

Screening of strong bicarbonate forming solvents for CO₂ capture

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Highlight

- 15 commercially strong bicarbonate forming solvents were tested
- 15 dissociation constants of strong bicarbonate forming solvents were reported
- Higher pKa value shows faster absorption rate and higher cyclic capacity
- 2-PPE and 1-(2HE)PRLD shows better performance than that of 30 mass% MEA

Abstract

15 bicarbonate forming solvents were tested and compared to 30 mass % MEA using a screening apparatus. Additionally the pKa values of each of the solvents at room temperature were measured. The overall evaluation was based on screening tests allowing estimation of cyclic capacity, pKa measurements and operative behavior of the system (foaming, high viscosity, precipitation). Based on the overall evaluation, two solvents, 2-PPE and 1-(2HE)PRLD, were chosen for further characterization.

The solvent concentration was optimized using the screening setup. The optimal solvent concentrations found were 50 mass % 2-PPE, and 40 mass % 1-(2HE)PRLD.

1. Introduction

Absorption using chemical absorbents has been widely used in natural gas acid gas removal for over 60 years. The best absorbents are the ones with high net cyclic capacity (high absorption and desorption rates are necessary), fast reaction/absorption rates for CO₂, low heat of reaction, high chemical stability, low vapor pressure and low corrosiveness. Several different types of amines have been used such as alkanolamines and polyamines. Alkanolamines are widely used as solvents for post-combustion CO₂-capture because the compounds have two functional groups which in combination give an increase of CO₂ solubility in water and thus higher absorption of CO₂ (Kohl and Nielsen, 1997). The most common alkanolamines studied for this purpose are 2-ethanolamine (MEA, CAS 141-43-5), diethanolamine (DEA, CAS 111-42-2), *N*-methyldiethanol-amine (MDEA, CAS 105-59-9), 2-amino-2-methylpropanol (AMP, CAS 124-68-5) and blends of these. Of the polyamines, piperazine has gotten increased attention during the last five years (Chen et al., 2013; Freeman et al., 2010; Nielsen et al., 2013).

In chemical absorption, CO₂ is bound as bicarbonate or carbamate. The formation reaction for the bicarbonate is given in reaction R₁ and for the carbamate in reaction R₂:



Where R_3N can be any amine component.



The base strength of the amine (R₃) determines the extent of bicarbonate formation of an amine:



Carbamate formation depends on the stability of the carbamate, which is expressed by the equilibrium given in reaction R₄, and the base strength (R₃).



The CO₂ absorption capacity is lower for amines forming stable carbamates since two amine molecules participate in the reaction with one CO₂ molecule (see reaction R₂). CO₂ absorption could be increased by hydrolysis of the carbamate. The degree of hydrolysis depends on amine concentration, pH of the solution and chemical stability of the carbamate (Caplow, 1968; Chakraborty et al., 1988; Ewing et al., 1980; Hook, 1997)

Carbamate stabilities and basicity of the amines are the two main equilibrium constants which to a large extent determine how a solvent will perform in CO₂ absorption (da Silva, 2011). A solution with higher bicarbonate ratio is expected to have higher CO₂ capacity, faster desorption rate and to give a leaner solution (Hook, 1997; Sartori and Savage, 1983).

Over the years several studies regarding the influence of amine structure on capacity for CO₂ capture as well as CO₂ absorption and desorption rate and carbamate stability have been performed (Bonenfant et al., 2003; Chakraborty et al., 1986; Chowdhury et al., 2009; Chowdhury et al., 2011; Chowdhury et al., 2013a; Chowdhury et al., 2013b; da Silva and Svendsen, 2006, 2007; Fernandes et al., 2012; Robinson et al., 2012; Sartori and Savage, 1983; Singh et al., 2009; Yang et al., 2012). The studies have discussed different factors as basicity, the pH, of the solution polarity and steric hindrance/structural characteristics of the compound (Bonenfant et al., 2003; Sartori and Savage, 1983). However, it is also important to include electron density, hydrogen bonding and solvation since these systems have an abundance of amino lone pair, hydroxyl group ions and water (Yamada et al., 2013). For example, high absorption capacity has been observed for amine formation unstable carbamate. Several research groups agrees that substituents at the α -carbon creates a carbamate (Chakraborty et al., 1986; Chakraborty et al., 1988; McCann et al., 2011; Sartori and Savage, 1983), but this instability has been explained using different terms. Sartori et al. suggest that the instability is caused by the steric hindrance these substituent introduces while Chakraborty et al. discussed the change in electron density caused by the substituents which, in this particular case, was expected to reduce the charge at the nitrogen atom

making it more susceptible to hydrolysis by the hydroxide in the solution (Chakraborty et al., 1986; Chakraborty et al., 1988; Singh et al., 2007).

Another important factor when selecting amine based absorbents for acid gas removal is acid and base strength represented respectively by the dissociation constant (pKa) and the basicity. There have been several molecular modelling studies investigating basicity of solvents, pKa and temperature dependency of these factors (da Silva, 2005; da Silva and Svendsen, 2003; Gupta et al., 2012; Mergler et al., 2011; Yamada et al., 2010). Gas phase basicities are related to solution phase pKa by solvation free energies (Jackson et al., 2011) is important Gas-phase basicities from quantum mechanical calculations taking into account the hydrogen bonding in poly functional molecules (Bouchoux, 2007; Jackson et al., 2011; Karpas, 1992) are generally in good agreement with experimental data (da Silva, 2005). In the work by da Silva (da Silva, 2005), the alkanolamines (MEA, DEA, 3-amino-1-propanol) and 1,2-ethanediol which were tested deviated from experimental values. Overall, the basicity and pKa of molecules can be explained based on evaluation of electron density e.g. charge density/dispersal, electronegativity, polarizability, resonance, substituents, orbitals, and aromaticity. The electron density are related to field and resonance effect where field effects operate through space electrostatic interaction and resonance effect operate through the π -electrons of the system (Carey and Sundberg, 2000).

When evaluating the amine performance for CO₂ capture shows that there is a trade-off between factors e.g. steric hindrance increases capacity while absorption rate is reduced and several factors that has been considered in literature when explaining the behavior observed during testing: molecular level (electron density), solution perspective (e.g. hydrogen bonding) or as in many cases from steric hindrance perspective.

To further investigate changes in performance, 15 commercial, strong bicarbonate forming amines or amines interesting for correlating amine structure and solvent performance were tested in screening setup. The amines are given in Table 1. These amines were selected based on earlier experimental or modelling work conducted in several research environments e.g. RITE in Japan (Chowdhury et al., 2011; Chowdhury et al., 2013a; Chowdhury et al., 2013b; Goto et al., 2011a; Goto et al., 2011b),

CSIRO in Australia (Fernandes et al., 2012; Puxty et al., 2009), Twente University and Procede Group BV (Singh et al., 2007, 2009) and NTNU (da Silva, 2005, 2011; da Silva and Svendsen, 2003; Gupta et al., 2012).

