy of absorption is directly linked with the energy demand of the stripper.

The enthalpy of absorption can either be measured experimentally, which was reported for MEA by Carson et al. (2000), Kim and Svendsen (2007) and Mathonat et al. (1998) or direct calculated from vapour–liquid equilibrium data using the van't Hoff equation, as reported for methyldiethanolamine (MDEA) by Ma'mun et al. (2005). Kim et al. (2009) and Kim and Svendsen (2007) discussed the disadvantages of this simplified method in detail.

Anthony et al. (2001), Cadena et al. (2004), Hou and Baltus (2007) and Wasserscheid and Welton (2008) used this approach for characterizing ionic liquids. Considering the effect of tempera-

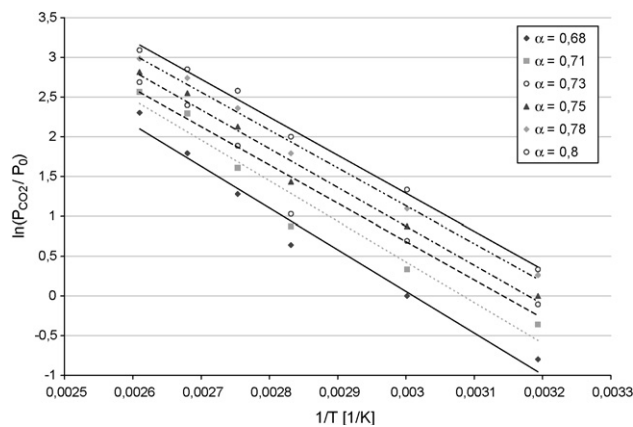


Fig. 6. Calculation of the enthalpy of absorption.

Table 2  
Process parameters for the baseline MEA process.

CO <sub>2</sub> fraction in flue gas	13.3 (vol.%)
CO <sub>2</sub> capture rate	90 (%)
MEA concentration	30 (w%)
Temperature absorber	35 (°C)
Temperature desorber	120 (°C)
CO <sub>2</sub> lean loading	0.242 (mol <sub>CO2</sub> /mol <sub>MEA</sub> )
CO <sub>2</sub> rich loading (50% regeneration)	0.484 (mol <sub>CO2</sub> /mol <sub>MEA</sub> )

ture on the gas solubility the van't Hoff equation can be expressed as:

$$\Delta H_{\text{Abs}} = R \cdot \left( \frac{\partial \ln p_{\text{CO}_2}}{\partial (1/T)} \right)_{\alpha} \quad (3)$$

Using Eq. (3) the enthalpy of absorption can be calculated directly from the vapour–liquid equilibrium curves at constant CO<sub>2</sub> solvent loading  $\alpha$ . The calculation from the equilibrium curve requires the assumption that the enthalpy of absorption is independent of the temperature. This is in fact not a correct assumption. However, for a basic comparison between the MEA and an ionic liquid based solvent, the temperature dependence can be neglected. To improve the validity of the calculation the enthalpy of absorption was determined for six different solution loadings between 0.68 and 0.8 mol<sub>CO2</sub>/mol<sub>IL</sub>. This implies that the enthalpy of absorption was calculated separately for six different solvent loadings in the mentioned region. This region was picked because in this area the fit of the equilibrium curves between 40 °C and 110 °C is still near the experimental measured points. Looking at lower solvent loadings would increase the uncertainty of low temperatures, because the CO<sub>2</sub> partial pressure is too low to measure. Conversely at higher solvent loadings the equilibrium partial pressure at higher temperatures is far out of the experimental measured range, which also increases the inaccuracy. Based on Eq. (3), the obtained

Table 3  
Comparison of the energy demand for stripping.

Process parameters	Literature [Abu-Zahra et al., 2007]	Present work	Deviation
	[GJ/ton <sub>CO2</sub> ]		
Baseline scenario	3.89	3.75	–3.60
Increasing MEA concentration to 40%	3.5	3.56	1.71
Increasing lean loading to 0.32 mol <sub>CO2</sub> /mol <sub>MEA</sub>	3.45	3.25	–5.80
Decreasing temperature to 108 °C–pressure to 0.9 bar	4.87	5.04	3.49
Decreasing temperature to 114 °C–pressure to 1.2 bar	4.24	4.14	–2.36
Average deviation			–1.31

Table 4  
Process parameters for IL–MEA comparison.

