New Polyalkylated Imidazoles Tailored for Carbon Dioxide Capture

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Abstract

Aqueous polyalkylated imidazoles have gained interest as potential CO_2 capture solvents due to their high oxidative stability and low vapor pressures compared to traditional amines. In this work, 21 aqueous solutions of polyalkylatedimidazoles were screened as absorbents for CO_2 capture and four solvent candidates were further characterized by measuring the vapor-liquid equilibria and the heat of absorption of CO_2. The pK_a values of the imidazoles were measured and a positive correlation between the absorption capacity and pK_a of polyalkylated imidazoles was found. Increasing the pK_a of imidazoles to 9 by alkylation improved the CO_2 absorption capacity significantly. Based on the equilibrium experiments, the cyclic capacities of the selected solvents varied from 0.8 to 2 mol CO_2/kg solvent. Furthermore, the heat of absorption of CO_2 of the studied imidazoles was lower compared to primary amines. In general, the tested polyalkylated imidazoles are more feasible for processes with partial pressures of CO_2 above 50 kPa. Trimethylimidazole that forms bicarbonate precipitate might be applicable for post combustion CO_2 capture as a high cyclic capacity is obtained even at CO_2 partial pressures around 10 kPa. The collected data indicates that the absorption rate of imidazoles is comparable to tertiary amines and promoters would most likely be required. The present study gives new important knowledge of the absorption properties of polyalkylated imidazoles.

1. Introduction

The predominant technology for CO_2 capture is the use of aqueous alkanolamine solutions for chemical absorption. Unfortunately, chemical absorption with these systems require substantial amounts of energy to regenerate the solvent system.[1] Hence, it is important to study the potential of other amines for CO_2 capture. An interesting class of compounds is imidazoles. Imidazoles are *N*-heterocyclic compounds and have not been extensively studied as absorbents for CO_2 capture. Recently, evolutionary de novo design has been applied to propose new imidazoles for investigation as potential aborbents.[2] The attention given to imidazoles has mainly been as precursor for imidazolium ionic liquids as physical absorbents for CO_2[3] or in imidazolium-based deep eutectic solvents for CO_2 capture.[4] Furthermore, incorporating imidazole into CO_2 selective membranes has shown promising results[5] and highly efficient absorption of SO_2 have been obtained with imidazoles.[6] Other uses of imidazoles include natural products[7] and as NHC-ligands in organometallic catalysis,[8] Shannon et al. have previously reported that pure, non-aqueous *N*-alkylimidazoles exhibit both lower viscosities and greater physical absorption than their imidazolium counterparts.[9] As neat liquids, *N*-alkylimidazoles do not demonstrate chemical reaction with CO_2. However, significantly improved CO_2 absorption capacity was obtained for monoethanolamine in *N*-butylamine compared to aqueous monoethanolamine solutions.[9] In aqueous solutions, imidazoles react with CO_2 as tertiary amines.[10] Chemical absorption of CO_2 with unsubstituted imidazole is not efficient due to imidazole not having sufficiently high pK_a (7), and has been scarcely studied. Investigation of imidazoles with increased pK_a is therefore of interest. The absorption capacity and cyclic capacity of imidazole/piperazine blends increase with higher pK_a of the imidazole.[11] Imidazoles can also be used to improve CO_2 mass-transfer rates into amine solvents[11] and have been applied to reduce the vapor pressure of volatile organic compounds in aqueous solution.[12] Very low vapor pressures are observed above neat alkylimidazole solutions.[13-14] Furthermore, the thermal stability of imidazoles is improved by additional number of alkyl substituents on the imidazole.[15] Imidazole has excellent oxidative stability compared to other amines.[16] As alkyl substitution increases both the thermal stability and the pK_a[17] of the imidazole, we decided to study the CO_2 absorption capacities of polyalkylated imidazoles. We have previously prepared a wide range (> 40) polyalkylated imidazoles in out laboratory for this purpose.[18]

In this work, we present newly synthesized imidazoles as potential candidates for CO_2 capture. The effect of increasing the number of alkyl substituents on pK_a and absorption capacity of imidazoles will be presented. The water solubility

of imidazoles will be discussed. Furthermore, the heat of absorption and vapor-liquid equilibrium (VLE) data of selected imidazoles will be given.

2. Experimental Section

2.1 Materials

The tested compounds **1**-**21** are presented in Table 1. Monoethanolamine (MEA), *N*-methyldiethanolamine (MDEA), imidazole **1**, 1-methylimidazole **2**, 2-methylimidazole **3**, 2-ethylimidazole **4**, 4(5)-methylimidazole **5**, 1,2-dimethylimidazole **6** and 2-ethyl-4-methylimidazole **7** were obtained from Sigma-Aldrich Merck (Germany). 1,2,4,5-Tetramethylimidazole **16** was obtained from TCI Europe (Belgium). Commercial compounds were used without further purification. Polyalkylated imidazoles **8-15**, **17-21** were readily prepared by a one-step procedure in our laboratory[18] from corresponding diketone, aldehyde and amine with ammonium sulfate or ammonium carbonate as ammonium source.

2.2 Acid dissociation constant, pK_a

Potentiometric measurements were conducted with a Mettler Toledo G20 compact titrator with a pH-electrode DSC-115 (uncertainty $\pm$ 0.02 pH) and temperature sensor DT100 (uncertainty $\pm$ 0.1 °C).[19] The temperature was controlled at 25 °C with a Julabo M4 heating circulator (temperature stability $\pm$ 0.1 °C). Deionized water was used as heat transfer medium. Calibration of the pH electrode was performed using buffer solutions traceable to the National Bureau of Standards (pH 4.01, 7.00, 9.21 and 11.00 from Mettler Toledo). MEA was used as reference compound to validate the calibration. MEA gave pKa value of 9.50, which agrees well with literature values varying between 9.44-9.50.[20-22] Aqueous amine solution (30-35 mL, 0.01 M) was automatically titrated with 0.1 M HCl solution. All measurements were performed in duplicate and the average values are reported. Average deviation of the duplicates were <1%. A dynamic equilibrium method was used to allow an incremental dosing of titrant with minimum 0.005 ml/min and maximum 0.3 ml/min to prevent a disturbance in temperature. Data was recorded using the LabX 3.1 software provided by Mettler Toledo. pK_a values were calculated as the pH at half equivalence.

2.3 CO₂ absorption capacity screening experiments

CO_2 absorption capacity screening experiments of the amine solutions were carried out in a 300 mL small-scale reactor as shown in Figure 1. This equipment was designed by SINTEF Materials and Chemistry in order to perform small-scale screening of series of compounds. An amine solution (1-2 mL, 30 wt%) was added to the liquid well. The liquid was set to stir slowly and the reactor closed. The reactor was degassed under vacuum at 20 °C before the experiment. Experiments were started at <5 kPa pressure.

The reactor was heated with current carrying metal rods in the four corners of the apparatus and two on the lid of the apparatus. The temperature in the reactor was measured at three points, the temperature in the liquid solution, bottom of the gas phase and top of the gas phase. Temperature control was performed using Labview 2016 and experiments were run at 40 ± 0.2 °C.

