Aminoalkyl-functionalized pyridines as high cyclic capacity CO_2 absorbents

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Abstract

Recent years have witnessed a growing academic interest in development of new CO_2 capture solvents to reduce the capture costs. This study focused on nine picolylamines (three commercial and six synthesized) and one imidazole-amine, most of which have not previously been reported as amine absorbents. The solvent performance was evaluated by measuring the absorption capacity, desorption tendency and pK_a. Several of the amines demonstrated CO_2 cyclic capacity significantly higher than that of 30 wt% MEA due to very lean CO_2 loadings, driven by low amine pK_a. The lean loadings can potentially mitigate solvent degradation. At the same time, absorption rates comparable to 30 wt% MEA were obtained for 3 M picolylamines. The results demonstrate the promising nature of picolylamines and derivatives for CO_2 capture.

1. Introduction

Aqueous alkanolamines are the conventional absorbents for post-combustion absorption of CO_2. Monoethanolamine (MEA) has been considered the benchmark since its introduction,[1] and together with diethanolamine (DEA) and *N*-methyldiethanolamine (MDEA) have seen wide implementation in gas separation technologies for the natural gas and oil industry.[2] The presence of an alcohol functionality affords low volatility and high aqueous solubility, allowing for high amine concentration, and thus high CO_2 capacity in MEA.[2] However, MEA has strong tendencies for degradation and corrosion.[3] Furthermore, significant energy is required to remove absorbed CO_2 from MEA solutions. Several new solvents have been developed to address the challenges with using MEA.[4] Piperazine (PZ) is used both as rate enhancing agent and as an absorbent, and is generally considered more stable than alkanolamines.[5] Benzylamine (BZA) is also useful to promote CO_2 capture into aqueous amine solutions, and shows high potential cyclic capacity. Furthermore, the aromatic moiety in BZA is highly resistant towards degradative behavior, and is an appealing absorbent for CO_2 capture. Unfortunately, BZA exhibits high volatility and is susceptible to phase-change and carbamate precipitation due to the large non-polar phenyl ring.[6] Similar behavior is observed for aqueous PZ solutions.[7] Improvement in CO_2 absorption-desorption performance compared with PZ has been achieved through targeted synthesis of amino-functionalized piperidines.[8] These results suggest a room for improvements within the molecular space of existing compounds. Development and investigation of absorbents retaining high aqueous solubility, high absorption rate and cyclic CO_2 capacity, but containing more robust structures, are of great interest. Apart from BZA, amino-functionalized aromatic compounds have been scarcely investigated for CO_2 capture,[9, 10] often being perceived as toxic and non-biodegradable. Recently, a strong argument was made for investigation into modified aromatic amines as a new class of absorbents for CO_2 capture, debunking preconceived notions regarding biodegradability and other characteristics.[9]
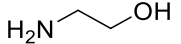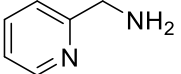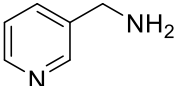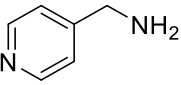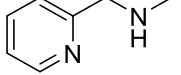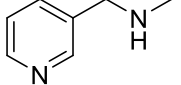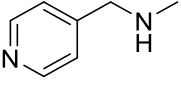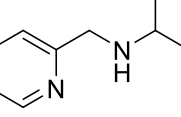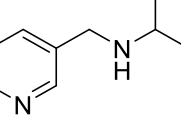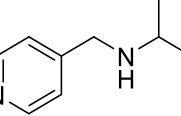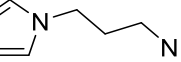
In the following study, the CO_2 absorption capacity, cyclic capacity and absorption rate of ten aminoalkyl-functionalized heterocycles in aqueous solution were investigated. Effects of substitution pattern, amine alkylation and steric hindrance were studied using both commercially available and in-house synthetized compounds. The results demonstrate that aminoalkyl-functionalized heterocycles are promising aqueous absorbents with respect to their high absorption rate throughout the absorption range and their outstanding cyclic capacity.