The non-toxic amines with different structure (ring, straight chain, variation in carbon chain and substituents) studied are expected to influence e.g. the bicarbonate ratio and pKa were tested. The amines are listed in Table 1. Steric hindrance effect on tBAE, IPAE, 3QUI, TMP-OL are expected to have high bicarbonate formation, particularly in tBAE, PAE and IPAE where different alkyl groups as steric hindrance (R-group) for amino group attached. It was already reported that PAE, IPAE, tBAE, 2PPM and 2PPE showed similar absorption rate as for MEA and may have lower heat of reaction (Chowdhury et al., 2011; Chowdhury et al., 2013a). DMAH, DEA-1P, DEA-1,2-PD, 1-(2HE)PP and 1-(2HE)PRLD reported to have moderate absorption rate, but high absorption capacity (Chowdhury et al., 2009; Chowdhury et al., 2013a). TM-1,4-DAB and DEAE-EO showed moderate absorption rate and low absorption capacity (Chowdhury et al., 2009; Chowdhury et al., 2013a), however they have structural features of interest and are therefore tested. DEAE-EO with ether group and TM-1,4-DAB with longer carbon chain between the amine molecules, the longer chain between amine molecules in polyamines has shown to increase the bicarbonate formation (Singh et al., 2007). Different structural features are also studied, such as: influence extra carbon between amino and alcohol function (DEEA and DEA-1P), influence of extra OH group (DEA-1,2-PD and DEA-1P), placement of substituents in the piperidine ring and carbon chain length between amine and alcohol function (1-(2HE)PP, 2-PPE and 2-PPM) and different ring size (1-(2HE)PP and 1-(2HE)PRLD). All tested solvent candidates have two different amine groups, i.e. secondary and tertiary. Secondary amine has ability to form carbamate and bicarbonate. Ratio of carbamate to bicarbonate (Ciftja et al., 2014) must be very small for secondary amine to be considered as strong bicarbonate forming solvent. When carbamate formed is low, absorption rate mostly depends on the carbamate formation, hence the system will also have low absorption rate. MEA, DEA and DEEA were used as reference solutions.

2. Experimental Section

2.1. Chemicals

Commercially available chemicals/ amines used in this study are presented in Table 1 and without any further purification, 30 mass % amines in aqueous solutions were prepared by dissolving them into DI-water for screening experiment while for pKa measurement 0.01 mol of amines were dissolved in 1 kg DI-water. TMP-OL was observed to have water solubility issue hence 11 mass% solution was prepared for screening test. IPAE has low purity and results should be use with extreme care. A gravimetric procedure in the solution preparation was recorded with the MS6002S Scale (with an uncertainty $\pm 10^{-5} kg$).

Table 1. Chemicals used in this work

NO.	Chemical Name	Abbreviation	CAS No.	Formula	M (g/mol)	Phase*	Supplier	Purity (%min)
R1	Monoethanolamine	MEA	141-43-5	C ₂ H ₇ NO	61.08	Liquid	SA	99
R2	Diethanolamine	DEA	111-42-2	C ₄ H ₁₁ NO	105.14	Liquid	SA	98.5
R3	2-(Diethylamino)ethanol	DEEA	100-37-8	C ₆ H ₁₅ NO	117.19	Liquid	SA	99.5
1	2-(Isopropylamino)ethanol	IPAE	109-56-8	C ₅ H ₁₃ NO	103.16	Liquid	SA	70**
2	2-(Propylamino)ethanol	PAE	16369-21-4	C ₅ H ₁₃ NO	103.16	Liquid	SA	98
3	2-(tert-Butylamino)ethanol	tBAE	4620-70-6	C ₆ H ₁₅ NO	117.19	Solid	SA	99
4	2-Piperidinemethanol	2-PPM	3433-37-2	C ₆ H ₁₃ NO	115.17	Solid	SA	97
5	2-Piperidineethanol	2-PPE	1484-84-0	C ₇ H ₁₅ NO	129.20	Solid	SA	97
6	2,2,6,6-Tetramethyl-4-piperidinol	TMP-OL	2403-88-5	C ₉ H ₁₉ NO	157.25	Cristal	SA	98
7	Potassium Pipecolinic	KPIP	535-75-1	C ₆ H ₁₁ NO ₂	129.16	Powder	SA	98
8	3-Diethylamino-1-propanol	DEA-1P	622-93-5	C ₇ H ₁₇ NO	131.22	Liquid	SA	97
9	3-(Diethylamino)-1,2-propanediol	DEA-1,2-PD	621-56-7	C ₇ H ₁₇ NO ₂	147.22	Liquid	SA	98
10	N,N,N',N'-Tetramethyl-1,4-butanediamine	TM-1,4-DAB	111-51-3	C ₈ H ₂₀ N ₂	144.26	Liquid	SA	98
11	2-(2-Diethylaminoethoxy)ethanol	DEAE-EO	140-82-9	C ₈ H ₁₉ NO ₂	161.16	Liquid	TCl	98
12	6-Dimethylamino-1-hexanol	DMAH	1862-07-3	C ₈ H ₁₉ NO	155.17	Liquid	TCl	95
13	1-(2-Hydroxyethyl)pyrrolidine	1-(2HE)PRLD	2955-88-6	C ₆ H ₁₃ NO	115.17	Liquid	SA	97
14	1-(2-Hydroxyethyl)piperidine	1-(2HE)PP	3040-44-6	C ₇ H ₁₅ NO	129.20	Liquid	SA	99
15	3-Quinuclidinol	3QUI	1619-34-7	C ₇ H ₁₃ NO	127.18	Powder	SA	99
16	Carbon Dioxide	CO ₂	124-38-9	CO ₂	44.01	Gas	AGA	99.999
17	Nitrogen	N ₂	7727-37-9	N ₂	28.02	Gas	AGA	99.998
*) at ambient								
**) Impurity: 30% of N-isopropyl ethanolamine (N-Isopropyl-2-2'-iminodiethanol) CAS : 121-93-7								
SA = Sigma Aldrich TCl = Tokyo Chemical Industry								

2.2. Equipment and Procedures

Screening Apparatus:

The existing screening apparatus was used during the screening experiments (Aronu et al., 2010; Brüder et al., 2011; Hartono et al., 2014a; Ma'mun et al., 2007). The screening apparatus mimics an absorption (40°C and 95% CO₂ captured) and desorption (80°C and 90% CO₂ removal) processes in CO₂ capture plant and thus allows solvent performances estimation (rich/ lean loading and cyclic capacity) of each solvent compared to the reference solvent(s). In this work MEA, DEA and DEEA were used as reference solvents. Additionally information related to foaming, precipitation and possible discoloration upon CO₂ loading are gathered.