CO_2 was added in two subsequent additions of $\Delta P = 50$ kPa CO_2 with a three-hour interval between injections from a storage cylinder (1000 mL) with recorded temperature. After the second injection, absorption of CO_2 was continued for an additional three hours to obtained equilibrium. Addition of CO_2 to the reactor was calculated from the difference in pressure in the storage cylinder. The amount of CO_2 absorbed was calculated from the final and initial pressures. The vapor pressures of water, solvent or amine were considered constant throughout the experiment and independent of CO_2 partial pressure. Imidazoles have been reported to have very low vapor pressures (below 1mbar)[13-14] and even a 10-fold increase during the CO_2 absorption would not have a significant effect on the results. The pressure was recorded with Keller LEO5 relative pressure gauge (-1-3 barg, accuracy 0.05% FS) in the reactor and Keller LEO5 pressure gauge (0-11 bara, accuracy 0.05% FS) in the storage cylinder.
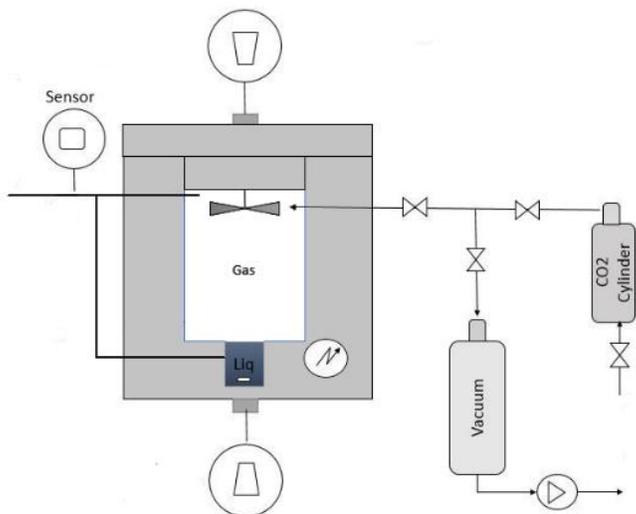
Figure 1: Small-scale reactor for CO_2 absorption measurements.

2.4 Heat of reaction, ΔH measurements

Heat of reaction measurements of aqueous solutions (30 wt%) were performed using CPA202 from Syrris (ChemiSens). A depiction of the apparatus and set-up is given in Figure 2. Experiments and uncertainties are in accordance with previously described procedures using the same apparatus.[23] A brief description of the apparatus and differences in procedures are given here. The CPA202 is a true heat-flow reaction calorimeter, measuring the heat flow to, or from, the system. A glass and stainless steel reactor with volume 270.4 ± 0.2 cm^3 submerged in an ethylene glycol thermostated bath was used for the experiments. The solution was stirred with a motoric stirrer. The pressure was recorded with SENSIT pressure gauge (1-10 bara, accuracy 0.15% FS) and the temperature in the reactor is measured with Pt-100 temperature sensor (accuracy 0.1 °C). In each experiment, the reactor was loaded with 130 mL of solution. The reactor was degassed under vacuum at 20 °C before the run. Then the solution was heated to desired temperature and the pressure recorded. Experiments were run at constant temperature at either 40 or 80 °C. CO_2 was injected into the reactor through a Bronkhorst Hightech mass flow controller (0.5 NL/min, accuracy 0.1% FS) from a 2300 mL storage cylinder. The CO_2 was stored at room temperature and the gas stream temperature was assumed equal to the cylinder temperature when injected into the apparatus. Corrections in the obtained heat of absorption values for the temperature of the introduced CO_2 were performed. The amount of CO_2 added was calculated from the change in pressure of the storage cylinder with known volume.

Injection of CO_2 was performed when the reaction system was considered to be at equilibrium. Determination of the equilibrium was automated by a script, which required the maximum deviation in pressure, temperature and true heat flow of the system to be below $\pm$ 0.5 kPa, $\pm$ 0.01 °C and $\pm$ 0.03 W over 10 min. ChemiCall software provided by Chemisens was used to record the operation parameters as a function of time.

Equilibrium partial pressure of CO_2 at each loading (α) was calculated from the total pressure data. This is possible, if it is assumed that the partial pressures of water and amine were constant throughout the experiment and thus independent of the CO_2 partial pressure. The same assumption has been used by several authors.[24,25,26]

The amount of CO_2 in the storage cylinder and the amount of unreacted CO_2 in the gas phase in the reactor was calculated from the Peng Robinson equation of state.[27] Vapor-liquid equilibrium (VLE) results obtained in the apparatus at low CO_2 pressures (<3 kPa) are considered inaccurate, since two almost equal numbers (with accuracy of 1.5 kPa) are subtracted from each other (total pressure – partial pressure of water and solvent). However, the CO_2 pressures obtained for the imidazoles during the calorimetric measurements were always higher than 3 kPa.
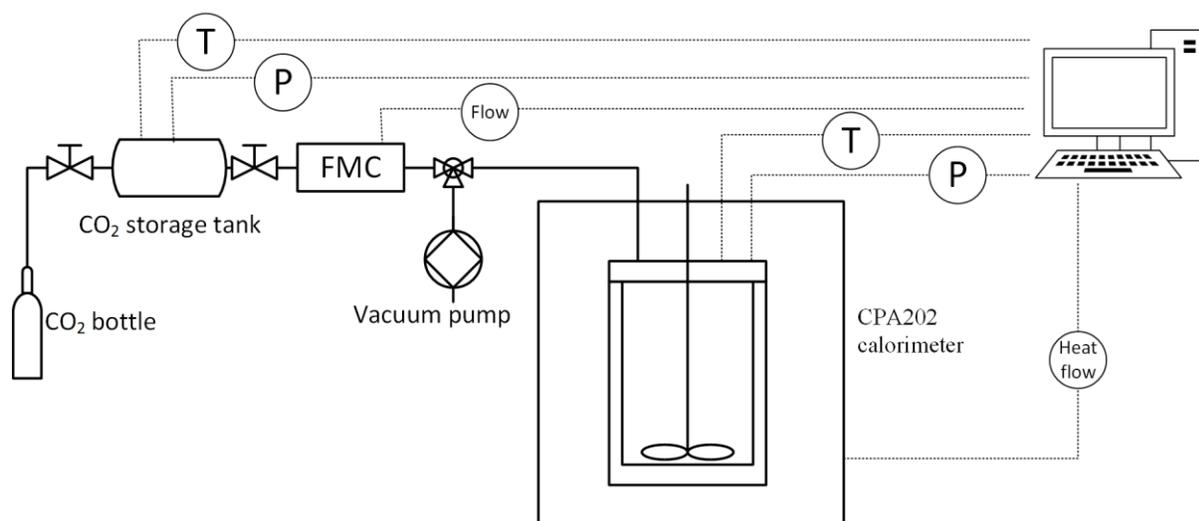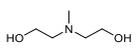

Figure 2: Schematics of calorimetric experiments.