CO <sub>2</sub> fraction in flue gas	13.3 (vol.%)
CO <sub>2</sub> capture rate	90 (%)
IL concentration	60 (w%)
MEA concentration	30 (w%)
Temperature absorber	40 (°C)
Temperature desorber	110 (°C)
Gas flow rate	1,000,000 (Nm <sup>3</sup> /h)

graphical results are shown in Fig. 6 where the enthalpy of absorption can directly be calculated from the slope of the linear trend lines multiplied with the universal gas constant.

For the used ionic liquid solution, the enthalpy of absorption within a 95% confidence interval was calculated to be:

$$\Delta H_{\text{Abs}} = 41.1 \pm 3.2 \text{ kJ/mol}_{\text{IL}}$$

The enthalpy of absorption for the MEA solvent is dependent on the CO<sub>2</sub> solvent loading and the temperature, and at room temperature is reported to be approximately 82 kJ/mol<sub>MEA</sub> (Carson et al., 2000). This agrees with the simplified calculation using the van't Hoff equation where an enthalpy of absorption of 80.5 kJ/mol was calculated for MEA solvent using the VLE data of Jou et al. (1995). According to this, the enthalpy of absorption for the ionic liquid solvent is only half of the MEA solvent. Lowering the enthalpy of absorption might be one of the suggested options to reduce the energy demand for CO<sub>2</sub> capture (Davidson, 2007).

### 3.4. Energy demand for stripping

Using the experimentally obtained vapour–liquid equilibrium curve and the calculated enthalpy of absorption, the total energy demand for supplying the stripping energy in the desorber can be estimated. The following calculation method was based on the work of Draxler et al. (2005) using Mathematica 7.0. It was originally used to determine the energy demand of a hypothetical amine for CO<sub>2</sub> absorption. The work by Draxler et al. (2005) was modified and supplemented by the activity coefficient model of Bromley (Bromley, 1973; Zemaitis, 1986), to simulate the CO<sub>2</sub> absorption with 30 w% MEA as a solvent. To ensure the accuracy of the calculation methodology, the energy demand of the baseline MEA process defined by Abu-Zahra et al. (2007) was calculated. The main process parameters are shown in Table 2.

Using this baseline process some of the parameters were adjusted, such as the lean loading, decreasing of temperature and pressure and increasing of the MEA concentration and the energy demands were re-calculated. All results were compared with the AspenPlus<sup>®</sup> modelling of Abu-Zahra et al. (2007) (see Table 3).

It can be seen, from the data presented in Table 3, that the calculation of the energy demand closely correlates with the values of the AspenPlus<sup>®</sup> simulation reported by Abu-Zahra et al. (2007). The mean deviation is only 1.3%, suggesting very good agreement. This comparison validates the calculation routine and that the

**Table 5**  
Comparison of the energy demand of ionic liquid and MEA solutions.

	60 w% ionic liquid in water		30 w% MEA in water	
	Equilibrium data from experiment		Bromley activity coefficient model	
Stages absorption	2	2	2	2
Stages desorption	4	8	4	8
Lean solvent loading [mol <sub>CO<sub>2</sub></sub> /mol <sub>solvent</sub> ]	0.65	0.68	0.242	0.242
Rich solvent loading [mol <sub>CO<sub>2</sub></sub> /mol <sub>solvent</sub> ]	0.93	0.93	0.56	0.56
Heat of absorption $\Delta H_{Abs}$ [kJ/mol <sub>CO<sub>2</sub></sub> ]	41.1	41.1	82	82
Cooling Abs/heating Des [MW]	61	61	119	119
Specific solvent flow rate [m <sup>3</sup> /ton <sub>CO<sub>2</sub></sub> ]	36	40	14.5	14.5
Energy demand for CO <sub>2</sub> stripping [GJ/ton <sub>CO<sub>2</sub></sub> ]	4.18	3.43	4.78	4.12

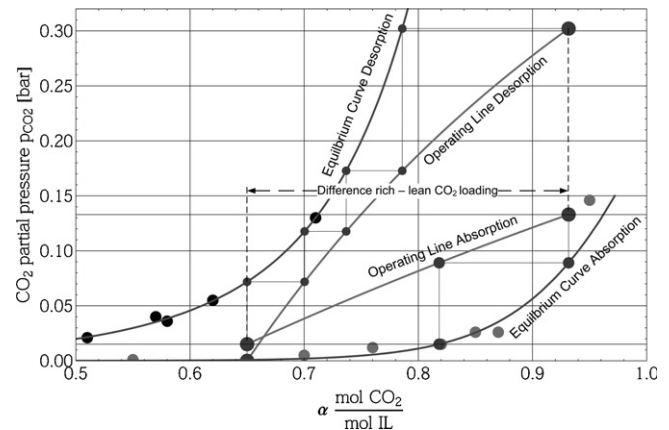
energy demand for the ionic liquid solution can similarly be estimated using this calculation routine.