2. Materials and methods

2.1 Chemicals

Carbon dioxide (CO_2) purity 99.999% and nitrogen (N_2) purity 99.998% were purchased from AGA. Monoethanolamine, 2-picolylamine (2-Pic), 3-picolylamine (3-Pic), 4-picolylamine (4-Pic), 1-(3-aminopropyl)imidazole and chemicals for synthesis were purchased from Sigma-Aldrich. Secondary amines were synthesized from corresponding pyridine carboxaldehydes and appropriate amines by reductive amination with $NaBH_4$, following a literature procedure.[11] By ^{1}H NMR, impurities in methylated picolylamines were determined to be mainly water.

Table 1. Studied molecules with corresponding pK_a values at 23 °C.

Compound	CAS-number	Structure	pK_a	Molecular mass [g/mol]	Purity
Monoethanolamine (MEA)	141-43-5		9.53	61.08	≥99%
2-Picolylamine (2-Pic)	3731-51-9		8.81	108.14	99%
3-Picolylamine (3-Pic)	3731-52-0		8.85	108.14	≥98%
4-Picolylamine (4-Pic)	3731-53-1		8.48	108.14	98%
n-Methyl-1-(pyridin-2-yl)methanamine (2-MePic)	20135-59-6		8.97	122.17	85%
n-Methyl-1-(pyridin-3-yl)methanamine (3-MePic)	20173-04-0		9.04	122.17	85%
n-Methyl-1-(pyridin-4-yl)methanamine (4-MePic)	6971-44-4		8.67	122.17	80%
n-(Pyridin-2-ylmethyl)propan-2-amine (2-iPrPic)	58669-30-0		9.17	150.23	96%
n-(Pyridin-3-ylmethyl)propan-2-amine (3-iPrPic)	19730-12-2		9.19	150.23	93%
n-(Pyridin-4-ylmethyl)propan-2-amine (4-iPrPic)	70065-82-6		8.86	150.23	95%
1-(3-Aminopropyl)imidazole (APIm)	5036-48-6		9.71, 6.57	125.18	≥97%

2.2 Potentiometric measurements

Potentiometric measurements were conducted with a Mettler Toledo G20 compact titrator with a pH-electrode DSC-115 (uncertainty ± 0.02 pH) and temperature sensor DT100 (uncertainty ± 0.1 °C).[12] The experiments were carried out at 23.0 ± 0.2 °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 10.01 from Mettler Toledo). Aqueous amine solution (50 mL, 0.01 M) was automatically titrated with 0.1 M H_2SO_4 solution. All measurements were performed in duplicate and the average values are reported. Average deviation of the duplicates

was < 0.01 pH. 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. Titration of MEA gave a pK_a value of 9.53, which agrees well with literature values varying between 9.44-9.508 at 25 °C.[13-15] Determined amine pK_a values are reported in Table 1. pK_a values for the pyridine protonations were not obtained because the amine concentrations were low, 0.01 M.

2.3 Screening apparatus

The absorption characteristics of the amines were measured using a screening apparatus, shown in Figure 1. The operations of this equipment has been described in several works.[15, 16] The methodology gives reasonable rich loadings and cyclic capacities even though the screening is performed between 40 and 80 °C instead of stripping the solvent at temperatures relevant for industrial use, 100-120 °C.[4, 17] An aqueous amine solution (3 M or 30 wt%, 140-150 mL) was added to the reactor, and the reactor was closed, except for the gas outlet. Upon starting the experiment, the CO_2 analyzer was calibrated by circulating a gas mixture containing 10 vol% CO_2 and 90 vol% N_2 through a bypass valve. The amine solution was heated to 40 ± 0.2 °C, after which the 10 vol% CO_2 in N_2 gas mixture was bubbled through the solution. The gas flow rate was controlled by a Bronkhors® High-Tech mass flow controller. A stirring rate of 400 rpm was maintained for all experiments to ensure good mixing and consistency. After being bubbled through the solution, the gas passed through a water condensers and subsequently one ice-bath condenser to prevent H_2O to enter a Fisher-Rosemount BINOS® 100 NDIR CO_2 analyzer from Emerson Process Management. When the outlet gas concentration reached 9.5 vol% CO_2, the absorption was stopped. The absorption endpoint was selected to mimic a post combustion CO_2 capture with 90% CO_2 removal. A sample (3-4 mL) was taken after absorption for amine and CO_2 analysis. Throughout the absorption sample temperature, inlet gas velocity and the CO_2 concentration in outlet gas as a function of CO_2 loading was logged using Labview. After absorption, CO_2 was desorbed from the amine solution at 80 °C by N_2 sparging. When the CO_2 concentration in the outlet gas dropped below 1.0 vol%, the desorption experiment was terminated. A sample for amine and CO_2 analysis was collected after the desorption.