3. Results and Discussion

3.1 Acid dissociation constant, pK_a

The obtained pK_a results for the imidazoles **1-21** are presented in Table 1. The pK_a of the alkylimidazoles was found to increase with additional number of substituents (Figure 3 and Table 1). The basicity of the alkylimidazoles decreases by alkylation in 2->4-/5->1-position, respectively. This effect may be explained by 2-position being α to both nitrogens, whereas 4- and 5-position are in α-position to one nitrogen and β-position to another. Alkyl substituents in 1-position do not significantly change the pK_a of the imidazole compared to hydrogen. By adding alkyl substituents, it is possible to raise the imidazole pK_a from 7.01 for unsubstituted imidazole **1** to 9.05 for tetrasubstituted imidazole **16**. Trialkylated imidazoles **8** and **9** had nearly as high pK_a as **16**. Contrary to results by Lenarcik et al.,[17] no clear trend was observed for the pK_a of the alkylimidazoles in this study. Possibly, because of the shorter alkyl chain lengths in this study, and the use of infinite dissolution versus 0.50 M fixed ionic strength.

Table 1: pK_a Values: a) lit. data[17] at 25 °C, b) measured at 25 °C and c) measured CO_2 loading (α) [mol CO_2/mol amine] at given pressure at 40 °C.

Compounds (purity wt%)		a) pK_a lit. data[1]	b) pK_a Measured[2]	c) CO_2 loading α [mol/mol] (pressure [kPa])
Monoethanolamine (99.5%)	MEA		9.50	0.56 (65)
N- Methyldiethanolamine (≥99%)	MDEA		8.57	0.75 (73)
Imidazole (≥99%)	**1**	6.95	7.01	0.21 (96)
1-Methylimidazole (99%)	**2**	7.21	7.04	0.12 (80)
2-Methylimidazole (99%)	**3**	7.85	7.92	0.36 (80)
2-Ethylimidazole (98%)	**4**	7.99	7.88	0.29 (84)
4(5)-Methylimidazole (98%)	**5**	7.69	7.58	0.29 (90)
1,2-Dimethylimidazole (98%)	**6**	8.21	8.05	0.36 (87)
2-Ethyl-4(5)-methylimidazole (95%)	**7**	8.68	8.38	0.47 (80)

Name	Structure			
2,4,5-Trimethylimidazole (98%)	**8**	8.92	8.90	0.61 (78)
4-Ethyl-2,5-dimethylimidazole (97%)	**9**	-	8.88	0.63 (84)
1,4,5-Trimethylimidazole (97%)	**10**	-	8.02	0.34 (87)
1-Ethyl-4,5-methylimidazole (98%)	**11**	-	8.24	0.33 (97)
4,5-Methyl-1-propylimidazole (97%)	**12**	-	8.18	0.31 (86)
1-Isopropyl-4,5-dimethylimidazole (97%)	**13**	-	8.04	0.31 (88)
1-(2-Hydroxyethyl)-4,5-dimethylimidazole (96%)	**14**	-	7.94	0.50 (84)
2,4,5-Triethylimidazole (95%)	**15**	-	7.99	0.24 (90)
1,2,4,5-Tetramethylimidazole (98%)	**16**	9.20	9.05	0.72 (89)
1-Ethyl-2,4,5-trimethylimidazole (98%)	**17**	-	8.68	0.71 (83)
2,4,5-Trimethyl-1-propylimidazole (98%)	**18**	-	8.89	0.68 (84)
1-Isopropyl-2,4,5-trimethylimidazole (95%)	**19**	-	8.80	0.58 (90)
2-Ethyl-1,4,5-trimethylimidazole (99%)	**20**	-	9.03	0.66 (84)
1,4,5-Trimethyl-2-propylimidazole (95%)	**21**	-	9.04	0.61 (81)

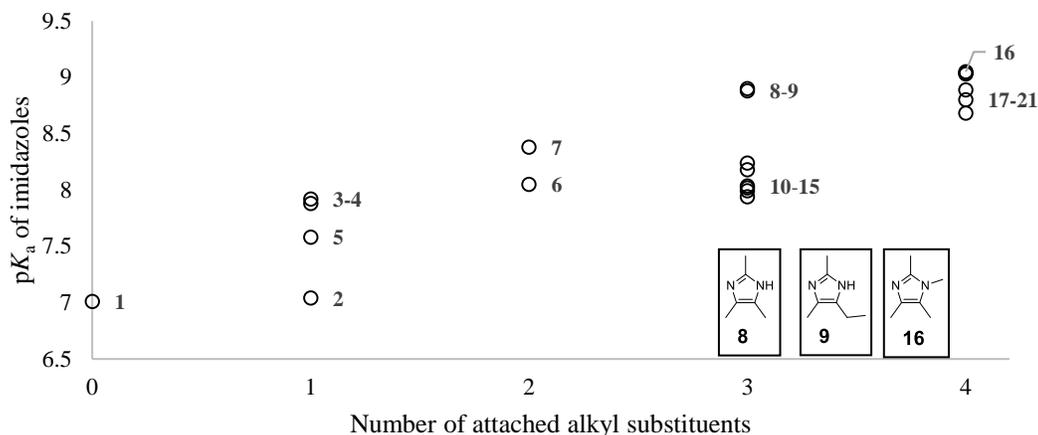[1] Fixed ionic strength, I = 0.5 (KNO_3)[17]

[2] Infinite dilution

Figure 3: Effect on pK_a by the increasing number of alkyl substituents on imidazole ring, based on Table 1.

3.2 Aqueous solubility

The water solubility of the alkylimidazoles was an important aspect in the screening study, as some imidazoles were not sufficiently water soluble to be tested as 30 wt% aqueous solution, see Supporting Info.

The solubility of imidazole **1** in water is 633 g/L at 20 °C. By alkylating the imidazole at different positions, it was expected that the general trend for imidazole solubility would be decreasing solubility with additional number of substituents and increasing size of the substituents. Alkylation in 1-position has been considered to have a greater impact on the water solubility than substitution in other positions, as this decreases the H-bonding ability of the imidazole. The lack of H-bonding is observed by the considerably lower melting points of 1-alkyl imidazoles compared to 1-H imidazoles.[18] Melted 1-H imidazoles had significantly higher viscosities than 1-alkyl imidazoles. However, when attempting to dissolve the imidazoles, the short-chained 1-alkylimidazoles, $C_n < 4$, were water-soluble at least up to 30 wt% in water, regardless of the number of methyl substituents on the imidazole ring. As shown by the solubility of imidazole **16**. The general trend for aqueous solubility of imidazoles was that longer alkyl chains reduced the solubility. An example is the reduction in solubility from alkylimidazole **10** (>50 wt% water soluble) to 1-butyl-4,5-dimethylimidazole (<30 wt% water soluble), see Supporting Info. 2,4,5-Triethylimidazole **15** was not completely soluble as a 30 wt% solution in water. An interesting observations was that the solid dialkyl compound **7** formed a liquid two-phase system when attempted dissolved as 30 wt% in water.

3.3 CO₂ absorption capacity screening

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Screening experiments of the CO_2 absorption capacity of imidazoles **1-21** were performed. The imidazole solutions were screened as 30 wt% solutions at 40 °C, with the exception of compound **9**, which was tested as a 20 wt% solution due to lower solubility. Absorption capacities in mol CO_2/mol amine, are presented in Figure 4 and values with corresponding CO_2 pressures are given in Table 1. Absorption capacities in mol CO_2/kg solution, are shown in Figure 5.