In this work a small (~150 cm³) jacketed glass reactor was used to reduce the solvent use and to better maintain a constant temperature during the experiments. About ~0.125 kg solvent was introduced into the reactor and Bronkhors® High-Tech mass flow controllers (MFC) of N₂ and CO₂ were used to control the composition of the feed gas (maximum flow of 1NL/min). To improve the liquid-gas contact, a magnetic stirrer at 450 rpm was used. All the gas was sent to a Fisher–Rosemount BINOS® 100 NDIR CO₂ analyzer. Screening equipment is shown in Figure 1.

Based on the logged data the amount of CO₂ absorbed can be calculated using equation:

$$Q_{CO_2} \left(\frac{mol CO_2}{s} \right) = n_{CO_2}^{in} - \frac{x_{CO_2}^{out} \cdot n_{N_2}^{in}}{1 - x_{CO_2}^{out}} \quad (1)$$

Where $n_{CO_2}^{in}$ and $n_{N_2}^{in}$ are the amounts of CO₂ and N₂ fed into the reactor, respectively and $x_{CO_2}^{out}$ is the volume % of CO₂ in the gas leaving the reactor. From this, the accumulated amount of CO₂ absorbed can then be integrated:

$$N_{CO_2} (mol CO_2) = \int_0^t Q_{CO_2} \cdot dt \quad (2)$$

The absorption and stripping rates can be calculated from:

$$r_{CO_2} \left(\frac{mol CO_2}{kg solution \cdot s} \right) = \frac{1}{W_S} \cdot Q_{CO_2} \quad (3)$$

Where W_S is the the amount of solvent in the reactor.

Finally cyclic capacity and loading can be estimated from the equations (4) and (5).

$$Q_{cyc} \left(\frac{mol CO_2}{kg solution} \right) = \alpha_{Rich} - \alpha_{Lean} \quad (4)$$

The rich and lean loadings required in the previous equation are calculated from the total amount of CO₂ absorbed (giving α_{Rich}) or from the total amount of CO₂ stripped (giving α_{Lean}) by dividing these with the total amount of solvent:

$$\alpha \left(\frac{\text{mol CO}_2}{\text{kg solution}} \right) = \frac{N_{CO_2}}{W_S} \quad (5)$$

$n_{CO_2}^{in}$, $n_{N_2}^{in}$ and $x_{CO_2}^{Out}$ were recorded from the Mass Flow controller and the CO₂ analyzer respectively, while the solvent amount (W_S) was recorded in the MS6002S Scale (with an uncertainty $\pm 10^{-5} \text{kg}$).

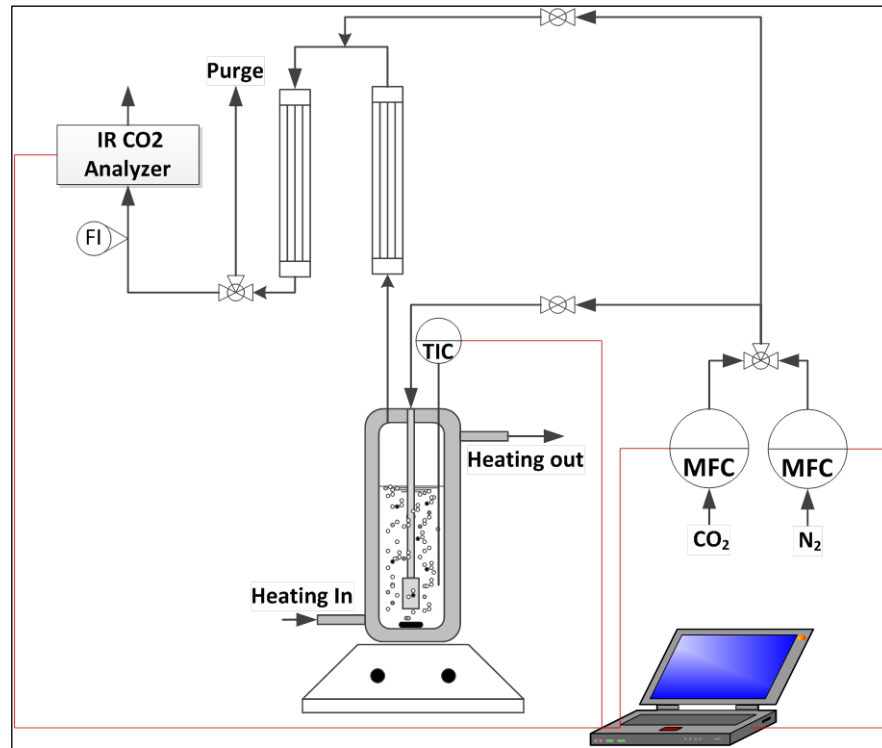


Figure 1: Screening Apparatus

Dissociation constant:

Amine reacts to any added acid in the system according to reaction (R₃) and the dissociation constant may then expressed as pK_a according to:

$$K_a = \frac{a_{Am} \cdot a_{H_3O^+}}{a_{AmH^+} \cdot a_{H_2O}} \quad (6)$$

This reaction can be observed in the pK_a determining apparatus (Figure 2). The set up (Kim et al., 2011) consists of a Mettler Toledo G20 compact titration unit with a pH-electrode DSC-115

(uncertainty ± 0.02 pH), temperature sensor DT100 (uncertainty ± 0.1 °C) and a heating water bath Julabo M4 unit. A jacketed glass reactor (100 ml volume) is connected to the heating circulator (temperature stability ± 0.1 °C). The glass pH-electrode is calibrated in advance at measuring temperature using buffer solutions traceable to the National Bureau of Standards (pH 4.01, 7.00, 9.21 and 11.0 from Mettler Toledo).

About 35 g of very dilute amine solution, concentration of 0.01 mol/kg H₂O, is titrated with 0.1 mol/l HCl solution. A dynamic equilibrium procedure provides an automatic adjustment of the amount HCl added into solution (minimum of 0.005 cm³/min and maximum of 0.3 cm³/min) to maintain a constant temperature (Hartono et al., 2014b). LabX 3.1 software provided by Mettler Toledo is used to calculate the pKa values as pH at half equivalence. At least two parallels experiments were performed. The pKa difference of the parallels was small, less than 0.1%.