For the comparison of the 60 w% ionic liquid and the 30 w% MEA solution the process parameters were set according to the vapour–liquid equilibrium measurements of the ionic liquid solution and shown in Table 4.

By keeping the basic parameters constant for both simulations, the results obtained for the required energy in the stripper were more comparable. This includes the absorption and the desorption temperature, the stages of absorption, the concentration of the active solvent, the CO<sub>2</sub> concentration in the flue gas, the gas flow rate and the capture rate. For the absorption of CO<sub>2</sub> an operating temperature of 40 °C was used, as typically desired for post-combustion capture. The desorption temperature of 110 °C was used that the experimental results from the earlier vapour–liquid equilibrium experiments could be used. The differences between the baseline scenario used for the validation of the calculation routine (see Table 2) and the actual MEA calculations for the comparison with the ionic liquid shown in Table 5, are mainly the absorption and desorption temperatures and the number of absorption stages. For comparison of the MEA and ionic liquid data the desorption temperature was decreased from 120 °C to 110 °C. However, the number of absorption stages was increased to two. At the baseline scenario of Abu-Zahra et al. (2007) the CO<sub>2</sub> loading of the rich MEA solution was set to 0.48 mol<sub>CO<sub>2</sub></sub>/mol<sub>MEA</sub> (equivalent to one absorption stage). These two modifications have opposing impacts. Decreasing the desorption temperature increases the energy demand and conversely, increasing the number of absorption stages decrease the energy demand. According to Table 5 the results are comparable with the baseline scenario and similar to the results available in literature (~4.2 GJ/ton<sub>CO<sub>2</sub></sub>).

The energy demand calculations were performed for different process parameters, namely by varying the stages of desorption and the lean solvent loading of the ionic liquid solution. The results for two different process variations, with either 4 or 8 desorption stages are presented in Table 5. For the 30 w% MEA, the lean solvent loading was set at 0.242 mol<sub>CO<sub>2</sub></sub>/mol<sub>MEA</sub> similar to Abu-Zahra et al. (2007). As a preliminary optimisation of the energy requirements for the 60 w% ionic liquid the lean solvent loading was varied between 0.6 and 0.7 mol<sub>CO<sub>2</sub></sub>/mol<sub>IL</sub>.

Comparison of the estimated energy demand of the 60 w% ionic liquid and 30 w% MEA solution suggested slightly better performance for the ionic liquid at the selected constant process parameters. Depending on the lean solvent loading and the number of desorption stages, the estimated energy demand varies between 3.43 GJ/ton<sub>CO<sub>2</sub></sub> and 4.18 GJ/ton<sub>CO<sub>2</sub></sub> for the ionic liquid solution and 4.12 GJ/ton<sub>CO<sub>2</sub></sub> to 4.78 GJ/ton<sub>CO<sub>2</sub></sub> for the MEA solution. In terms of the specific solvent flow rate, MEA shows better results mainly because of the higher cycling capacity of the solvent, expressed as the difference between rich and lean CO<sub>2</sub> loading. Achieving a higher cycling capacity leads to a lower required



**Fig. 7.** Operating lines for the absorption process at 40 °C and the desorption process at 110 °C of the 60 w% ionic liquid solution.

solvent circulation flow rate, as more CO<sub>2</sub> can be captured per unit volume of solvent. This difference is due to the high heat of absorption (see Eq. (3)). Hence, the higher specific flow rate of the ionic liquid solution required to achieve comparable performance, leads to the requirement for bigger pumps, heat exchanger, pipes and other internals. In this respect, the MEA solution has a definite advantage in comparison to the ionic liquid solution. Hence, a higher heat of absorption does not necessarily imply a higher energy demand for solvent regeneration. The calculated specific solvent flow rate of the MEA solution is lower than the values reported by Abu-Zahra et al. (2007). This is mainly because of the higher solvent loading of the CO<sub>2</sub> rich flow, in this case caused by a two-stage absorption and the assumption that equilibrium is nearly obtained.

Presented in Fig. 7 is a typical graph for the absorption and the desorption process of the 60 w% ionic liquid with the inclusion of the equilibrium and the operating lines.