MEA (30 wt%) was tested as a standard to validate the screening results obtained in the reactor. Seven experiments with MEA were performed and the obtained CO_2 loadings for the 30 wt% MEA solutions at final CO_2 pressure was 0.56 ± 0.02 mol CO_2/mol amine at 65 kPa CO_2, which fits well with the equilibrium model value of 0.57 mol CO_2/mol amine at this pressure.[28] To compare the behavior of the imidazoles with other tertiary amines, MDEA (30 wt%) was used as a reference. The obtained absorption capacity of MDEA was 0.75 mol CO_2/mol amine at 73 kPa CO_2 partial pressure, in agreement with the VLE data presented in Figure 8. Thus, the equilibrium loadings for MEA and MDEA are reached in this equipment and equilibrium for tertiary imidazoles can be obtained with the experimental procedure if the tested imidazole absorbs CO_2 as fast as MDEA. Hence, the results are considered pseudo equilibrium.
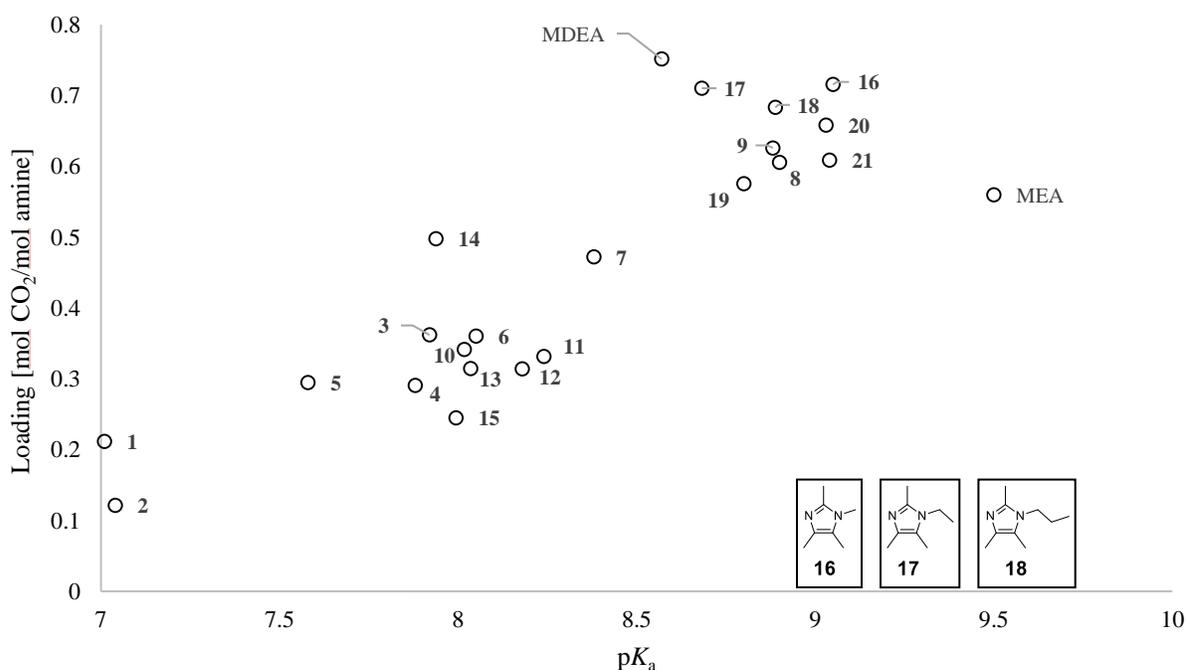

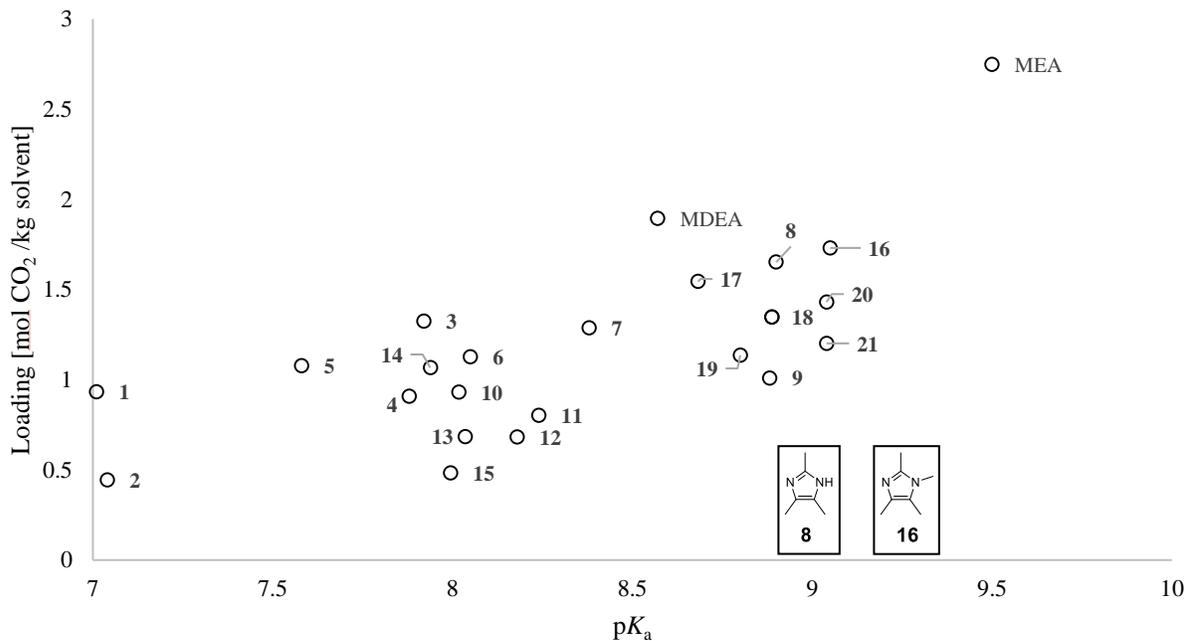Figure 4: CO_2 loading [mol/mol amine] of imidazoles **1-21**, MDEA and MEA at 65-97 kPa CO_2 pressure.

Figure 5: CO_2 loading [mol/kg solution] of imidazoles **1**-**21**, MDEA and MEA at 65-97 kPa CO_2 pressure.

From the screening experiments, a strong correlation between the pK_a of the imidazoles and their respective CO_2 absorption capacity was observed (Figure 4 and Figure 5). By increasing the imidazole pK_a from 7 to 8, the loading was raised from 0.1-0.2 mol CO_2/mol amine to 0.3-0.5. An imidazole pK_a of 9 enhanced the loading to 0.6-0.8 mol CO_2/mol amine. The improvement in capacity per kg solution is somewhat lower than per mole amine, due to the higher molecular weights of the more substituted imidazoles. Compounds **16** (0.72 mol CO_2/mol amine), **17** (0.71 mol CO_2/mol amine) and **18** (0.68 mol CO_2/mol amine) obtaining the highest molar absorption capacity. A longer alkyl chain in 2-position appeared to decrease the absorption capacity more than in 1-position, as substrates **20** and **21** obtained absorption capacities of 0.66 and 0.61 mol CO_2/mol amine, respectively. The highest CO_2 capacities on weight basis were obtained for imidazoles **8** and **16** with 1.65 and 1.73 mol CO_2/kg solution. This is a substantial increase from imidazole **1**. Addition of a hydroxyl functionality, **14**, improved the CO_2 absorption capacity per mol imidazole considerably more than an alkyl chain, however, the effect was smaller than addition of a methyl substituent in 2-position.