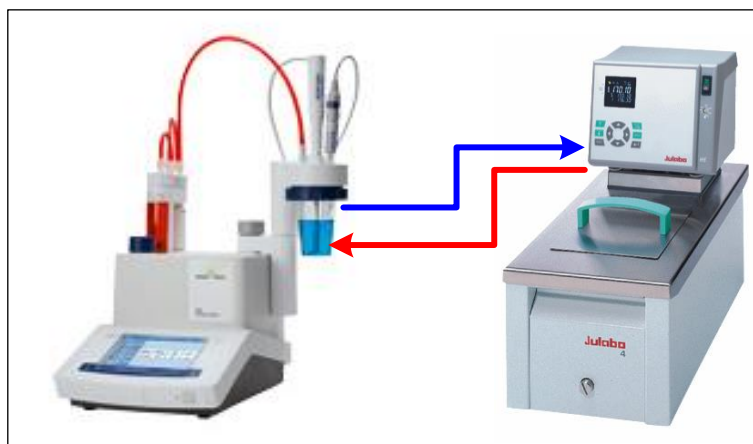


Figure 2: pKa determining Apparatus

3. Results and Discussion

3.1. Screening experiments

3.1.1. Secondary amines tested

In Table 2 the tested, seven secondary amines are listed and in Figure 3 the absorption and desorption curves are shown. In the table some general characteristics like foaming and color during screening

experiments are given. No precipitation, discoloration or high viscosity was observed. However, foaming was a major issue for IPAE, TMP-OL and tBAE. This is also clearly seen from the shape of the absorption curves in Figure 3. Based on the results, MEA derivate molecules which have tertiary or quaternary carbon attached to the amino group (i.e. IPAE and tBAE) tends to give more serious foaming issues than that attached in the secondary carbon, like PAE.

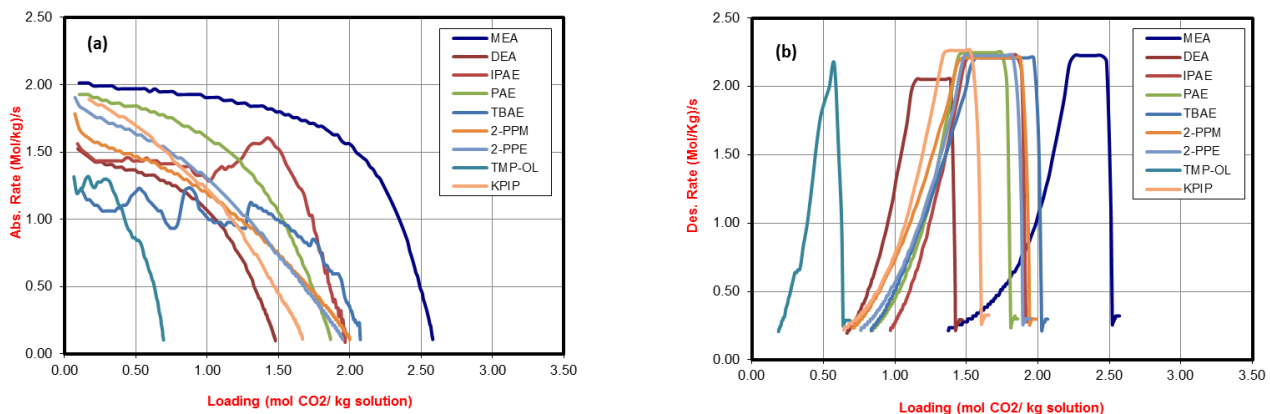
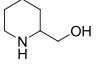
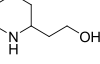
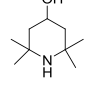
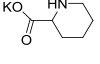


Figure 3. Absorption rate (a) and desorption rate (b) of secondary amine solvents as function of loading at 40°C and 80°C

Table 2. Characteristics of absorption and desorption at process conditions for secondary amines

No	Solvent		Characteristics	
	Name	Structure	Absorption	Desorption
1	IPAE	<chem>CC(C)NCCO</chem>	<ul style="list-style-type: none"> •Clear liquid •30 % impurity •DEA~Abs. Rate*<MEA •DEA<Rich loading<MEA •Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •DEA~Des. Rate**<MEA •DEA<Lean loading<MEA •Foaming issue •No discoloration
2	PAE	<chem>CCCNCCO</chem>	<ul style="list-style-type: none"> •Clear liquid •DEA<<Abs. Rate*<MEA •DEA<Rich loading<MEA •No foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •DEA~Des. Rate**<MEA •DEA<Lean loading<MEA •Foaming issue •No discoloration
3	tBAE	<chem>CC(C)(C)NCCO</chem>	<ul style="list-style-type: none"> •Light yellowish liquid •Abs. Rate*<DEA<MEA •DEA<Rich loading<MEA •Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Light yellowish liquid •Des. Rate**<DEA<MEA •DEA<Lean loading<MEA •Foaming issue •No discoloration

4	2-PPM		<ul style="list-style-type: none"> •Light yellowish liquid •DEA<Abs. Rate*<MEA •DEA<Rich loading<MEA •No foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Light yellowish liquid •Des. Rate**<DEA< MEA •DEA~Lean loading<MEA •No foaming issue •No discoloration 	
5	2-PPE		<ul style="list-style-type: none"> •Light yellowish liquid •DEA<<Abs. Rate*<MEA •DEA<Rich loading<MEA •No foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Light yellowish liquid •Des. Rate**<DEA< MEA •DEA<Lean loading<MEA •No foaming issue •No discoloration 	
6	TMP-OL		<ul style="list-style-type: none"> •Solubility issue •Light yellowish liquid •Abs. Rate*<DEA<MEA •Rich loading<DEA<MEA •Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Light yellowish liquid •Des. Rate**<<DEA< MEA •Lean loading<DEA< MEA •Foaming issue 	
7	KPIP		<ul style="list-style-type: none"> •Neutralized amino acid •Clear liquid •DEA<<Abs. Rate*<MEA •DEA<Rich loading< MEA •No Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •DEA~Des. Rate**<MEA •DEA~Lean loading<MEA •No foaming issue •No discoloration 	
		*Abs. Rate is estimated at lean loading		**Des. Rate is estimated at rich loading	

3.1.2. Tertiary amines

Eight different tertiary amine solvent candidates (5 linear carbons and 3 cyclic carbons) were tested in this work. The results can be seen in Figure 4 and summarized in Table 3. During absorption process, 6 solvent candidates showed visible foaming issue. The solvent candidates were: DEA-1P, DEA-1,2-PD, TM-1,4-DAB, DEAE-EO, 1-(2HE)PP and DMAH. Only 1-(2HE)PRLD and 3QUI did not have any foaming issues. For all solvents, the initial absorption rates as well as rich loading are lower than those of DEEA. TM-1,4-DAB reached higher rich loading than DEEA, but this is most likely due to enhancement caused by the foam. No precipitation and no discoloration were observed. During desorption process, all solvents except TM-1,4-DAB gave lower lean loading than that of DEEA. 3QUI solvent shows low desorption rate.