The amine concentration in samples was measured by titration with 0.1 M H_2SO_4 by a Mettler Toledo G20 titrator, and using Lab X3.1 software to determine the equivalence point. Titrations were performed in duplicate and deviation between samples were < 1%. A thorough description of the procedure and uncertainties are given by Kim et al.[18] Determination of CO_2 concentration in the liquid phase was performed using a Shimadzu TOC-L Total Organic Carbon Analyzer. The CO_2 was detected with a non-dispersive infrared (NDIR) sensor, measuring IR radiation of the CO_2 specific absorption wavelength. Inorganic carbon samples were placed in a Shimdazu ASI-L Auto-sampler. Samples were diluted to 10-500 ppm with MQ water (18.2 Ω). During analysis, samples were acidified using HCl or H_3PO_4, and were sparged with N_2 to remove CO_2. All samples were measured in two parallels. When analyzing each parallel, 4-5 injections were performed and the results were averaged. Deviations between parallels were < 2%. A calibration curve was established using 10, 25, 50, 100, 200 and 500 ppm C solutions. Carbon solutions were prepared from $NaHCO_3$ (ACS reagent $\geq$ 99.7%). Between every three samples, one sample of both MQ water and calibration standard was run to confirm repeatability of measurements.
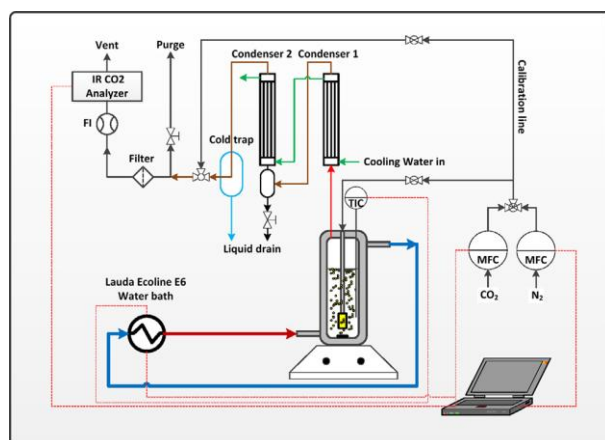
Figure 1. Schematics of the screening apparatus.[15]

The amount of CO_2 absorbed and desorbed throughout the experiments were logged as a function of time by Eq. 1. Where $n_{CO_2}^{in}$ and $n_{N_2}^{in}$ are the molar flows of CO_2 and N_2 to the reactor, respectively, while $x_{CO_2}^{out}$ is the volume fraction of CO_2 leaving the reactor. The accumulated amount of CO_2 absorbed or desorbed was obtained by integrating Eq. 1, Eq. 2.

$$Q_{CO_2}\left[\frac{mol}{s}\right] = n_{CO_2}^{in} - \frac{x_{CO_2}^{out} n_{N_2}^{in}}{1 - x_{CO_2}^{out}} \tag{1}$$

$$N_{CO_2}[mol] = \int_0^t Q_{CO_2}\, dt \tag{2}$$

Eq. 3 converted CO_2 loadings to mol CO_2/mol amine, α. $N_{amine,liq}$ is the number of moles of amine in the liquid phase.