When extending the reaction time from three to nine hours after the second injection for compound **8**, it was possible to achieve a loading of ~0.9 mol CO_2/mol amine at 73 kPa. The increased absorption at extended reaction times was due to formation of a solid layer on top of the amine solution, as precipitation had occurred. Imidazole **8** was the only imidazole where absorption of CO_2 resulted in precipitation. Since imidazole **8** was soluble in distilled water in up to 50 wt% and solutions of 20, 40 and 50 wt% **8** were screened. In all cases, precipitation was observed and loadings of 0.9 mol CO_2/mol amine could be obtained for all solutions. The high loading and reproducibility for imidazole **8** makes it highly interesting in a process utilizing precipitation, as has been proposed for several amino acid solvents.[29] ^{13}C-NMR (Supporting info) of the precipitate showed a characteristic HCO_3^-/CO_3^{2-} signal at 160.2 ppm, indicating a HCO_3^-/CO_3^{2-} equilibrium shifted towards HCO_3^-.[30-31] No H-C-carbamate couplings were observed by HMBC. FTIR of the **8**-HCO_3 precipitate showed overlapping peaks with $NaHCO_3$ (Supporting info). Peaks in the IR-spectrum not overlapping with those of $NaHCO_3$, overlapped with the peaks of pure alkylimidazole **8**. HRMS (ESI) gave the protonated imidazolium as the only identifiable compound. Hence, it seems that imidazole **8** readily forms a solid bicarbonate salt in CO_2 solutions. The imidazole and CO_2 can readily be regenerated from the bicarbonate, as the precipitate rapidly dissolves at 90 °C.

Absorption of CO_2 into aqueous solution of compound **7** gave a transition from a two-phase system to a single phase whereas the opposite behavior of what was described above for imidazole **8.** Furthermore, aqueous solution of compound 15 (1,4,5-triethylimidazole) did not completely solvate upon absorption of CO_2.

The alkylimidazoles **8** and **16** with the highest absorption capacity at 40 °C were selected for additional studies. Also, compounds **3** and **7** were chosen. Although they did not have a very high absorption capacity, comparing with the more alkaline imidazoles **8** and **16** would give insight into the effect of pK_a on absorption properties of alkylimidazoles. The tetraalkylated imidazoles **17**-**21** are expected to have similar heat of absorption and VLE as compound **16** and were not chosen for further studies.

3.4 Calorimetric measurements

Experiments to measure the heat of absorption of CO_2 were performed for alkylimidazoles **3**, **7**, **8** and **16**, at 40 and 80 °C, while MEA and MDEA were measured for reference. Both MDEA and MEA data was comparable to previously reported.[32-33] All systems were tested as 30 wt% solutions and the CO_2 loading was calculated following each CO_2 injection. The heat of absorption for imidazoles **3**, **7** and **16** as a function of loading is depicted in Figure 6. The heat of absorption for the imidazole **8** is shown in Figure 7. The integral heat of absorption for compounds **3**, **7**, **8**, **16** and MDEA is presented in Table 2.

The integral heat of absorption for the imidazoles at 40 °C was, respectively, for **3**, 55.3 kJ/mol CO_2 (lit.[34] 59.1 kJ/mol), for **7**, 54.7 kJ/mol CO_2, for **8**, 68.9 kJ/mol and for **16**, 53.0 kJ/mol CO_2, similar to data reported in literature: 46-59 kJ/mol CO_2.[34] Furthermore, the heat of absorption of MDEA, 52.3 kJ/mol CO_2, was comparable to previously obtained results[32-33] The heat of absorption for imidazole **16** is lower than compounds **3** and **7** at 40 °C, because of the *N*-methyl substituent on **16**. *N*-Alkylimidazoles have a lower heat of absorption at 40 °C than *N*H-imidazoles.[34] The higher heat of absorption for imidazole **8** is caused by precipitation during the reaction. The heat of absorption for compound **8** rises from 50 to 80 kJ/mol CO_2 upon onset of precipitation. This gives a heat of crystallization at ~30 kJ/mol. For **3**, **7** and **16** the heat of absorption increased from 40 to 80 °C. The temperature dependency on the heat of absorption for imidazole **16** is greater than the other imidazoles, with a $\Delta(-\Delta H_{abs})$ of 11.2 kJ/mol CO_2 from 40 to 80 °C. As shown in Figure 6, the heat of absorption of CO_2 for the imidazoles are slightly higher than MDEA and significantly lower than for MEA.

Table 2: Experimentally determined integral heat of absorption ($-\Delta H_{abs}$) of CO_2 in 30 wt% solutions of imidazoles **3**, **7**, **8** and **16** and MDEA over the loading range, at 40 and 80 °C.

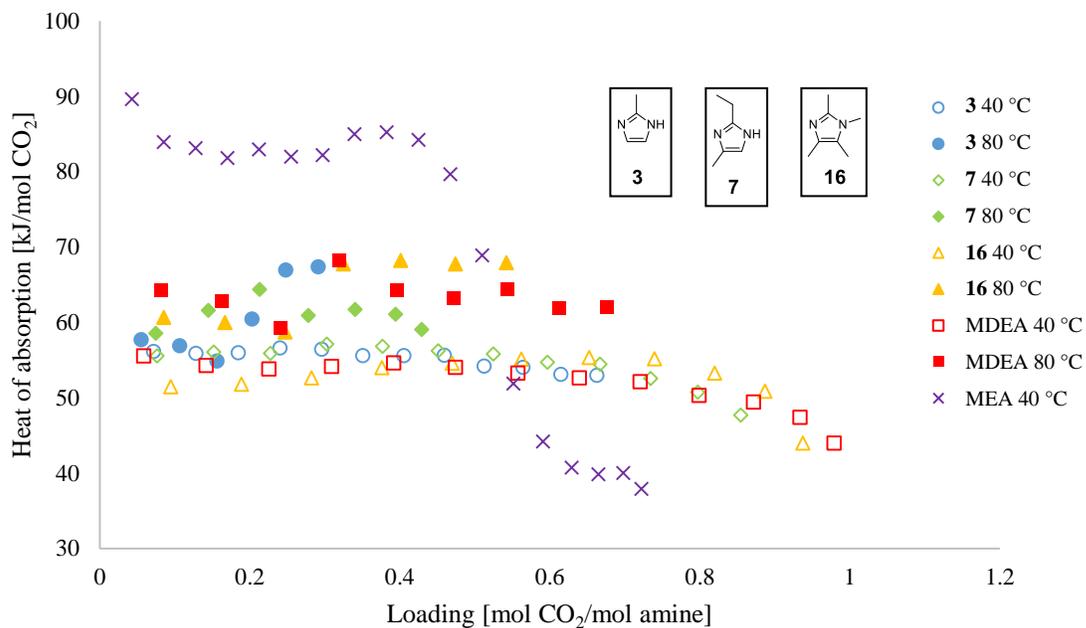|		Imidazole			
	MDEA	3	7	8	16
T (°C)	$-\Delta H_{abs}$ (kJ/mol CO_2)	$-\Delta H_{abs}$ (kJ/mol CO_2)	$-\Delta H_{abs}$ (kJ/mol CO_2)	$-\Delta H_{abs}$ (kJ/mol CO_2)	$-\Delta H_{abs}$ (kJ/mol CO_2)
40	52.3 (α = 0-0.979)	55.3 (α = 0-0.663)	54.7 (α = 0-0.855)	68.9 (α = 0-1.000)	53.0 (α = 0-0.937)
80	63.4 (α = 0-0.677)	60.4 (α = 0-0.291)	61.1 (α = 0-0.429)	61.7 (α = 0-0.543)	64.2 (α = 0-0.542)