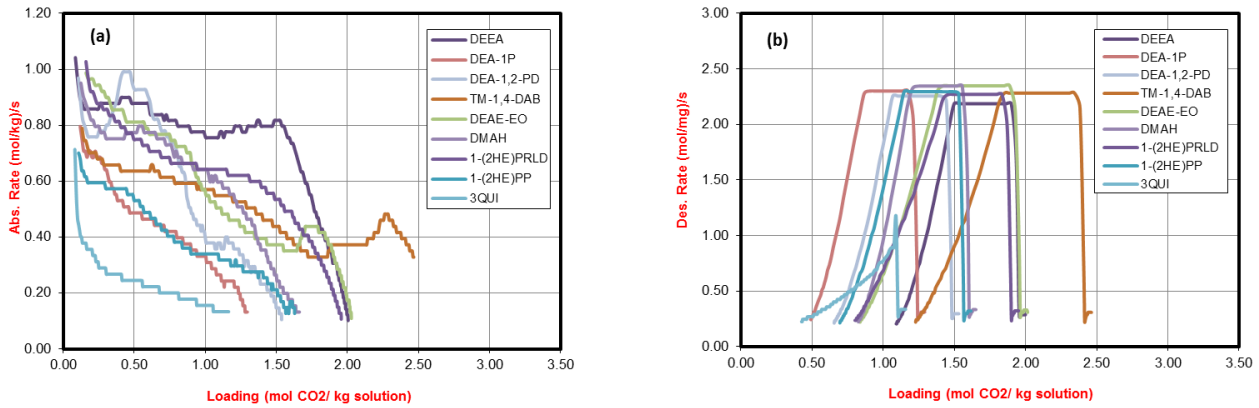




Figure 4. Absorption rate (a) and desorption rate (b) of secondary amine solvents as function of loading at 40°C and 80°C

Table 3. Characteristics of absorption and desorption at process conditions for tertiary amines

No	Solvent		Characteristics	
			Absorption	Desorption
1	DEA-1P	<chem>CCN(CC)CCO</chem>	<ul style="list-style-type: none"> •Dark yellowish liquid •Abs. Rate*<DEEA<<< MEA •DEEA<Rich loading<MEA •Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Dark yellowish liquid •DEEA<Des. Rate**<MEA •Lean loading<DEEA<MEA •Foaming issue
2	DEA-1,2-PD	<chem>CCN(CC)C(O)CO</chem>	<ul style="list-style-type: none"> •Clear liquid •DEEA~Abs. Rate*<<<MEA •DEEA<Rich loading<MEA •Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •DEEA<Des. Rate**<MEA •Lean loading<DEEA<MEA •Foaming issue
3	TM-1,4-DAB	<chem>CN(C)CCCCN(C)C</chem>	<ul style="list-style-type: none"> •Clear liquid •Abs. Rate*<DEEA<<< MEA •DEEA<Rich loading~MEA •Foaming issue at the end •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •Des. Rate**<DEEA<MEA •DEEA<Lean loading~MEA •Foaming issue
4	DEAE-EO	<chem>CCN(CC)CCOCCO</chem>	<ul style="list-style-type: none"> •Dark yellowish liquid •DEA~Abs. Rate*<<<MEA •DEEA~Rich loading<MEA •Foaming issue at the end •No viscosity issue 	<ul style="list-style-type: none"> •Dark yellowish liquid •DEEA~Des. Rate**<MEA •Lean loading<DEEA<MEA •Foaming issue
5	DMAH	<chem>CN(C)CCCCCO</chem>	<ul style="list-style-type: none"> •Very light yellowish liquid •DEEA~Abs. Rate*<<<MEA •DEEA<Rich loading<MEA •Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Very light yellowish liquid •DEEA<Des. Rate**<MEA •Lean loading<DEEA<MEA •Foaming issue
6	1-(2HE)PRLD	<chem>C1CCN(C1)CO</chem>	<ul style="list-style-type: none"> •Clear liquid •DEEA~Abs. Rate*<MEA •DEEA~Rich loading<MEA •No Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •DEEA~Des. Rate**<MEA •Lean loading<DEEA<MEA •No foaming issue

7	1-(2HE)PP		<ul style="list-style-type: none"> •Yellowish liquid •Abs. Rate*<DEEA<<<MEA •DEEA<Rich loading<MEA •Foaming issue at the end •No viscosity issue 	<ul style="list-style-type: none"> •Yellowish liquid •DEEA<Des. Rate**<MEA •Lean loading<DEEA<MEA •Foaming issue
8	3QUI		<ul style="list-style-type: none"> •Clear liquid •Abs. Rate**<<DEEA<<<MEA •Rich loading<<DEEA<MEA •More than 5 hours operation •No Foaming issue •No viscosity issue 	<ul style="list-style-type: none"> •Clear liquid •Des. Rate**<<DEEA<MEA •Lean loading<DEEA<MEA •No Foaming issue
*Abs. Rate is estimated at lean loading			**Des. Rate is estimated at rich loading	

3.1.3. Screening Performance of the solvent candidates

For Figure 5, it is seen that the rich loadings of most the solvent was lower compared to MEA. Only TM-1,4-DAB has rich loading comparable to MEA. All solvents have lower lean loading after the stripping process compared to MEA. This indicates that the solvents have good potential of releasing CO₂ during the desorption process.