The illustrated figure, Fig. 7, is identical with the first column presented in Table 5 with a total energy demand of 4.18 GJ/ton<sub>CO<sub>2</sub></sub> for the CO<sub>2</sub> capture. The points indicated on or near the equilibrium curve are the measured points from the earlier vapour–liquid equilibrium experiments. The slope of the operating lines is equal to the liquid-to-gas ratio for the absorption or gas-to-steam ratio for stripping. Based on these ratios, the solvent circulation rate and steam consumption can be calculated, from this it is possible to estimate the total energy consumption for stripping (see Table 5).

#### 4. Discussion and conclusion

The main goal of the present work was to compare the performance of a 30 w% MEA solution and a task specific ionic liquid as a potential solvent for post-combustion CO<sub>2</sub> capture from flue gases. The required energy demand for stripping the absorbed

CO<sub>2</sub> reflects the performance of an absorption solvent and is the characteristic parameter for validating the total costs and efficiency reduction of the power plant. In a detailed screening process, 80 different ionic liquids and blends of ionic liquids were tested and their CO<sub>2</sub> absorption performance was determined. Even if the operating conditions in the screening tests do not reflect real conditions in the application, these experiments give a good estimation of the absorption capability and kinetics of a liquid. From these tests it was obvious that the viscosity of pure ionic liquids is too high, hence a use as CO<sub>2</sub> absorption solvents is not possible. After lowering the viscosity to a proper value by adding water, comparable screening results were obtained. Based on these tests, the most promising ionic liquid blend with a concentration of 60 w% in water was selected for further use. By measuring the vapour–liquid equilibrium curve, calculating the enthalpy of absorption and finally determining the energy requirement in the stripper, a basic comparison between the 30 w% MEA and the 60 w% ionic liquid solutions was possible. With the developed calculation procedure a very detailed optimisation of the CO<sub>2</sub> absorption process is not possible, but for basic valuations it is applicable. It must be emphasized that this comparison of the used IL solution with the MEA solution was done for same absorption and desorption conditions and not for optimum conditions for each solvent. All calculations are based on an isothermal temperature profile and plug flow for the absorber and desorber. Based on these assumptions the calculation routine works with energy and mass balance, with consideration of equilibrium constants, rate constants and activity models for every reaction.

The important goal was to compare whether the selected ionic liquid solution is in the same range as the reference MEA solution concerning the energy demand. This calculation is the basis for further work on ionic liquids used for CO<sub>2</sub> capture. The developed calculation procedure is relying on some simplifications. Kinetic effects of the CO<sub>2</sub> absorption are not considered in this work. All calculations are based on equilibrium conditions. In the energy calculations two theoretical stages in the absorber were applied, which ensures that the equilibrium loading is nearly obtained. For a real application kinetic effects have major impact on the height of the column. This effect will be investigated during further pilot plant testing. The determination of the enthalpy of absorption using the van't Hoff equation is also a simplification and neglects its temperature dependence. In the literature of ionic liquids this simplification is widely used to investigate their enthalpy of absorption. Other important parameters for the validation of the overall CO<sub>2</sub> capture costs, like corrosion and viscosity problems were partly investigated but there is still more work to do.

From this work it can be concluded that ionic liquids are an interesting and promising option for post-combustion CO<sub>2</sub> capture. For full scale industrial application some technical and economical problems have to be solved. Especially the high viscosity is one of the major technical barriers today. The viscosity will effect the distribution of the ionic liquids in the columns and will increase the energy input for pumping. Despite the higher expected pumping costs, the major part of the costs results from the regeneration of the solvent in the desorber, which has the highest optimisation potential. Considering economics, the price of the solvent is the major issue. Since ionic liquids are only produced in small amounts for laboratory testing, the actual price is high but will decrease if a task specific ionic liquid is produced in industrial quantities. It is obvious that the price of the solvent is very important for the investment costs but if ionic liquids show significant cost reduction benefits during operation, this should overcome the higher investment. The research area of ionic liquids is relatively young and a lot of effects and problems are not investigated or solved yet. With more research the application for CO<sub>2</sub> capture can be more attractive in the near future.

## 5. Outlook

Considering this project, pilot plant test directly at a hard coal fired power plant will be performed with the investigated ionic liquid in the end of 2009. After this test period a comparison under real flue gas conditions and an energetic balance of the whole capture unit will be possible. This should also lead to answers about the long term stability, degradation, corrosion and other process related parameters.

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