Figure 6: Differential heat of absorption of 30 wt% of imidazoles **3**, **7**, **16** and MDEA at 40 and 80 °C, and of MEA at 40 °C.
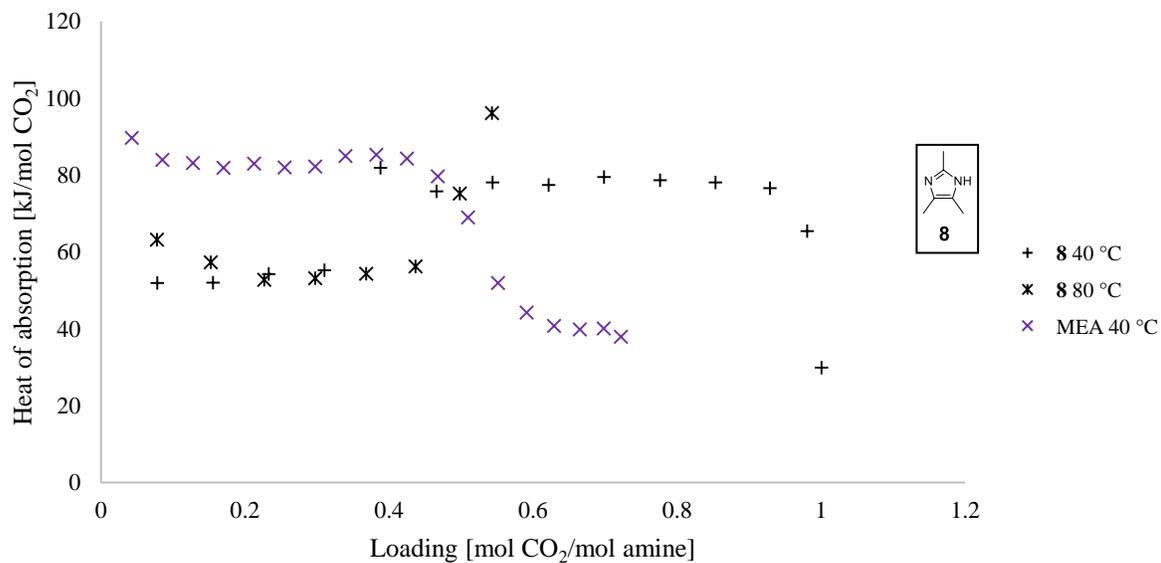

Figure 7: Differential heat of absorption of 30 wt% of imidazole **8** at 40 and 80 °C and of MEA at 40 °C.

From the parameters measured by the calorimeter, it is possible to obtain vapor-liquid equilibrium (VLE) curves for the reactions by plotting loading vs CO_2 partial pressure (Figure 8). The CO_2-H_2O-imidazole VLE shifts clearly towards increased absorption of CO_2 into the aqueous imidazole solution with increasing pK_a of the imidazole. This is in accordance with expected results and loadings obtained for the screening experiments.

The VLE curves obtained for the calorimetric measurements, Figure 8, were used to estimate the cyclic capacities, $\Delta\alpha_s$. The cyclic capacities (mol CO_2/kg solution) for imidazoles **3**, **7**, **8**, **16** and MDEA were determined as the difference between equilibrium loadings at 40 °C/50kPa and 80 °C/50kPa and are presented in Figure 9. The cyclic capacity $\Delta\alpha_s$ of **3** was 0.81, whereas **7** and **16** have $\Delta\alpha_s$ values of 0.89 and 0.97, respectively. Compound **8** performed exceptionally well with a $\Delta\alpha_s$ of 2.00 at 50 kPa between 40 and 80 °C. The cyclic capacity of the imidazoles, with the exception of imidazole **8**, are slightly lower than for MDEA, $\Delta\alpha_s = 1.08$, at the studied conditions. The formation of the precipitate shifts the VLE of the **8** solution towards a high solubility of CO_2 in the liquid/solid phase. The VLE (Figure 8) shows that the solubility of CO_2 in aqueous solution of imidazole **8** decreases considerable from 40 to 80 °C. Precipitation occurs at a higher loading (0.4-0.5 mol CO_2/mol amine) at 80 °C than at 40 °C (0.3 mol CO_2/mol amine) and at notably higher CO_2 pressures, 200 kPa vs 5-6 kPa. Imidazole **8** had an absorption capacity of 2.11 mol CO_2/kg solution at 40 °C at 10 kPa CO_2. The CO_2 absorption capacity of **8** is significantly higher compared to other precipitating amines, such as sarcosine[35], taurine[36], lysine[37] and proline[37].

In the current work, the partial pressure of CO_2 at 40 °C used to determine the rich loading of the imidazoles is higher than commonly used for solvents for post combustion CO_2 capture with 10-14 kPa of CO_2 in the gas phase and the characterized imidazoles, with the exception of substance **8**, would not be suitable for post combustion CO_2 capture. If the imidazoles tested here would be used, the rich loading would be 0.1-0.3 mol/mol imidazole (at 10 kPa) leading into a small cyclic capacities. It is concluded that the tested imidazoles are more suitable for applications with at least 50 kPa CO_2 available, such as biogas upgrading processes and high pressure applications. Imidazole **8** could be also suitable for applications with lower partial pressures of CO_2.

The developed solvents, **3,7** and **16**, have cyclic capacities similar to 30wt% MEA, 0.8-1.2 mol/kg[22,38, 39] depending on the experimental conditions. Whereas, the cyclic capacity of **8** is significantly higher. No discoloring was observed

in any of the experiments, and the viscosities of all samples were low, typically below 4 cP up to loading 0.5 mol CO_2/mol amine (at 40 °C), The viscosities of the fully loaded solutions were not measured. Loaded solution of imidazole **8** formed a more viscous slurry, which did not cause stirring problems at 500 rpm.
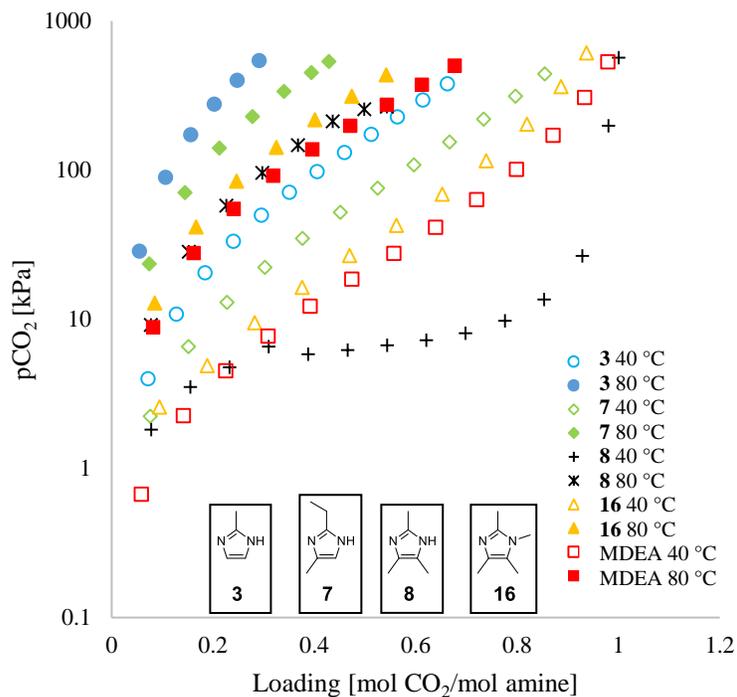