$$\alpha_{screening}\left[\frac{mol\ CO_2}{mol\ amine}\right] = \frac{N_{CO_2}}{N_{amine,liq}} \tag{3}$$

The CO_2 loadings from the liquid analysis were considered more accurate. The screening results were corrected by multiplying with the ratio between liquid analysis loading and screening loadings, r, Eq. 4.

$$\alpha_{corrected}\left[\frac{mol\ CO_2}{mol\ amine}\right] = \alpha_{screening} \cdot r \tag{4}$$

Average absorption rate was calculated in accordance with Eq. 5.

$$Q_{average,CO_2}\left[\frac{mol}{s}\right] = \frac{1}{\alpha_1 - \alpha_o}\int_{\alpha_0}^{\alpha_1} Q_{CO_2}\, d\alpha \tag{5}$$

3. Results and Discussion

3.1 Absorption and cyclic capacities

The CO_2 absorption and cyclic capacities of 3 M aqueous heterocyclic amines are presented in Figure 2. MEA (30 wt%) was used as a reference. The results for 30 wt% MEA (α_{rich} = 0.51 mol CO_2/mol amine) are in good agreement with previously reported values.[16, 19] The absorption capacity of the primary picolylamines 2-Pic, 3-Pic and 4-Pic (α_{rich} = 0.46-0.48 mol CO_2/mol amine) was comparable to that of the methylated picolylamines 2-MePic, 3-MePic and 4-MePic (α_{rich} = 0.44-0.47 mol CO_2/mol amine). Improved rich loading was obtained for 4-MePic compared to 4-Pic, due to higher pK_a (Table 1 and Figure 2). The isopropyl-functionalized amines had low absorption rates and the absorption capacity is drastically reduced. The more sterically hindered isopropyl picolylamines do not form stable carbamates and instead absorbs CO_2 as bicarbonate, explaining the low absorption rates (Figure 3). 3-iPrPic appeared to form a slightly more stable carbamate, due to either less steric hindrance or the higher amine pK_a. APIm obtained a higher absorption capacity (α_{rich} = 0.56 mol CO_2/mol amine) than MEA, due to favorable interactions between the imidazole moiety and the carbamate. In APIm, the imidazole is sufficiently alkaline to be protonated by CO_2. Both pyridines and imidazoles are weakly basic and do not react with CO_2 to form carbamate.[20] Picolylamine absorption capacities suggest that the pyridine moiety does not enhance CO_2 absorption capacity, in agreement with reported pyridine CO_2 loadings.[21]

The primary and methylated picolylamines experienced 46-63% higher cyclic capacities than MEA, due to very lean CO_2 loadings (α_{lean} = 0.02-0.07 mol CO_2/mol amine) after desorption (Figure 2). The picolylamine lean loadings are comparable to that of tertiary amines tested in the same system, α_{lean} = 0.01-0.05, a property rarely observed among primary and secondary amines.[4, 16, 22] 4-Pic and 4-MePic had higher cyclic capacities than the other substituent patterns, because less alkaline amines have reduced carbamates stability.[4] These results indicate that picolylamines can be regenerated substantially easier than other primary and secondary amines, and in agreement with what was proposed for aromatic amines a recent work.[9] The picolylamines obtain very lean loadings due to their relatively low pK_a compared with other amines, and possibly the high heat of protonation for aromatic amines.[9, 22] Reduced