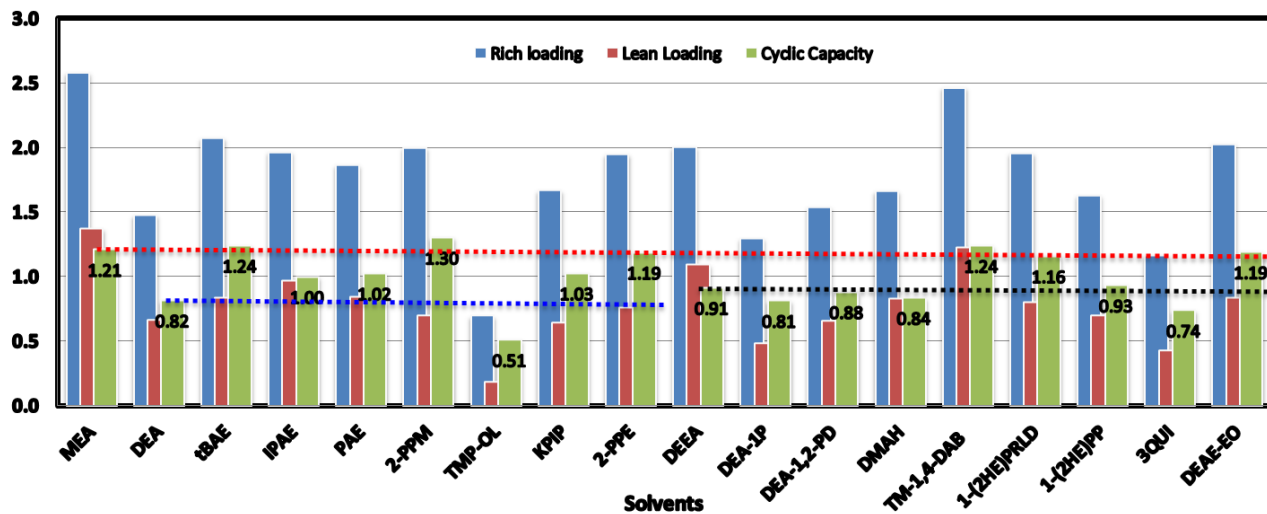


Figure 5. Screening performance of solvent candidates

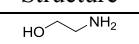
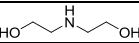
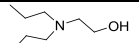
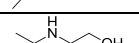
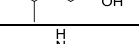
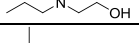
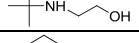
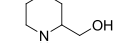
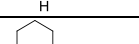
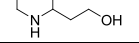
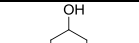
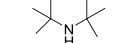
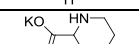
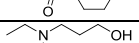
The cyclic capacity was estimated from the rich and lean loadings. Only one solvent candidate (2-PPM) showed clearly higher cyclic capacity than MEA while tBAE, 2-PPE, TM-1,4-DAB, 1-(2HE)PRLD and DEEA-EO have cyclic capacity comparable to MEA. From these solvent candidates

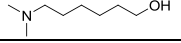
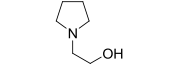
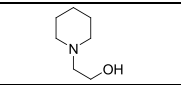
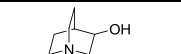
tBAE, TM-1,4-DAB and DEEA-EO has foaming issue. Furthermore, 2-PPM has high melting point which may become an issue (solidification) in plant operation during shutdowns.

3.2. Dissociation constant (pKa)

pKa values was used as one of the factors for solvent recommendations. To confirm the literature values and to measure pKa for those solvent candidates for which pKa values were not available, the dissociation constants of all tested solvent candidates were measured at low concentration $\sim 0.01\text{m}$ (assuming as an infinite solution) and at 25°C . The results along with available data are collected in Table 4. For MEA, DEA, DEEA and 1-(2HE)PRLD the results agree well with literature. Some disagreements were seen between our data and the reported data in literature. This is because different experiment conditions used i.e. temperature (23 and 26°C) and most probably solvent concentration. It is known that if higher concentrations are used, the initial pH and pKa values become higher.

Table 4. Measured pKa values at 0.01 m and at 25°C (NA = Not Available).

No	Solvent		pKa value	
	Name	Structure	This work	Literature(s)
R1	MEA		9.50	9.44(Hamborg and Versteeg, 2009)
R2	DEA		8.92	8.88(Vincent E. Bower, 1962)
R3	DEEA		9.75	9.76(Hamborg and Versteeg, 2009)
1	IPAE		9.78	NA
2	PAE		9.89	9.90(Perrin, 1965)
3	tBAE		10.04	NA
4	2-PPM		10.12	NA
5	2-PPE		10.42	10.14(Xu et al., 1992) 10.48(Fernandes et al., 2012)
6	TMP-OL		9.99	10.05 (Perrin, 1965)
7	KPIP		10.50	NA
8	DEA-1P		9.67	10.29(Chowdhury et al., 2013a)
9	DEA-1,2-PD		9.68	9.89(Chowdhury et al., 2013a)
10	TM-1,4-DAB		9.73	NA
11	DEAE-EO		10.15	NA

12	DMAH		10.01	NA
13	1-(2HE)PRLD		9.80	9.86(Chowdhury et al., 2013a)
14	1-(2HE)PP		9.57	9.76(Chowdhury et al., 2013a)
15	3QUI		9.77	NA

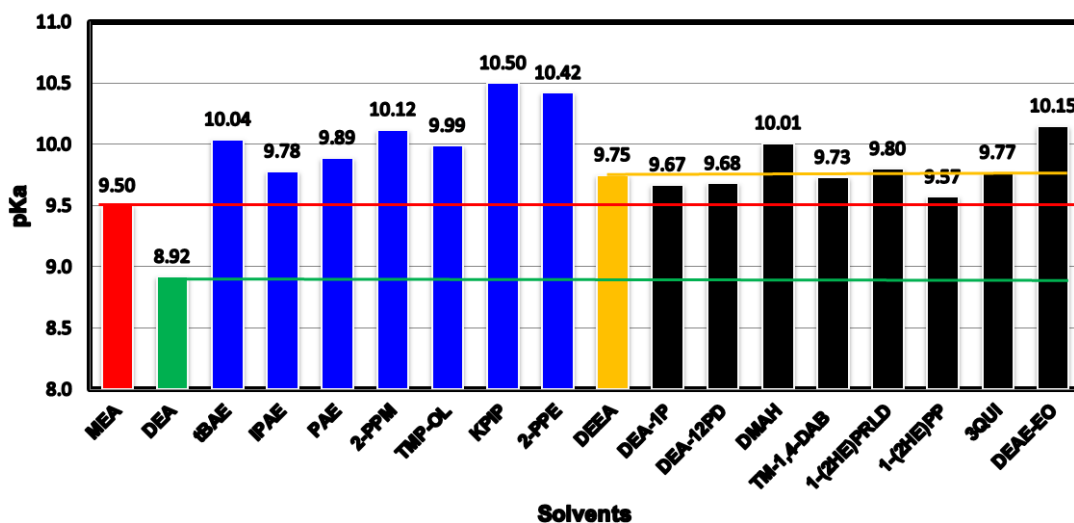


Figure 6. pKa values (at ~0.01 m and 25°C) for different solvent candidates (blue bars, secondary amines; black bars, tertiary amines; red line, pKa of MEA; green line, pKa of DEA; yellow line, pKa of DEEA)

All solvent candidates have higher pKa value than that of MEA and DEA. Seven solvents showed higher pKa values than that of DEEA and further eight solvents showed comparable value to that of DEEA (see in Figure 6). 2-PPE shows clearly higher pKa compared to the reference solvents, whereas the other solvent chosen for characterization, 1-(2HE)PRLD, has pKa values similar to DEEA.