Figure 8: Vapor-liquid equilibrium data (VLE) obtained from calorimeter for 30 wt% solutions of imidazoles **3**, **7**, **8**, **16** and MDEA at 40 and 80 °C.
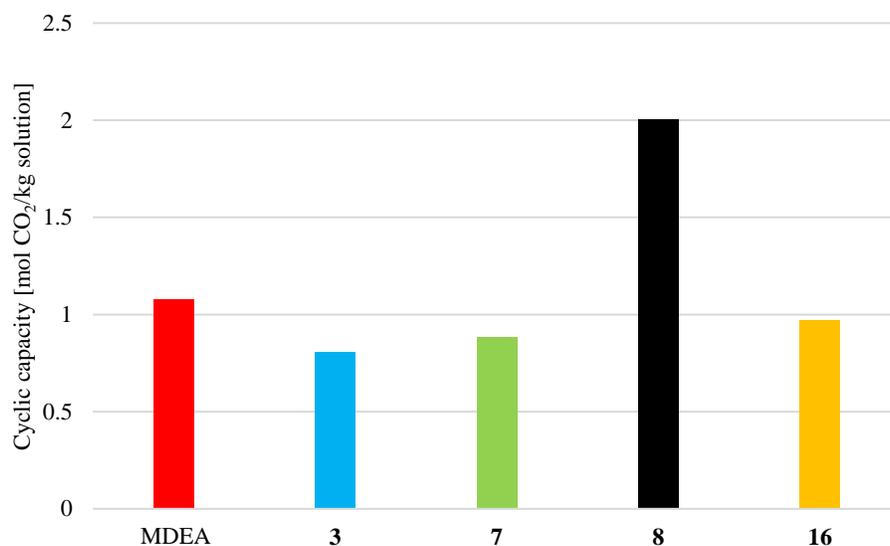
Figure 9: Cyclic capacity of 30 wt% solutions of imidazoles **3**, **7**, **8**, **16** and MDEA between 50 kPa at 40 and 80 °C.

4. Conclusions

A total of 21 polyalkylatedimidazoles were screened as absorbents for CO_2 capture. The measurements show that increasing the pK_a of imidazoles to 9 by alkylation improved the CO_2 absorption capacity considerably. Based on the equilibrium experiments, the cyclic capacities of the developed solvents varied from 0.8 to 2 mol CO_2/kg solvent. Furthermore, the heat of absorption of the studied imidazoles ranged from 53 to 69 kJ/mol CO_2 at 40-80 °C, being significantly lower compared primary amines such as 30 wt% MEA. The results show that the tested polyalkylated imidazoles are more feasible for processes with higher partial pressures of CO_2 (above 50 kPa). Already at low partial pressures of CO_2 one of the tested imidazoles, trimethylimidazole, forms bicarbonate precipitate and very high cyclic capacity is obtained even at low CO_2 partial pressures. The absorption rate of imidazoles is expected to be comparable to tertiary amines and promoters would most likely be required in a real process. Further investigations of imidazoles with promotors are currently being performed in our laboratories.

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Bibliography

1.   Svendsen, H. F.; Hessen, E. T.; Mejdell, T., Carbon dioxide capture by absorption, challenges and possibilities. *Chem Eng J* **2011,** *171* (3), 718-724.
2.   Venkatraman, V.; Gupta, M.; Foscato, M.; Svendsen, H. F.; Jensen, V. R.; Alsberg, B. K., Computer-aided molecular design of imidazole-based absorbents for CO2 capture. *International Journal of Greenhouse Gas Control* **2016,** *49*, 55-63.
3.   Ramdin, M.; de Loos, T. W.; Vlugt, T. J. H., State-of-the-Art of CO2 Capture with Ionic Liquids. *Ind Eng Chem Res* **2012,** *51* (24), 8149-8177.
4.   Cao, L.; Huang, J.; Zhang, X.; Zhang, S.; Gao, J.; Zeng, S., Imidazole tailored deep eutectic solvents for CO2 capture enhanced by hydrogen bonds. *Physical Chemistry Chemical Physics* **2015,** *17* (41), 27306-27316.
5.   Lin, C.; Stedronsky, E. R.; Regen, S. L., pK(a)-Dependent Facilitated Transport of CO2 across Hyperthin Polyelectrolyte Multilayers. *Acs Appl Mater Inter* **2017,** *9* (23), 19525-19528.
6.   Shannon, M. S.; Irvin, A. C.; Liu, H. N.; Moon, J. D.; Hindman, M. S.; Turner, C. H.; Bara, J. E., Chemical and Physical Absorption of SO2 by N-Functionalized Imidazoles: Experimental Results and Molecular-level Insight. *Ind Eng Chem Res* **2015,** *54* (1), 462-471.
7.   Zhang, L.; Peng, X.-M.; Damu, G. L. V.; Geng, R.-X.; Zhou, C.-H., Comprehensive Review in Current Developments of Imidazole-Based Medicinal Chemistry. *Medicinal Research Reviews* **2014,** *34* (2), 340-437.
8.   Fortman, G. C.; Nolan, S. P., N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: a perfect union. *Chemical Society Reviews* **2011,** *40* (10), 5151-5169.
9.   Shannon, M. S.; Bara, J. E., Properties of Alkylimidazoles as Solvents for CO2 Capture and Comparisons to Imidazolium-Based Ionic Liquids. *Industrial & Engineering Chemistry Research* **2011,** *50* (14), 8665-8677.
10.   Tomizaki, K.; Kanakubo, M.; Nanjo, H.; Shimizu, S.; Onoda, M.; Fujioka, Y., (13)C NMR Studies on the Dissolution Mechanisms of Carbon Dioxide in Amine-Containing Aqueous Solvents at High Pressures toward an Integrated Coal Gasification Combined Cycle-Carbon Capture and Storage Process. *Ind Eng Chem Res* **2010,** *49* (3), 1222-1228.
11.   Du, Y.; Yuan, Y.; Rochelle, G. T., Capacity and absorption rate of tertiary and hindered amines blended with piperazine for CO2 capture. *Chem Eng Sci* **2016,** *155*, 397-404.
12.   Puxty, G.; Richner, G.; Maria, P. H. Absorbent Solution for Absorption of Acid Gas and Process for Absorption of Acid Gas. US2015/0367281A1, **2015**.
13.   Emel'yanenko, V. N.; Portnova, S. V.; Verevkin, S. P.; Skrzypczak, A.; Schubert, T., Building blocks for ionic liquids: Vapor pressures and vaporization enthalpies of 1-(n-alkyl)-imidazoles. *The Journal of Chemical Thermodynamics* **2011,** *43* (10), 1500-1505.
14.   Emel'yanenko, V. N.; Portnova, S. V.; Verevkin, S. P.; Skrzypczak, A., Building Blocks for Ionic Liquids: A Study of Alkyl Chain Length Dependence of Vaporization Enthalpies of 1-(n-Alkyl)-2-methylimidazoles. *Journal of Chemical & Engineering Data* **2011,** *56* (9), 3532-3540.
15.   Du, Y.; Wang, Y. K.; Rochelle, G. T., Thermal degradation of novel piperazine-based amine blends for CO2 capture. *International Journal of Greenhouse Gas Control* **2016,** *49*, 239-249.
16.   Martin, S.; Lepaumier, H.; Picq, D.; Kittel, J.; de Bruin, T.; Faraj, A.; Carrette, P. L., New Amines for CO2 Capture. IV. Degradation, Corrosion, and Quantitative Structure Property Relationship Model. *Ind Eng Chem Res* **2012,** *51* (18), 6283-6289.
17.   Lenarcik, B.; Ojczenasz, P., The influence of the size and position of the alkyl groups in alkylimidazole molecules on their acid-base properties. *Journal of Heterocyclic Chemistry* **2002,** *39* (2), 287-290.
18.   Evjen, S.; Fiksdahl, A., Syntheses of polyalkylated imidazoles. *Synthetic Communications* **2017,** *47* (15), 1392-1399.
19.   Kim, I.; Jens, C. M.; Grimstvedt, A.; Svendsen, H. F., Thermodynamics of protonation of amines in aqueous solutions at elevated temperatures. *The Journal of Chemical Thermodynamics* **2011,** *43* (11), 1754-1762.
20.   Hamborg, E. S.; Versteeg, G. F., Dissociation Constants and Thermodynamic Properties of Amines and Alkanolamines from (293 to 353) K. *J Chem Eng Data* **2009,** *54* (4), 1318-1328.
21.   Kim, J. H.; Dobrogowska, C.; Hepler, L. G., Thermodynamics of Ionization of Aqueous Alkanolamines. *Can J Chem* **1987,** *65* (8), 1726-1728.
22.   Hartono, A.; Vevelstad, S. J.; Ciftja, A.; Knuutila, H. K., Screening of strong bicarbonate forming solvents for CO2 capture. *International Journal of Greenhouse Gas Control* **2017,** *58*, 201-211.