Higher pKa value is expected to give faster absorption rate. Therefore, the absorption rate and the cyclic capacity from the screening experiments were plotted as a function of pKa. From Figure 7, we can see that 2-PPE shows high absorption capacity and can be found in the upper right corner in Figure 7(a) whereas 1-(2HE)PRLD with lower pKa had much lower absorption rate and can therefore be found

in the middle of the figure together with the other tertiary amines. Based on this figure PAE shows somewhat unexpectedly high absorption rate. Furthermore, based purely on this figure KPIP, PAE and 2-PPE are showing good performance. However KPIP was not considered to be a promising solvent due to low cyclic capacity (less than that of MEA), as shown in Figure 5, a possible precipitation issues at higher loadings and concentrations as well as due to its high carbamate to bicarbonate ratio making it not very strong bicarbonate former. Also PAE have low cyclic capacity making it not suitable, see Figure 5. In Figure 7(b) the cyclic capacities are plotted as a function of pKa. As already discussed previously tBAE, 2-PPM, 2-PPE, TM-1,4-DAB, 1-(2HE)PRLD and DEEAE-EO have cyclic capacity comparable to MEA. However due to foaming issues and high melting point most of these solvents were not taken for further studies and only 2-PPE and 1-(2HE)PRLD were chosen for further characterization.

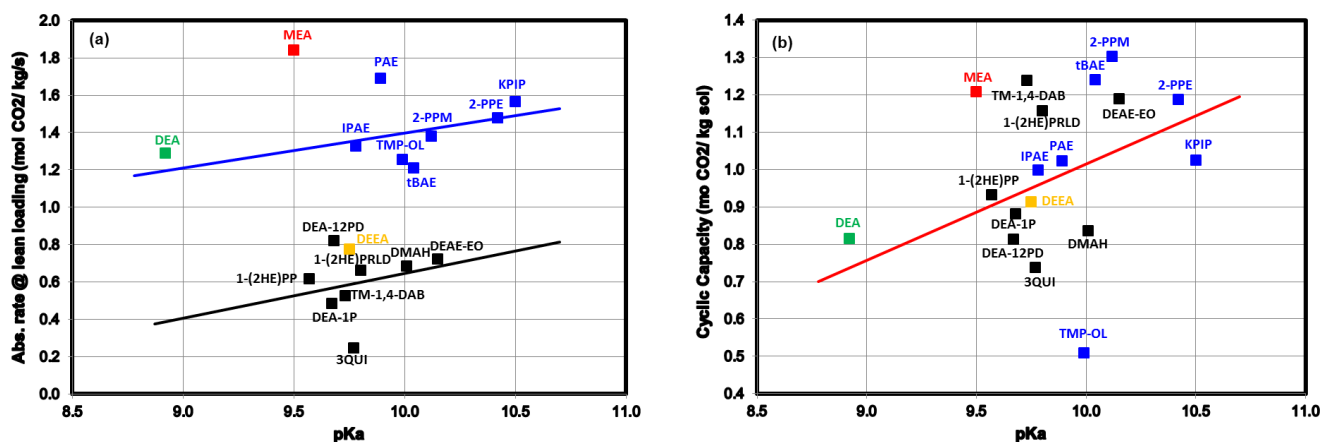


Figure 7. Absorption rate (a) and cyclic capacity (b) as a function of pKa value (■, Secondary amines, ■; tertiary amines; solid lines, trend lines)

3.3. Further characterization

To further study of these solvents, a screening apparatus was used to optimize the concentration of the solvent. Four different concentrations (30 to 60 mass % of solvent) were performed and the results are shown in Figure 8 for 2-PPE and in Figure 10 for 1-(2-HE)PRLD.

Initial absorption rate of 2-PPE solutions were faster than that of DEA but lower than that of MEA. The initial absorption rates at 50 and 60 mass % aqueous solutions of 2-PPE are slightly lower than those of 30 and 40 mass% aqueous solutions. This most likely due to increase in viscosity. However, at the same time the 50 and 60 mass % solutions showed higher rich loadings compared to 30 mass % MEA. No foaming, precipitation and discoloration issues were observed during the experiment. During the desorption process, 30 mass % 2-PPE showed lowest lean loading. Additionally the lean loading of 50 and 60 mass % 2-PPE was almost the same and similar to that of DEEA. There was no foaming issue. As a summary of the results it can be concluded that the both the rich loading and lean loading increased with concentration from 30 to 50mass% as shown in Figure 9(a). No further improvement was seen with 60 mass % solution. The maximum cyclic capacity (~ 1.77 mol CO₂/ kg solvent) is seen at 50 mass % solution. The cyclic capacity of 50 mass% 2-PPE is almost 40% higher compared to 30 mass% MEA (~ 1.21 mol CO₂/ kg solvent).

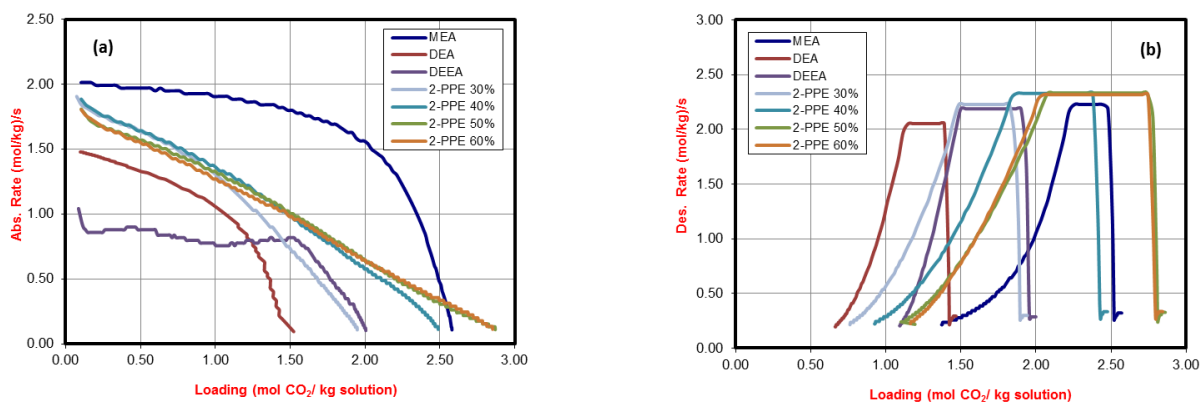


Figure 8. Absorption rate (a) and desorption rate (b) of 2-PPE solvents as function of loading at 40°C and 80°C