23.   Svensson, H.; Hulteberg, C.; Karlsson, H. T., Heat of absorption of CO2 in aqueous solutions of N-methyldiethanolamine and piperazine. *International Journal of Greenhouse Gas Control* **2013,** *17*, 89-98.

24.   Kim, I.; Hoff, K. A.; Mejdell, T., Heat of Absorption of CO2 with Aqueous Solutions of MEA: New Experimental Data. *Energy Procedia* **2014,** *63*, 1446-1455.

25.   Knuutila, H. K.; Nannestad, Å., Effect of the concentration of MAPA on the heat of absorption of CO2 and on the cyclic capacity in DEEA-MAPA blends. *International Journal of Greenhouse Gas Control* **2017,** *61*, 94-103.

26.   Aronu, U. E.; Gondal, S.; Hessen, E. T.; Haug-Warberg, T.; Hartono, A.; Hoff, K. A.; Svendsen, H. F., Solubility of CO_2 in 15, 30, 45, and 60 mass% MEA from 40°C to 120°C and model representation using the extended UNIQUAC framework. *Chem. Eng. Sci.* **2011,** *66* (24), 6393-6406.

27.   Peng, D.; Robinson, D. B., A New Two-Constant Equation of State. *Ind Eng Chem Fund* **1976,** *15* (1), 59-64.

28.   Bruder, P.; Lauritsen, K. G.; Mejdell, T.; Svendsen, H. F., CO2 capture into aqueous solutions of 3-methylaminopropylamine activated dimethyl-monoethanolamine. *Chemical Engineering Science* **2012,** *75*, 28-37.

29.   Sanchez-Fernandez, E.; Heffernan, K.; van der Ham, L.; Linders, M. J. G.; Brilman, D. W. F.; Goetheer, E. L. V.; Vlugt, T. J. H., Analysis of Process Configurations for CO2 Capture by Precipitating Amino Acid Solvents. *Ind Eng Chem Res* **2014,** *53* (6), 2348-2361.

30.   Ciftja, A. F.; Hartono, A.; Svendsen, H. F., C-13 NMR as a method species determination in CO2 absorbent systems. *International Journal of Greenhouse Gas Control* **2013,** *16*, 224-232.

31.   Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010,** *29* (9), 2176-2179.

32.   Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J. P. E., Enthalpies of absorption and solubility of CO2 in aqueous solutions of methyldiethanolamine. *Fluid Phase Equilibria* **1997,** *140* (1), 171-182.

33.   Kim, I.; Svendsen, H. F., Comparative study of the heats of absorption of post-combustion CO2 absorbents. *International Journal of Greenhouse Gas Control* **2011,** *5* (3), 390-395.

34.   Tomizaki, K.; Shimizu, S.; Onoda, M.; Fujioka, Y., Heats of Reaction and Vapor-Liquid Equilibria of Novel Chemical Absorbents for Absorption/Recovery of Pressurized Carbon Dioxide in Integrated Coal Gasification Combined Cycle-Carbon Capture and Storage Process. *Ind Eng Chem Res* **2010,** *49* (3), 1214-1221.

35.   Fernandez, E. S.; Heffernan, K.; van der Ham, L. V.; Linders, M. J. G.; Eggink, E.; Schrama, F. N. H.; Brilman, D. W. F.; Goetheer, E. L. V.; Vlugt, T. J. H., Conceptual Design of a Novel CO2 Capture Process Based on Precipitating Amino Acid Solvents. *Ind Eng Chem Res* **2013,** *52* (34), 12223-12235.

36.   Kumar, P. S.; Hogendoorn, J. A.; Timmer, S. J.; Feron, P. H. M.; Versteeg, G. F., Equilibrium solubility of CO2 in aqueous potassium taurate solutions: Part 2. Experimental VLE data and model. *Ind Eng Chem Res* **2003,** *42* (12), 2841-2852.

37.   Shen, S. F.; Yang, Y. N.; Wang, Y.; Ren, S. F.; Han, J. Z.; Chen, A. B., CO2 absorption into aqueous potassium salts of lysine and proline: Density, viscosity and solubility of CO2. *Fluid Phase Equilibria* **2015,** *399*, 40-49.

38.   Aronu, U. E.; Hoff, K. A.; Svendsen, H. F., CO2 capture solvent selection by combined absorption-desorption analysis. *Chemical Engineering Research and Design* **2011,** *89* (8), 1197-1203.

39.   Yamada, H.; Chowdhury, F. A.; Goto, K.; Higashii, T., CO2 solubility and species distribution in aqueous solutions of 2-(isopropylamino)ethanol and its structural isomers. *International Journal of Greenhouse Gas Control* **2013,** *17*, 99-105.