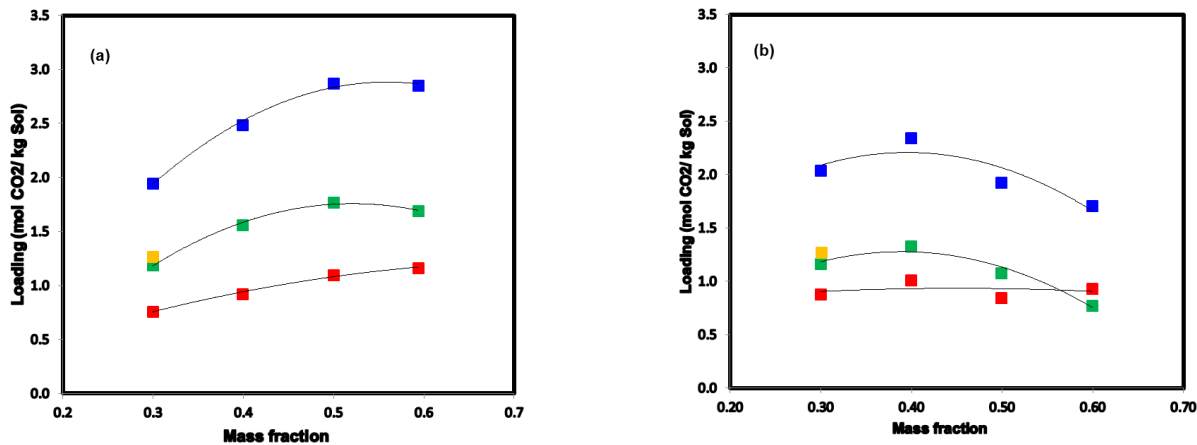


Figure 9. Screening performances of (a) 2-PPE (b) 1-(2HE)PRLD solvents at different concentrations (■, rich loading; ■, lean loading; ■, cyclic capacity; ■, cyclic capacity of 30 mass % MEA; Solid lines, trend lines).

1-(2HE)PRLD showed lower initial absorption rates than the tertiary amine DEEA and 2-PPE. The initial absorption rate of 30 mass % aqueous 1-(2HE)PRLD was faster compared to the higher concentrations. This is most likely related to the viscosity. For all tested concentrations, the rich loadings were lower than that of 30 mass % of MEA. No precipitation and discoloration issues were observed during the experiment. However there was some foaming during the testing of 30 and 40 mass % 1-(2HE)PRLD. Overall, the lean loading was independent of the concentration, but rich loading slightly increased when the concentration was increased to 40 mass %. At higher concentrations the rich loading decreased significantly as seen from Figure 9(b). Thus the highest cyclic capacity was found with 40 mass % of 1-(2HE)PRLD (~ 1.33 mol CO₂/ kg solvent).

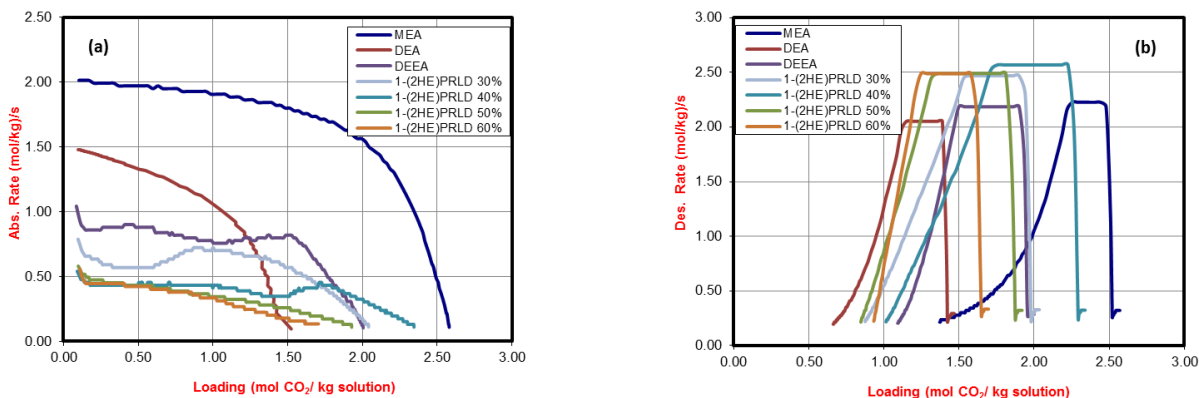


Figure 10. Absorption rate (a) and desorption rate of (b) of 1-(2HE)PRLD solvents as function of loading at 40°C and 80°C.

4. Conclusion

15 solvent candidates were tested in the screening apparatus where an absorption and a desorption process in CO₂ capture plant were mimicked. Absorption was done at 40°C and 95% CO₂ captured while desorption process was done at 80°C and 90% CO₂ removal. Fast and reliable solvent performance estimations (rich/ lean loading and cyclic capacity) of each solvent are calculated and compared to the reference solvent (MEA, DEA and DEEA). In addition, solvent appearances during the process were also reported, such as: solidification, foaming, discoloration and viscosity change. No discoloration, viscosity change and solidification issues were observed. Only foaming issues was the most challenge faced during the experiments. One solvent (TMP-OL) has water solubility issue during solution preparation.

The screening result shows that 6 solvent candidates were observed to have comparable cyclic capacity to MEA, i.e three secondary amines solvents (tBAE, 2-PPM and 2-PPE) and three tertiary amine solvents (TM-1,4-DAB, 1-2(HE)PRLD and DEAE-EO). Three solvents (tBAE, TM-1,4-DAB and DEAE-EO) were observed have foaming issue. 2-PPM has the highest cyclic capacity but it has high melting point.

Dissociation constants were also measured at low concentration (0.01 m) and at 25°C. It was observed that the pKa values are larger than that of MEA. Together with screening result, it is seen that cyclic capacity increases with pKa value as well as the absorption rate.

From the screening and pKa measurements, the two solvents (2-PPE and 1-2(HE)PRLD) were selected and then the second screening measurements expect to give optimum concentration where maximum cyclic capacity of the solvents achieved. The highest cyclic capacity was reached with 50 mass % 2-PPE and with 40 mass % 1-(2HE)PRLD.

ACKNOWLEDGMENT

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APPENDICES

Table 1. Chemicals used in this work

Figure 1: Screening Apparatus

Figure 2: pKa determining Apparatus

Table 2. Characteristics of absorption and desorption at process conditions for secondary amines

Figure 3. Absorption rate (a) and desorption rate (b) of secondary amine solvents as function of loading at 40°C and 80°C

Table 3. Characteristics of absorption and desorption at process conditions for tertiary amines

Figure 4. Absorption rate (a) and desorption rate (b) of secondary amine solvents as function of loading at 40°C and 80°C

Figure 5. Screening performance of solvent candidates

Table 4. Measured pKa values at 0.01 m and at 25 °C

Figure 6. pKa values (at 0.01 m and 25°C) for different solvent candidates

Figure 7. Absorption rate (a) and cyclic capacity (b) as a function of pKa value

Figure 8. Absorption rate (a) and desorption rate (b) of 2-PPE solvents as function of loading at 40°C and 80°C

Figure 9. Absorption rate (a) and desorption rate of (b) of 1-(2HE)PRLD solvents as function of loading at 40°C and 80°C

Figure 10. Screening performances of (a) 2-PPE (b) 1-(2HE)PRLD solvents at different concentrations.

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