carbamate stability has been proposed for aromatic amines, caused by the structural rigidity of the carbamate.[9] The lower carbamate stability of aromatic amines compared with alkylamines is demonstrated by the change in absorption mechanism for isopropyl picolylamines. Isopropyl ethanolamine (IPAE) forms carbamate during CO_2 absorption.[15, 23] APIm, where the distance between the amine and heterocyclic functionality is greater, CO_2 is not as readily desorbed, and the lean loading is closer to MEA. Nevertheless, APIm is more readily regenerated than MEA and possesses 35% better cyclic capacity.
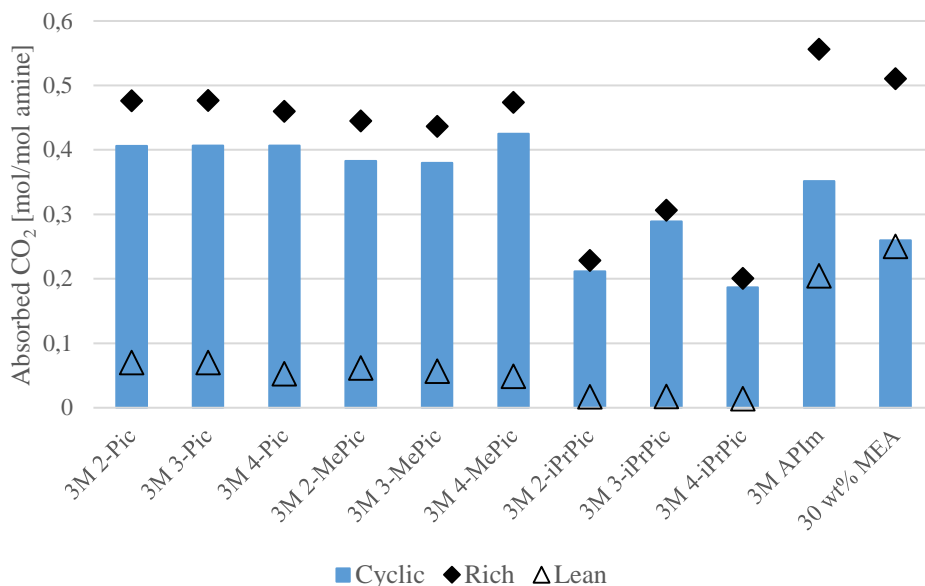

Figure 2. CO_2 absorption performance of amines: Rich loading at 40 °C, 9.5 vol% CO_2, lean loading at 80 °C, 1 vol% CO_2, and cyclic capacity (mol CO_2/mol amine) of aqueous 3 M aminoalkyl-functionalized heterocycles and 30 wt% MEA.

3.2 Absorption rate

The CO_2 absorption rate of amines as a function as CO_2 loading, α, is shown in Figure 3. MEA (30 wt%) has the fastest absorption rate, but also higher amine concentration. The most alkaline amine, APIm, had the highest absorption rate of the 3 M solutions. 3-MePic was the fastest absorbing picolylamine. In general, the CO_2 absorption rates of the amines correlated well with amine pK_a values. All three methylated picolylamines had higher absorption rates than their unsubstituted counterparts. A substantial increase in absorption rate was obtained for 2-MePic compared with 2-Pic. The reason for the low rate of 2-Pic could be the result of steric effects, but considering the higher rate of 2-MePic, it is unlikely. The impact of steric hindrance is clear on the absorption behavior of the isopropyl amines, with 3-iPrPic absorbing considerably faster than 2-iPrPic and 4-iPrPic (Figure 3).

In most absorption processes, the initial rate of absorption is of minor importance, as the complete desorption of CO_2 during the solvent regeneration is neither obtained nor targeted. Of greater interest is the average absorption rate throughout the absorption or within the absorption-desorption range. In an industrial process, the amine solutions will typically be operated in the range between the rich and lean loadings. The CO_2 content in the amine solution entering the absorber will be determined by the stripper lean loadings, α_{lean}. The average CO_2 absorption rate over the absorption ($\alpha = 0.0$ to $0.95\ \alpha_{rich}$) for the studied amines are depicted in Figure 4 together with the average absorption rate between lean loading and rich loading ($\alpha = \alpha_{lean}$ to $0.95\ \alpha_{rich}$). In both cases a cut-off of $\alpha = 0.95\ \alpha_{rich}$ was used as the rates at higher loadings decreased significantly and these loadings are thus less suitable for industrial operations. The lean loading, α_{lean}, of each solvent was selected as the loading after desorption.

MEA had the fastest absorption rate of the amine solutions over the full loading range, $\alpha = 0.0$ to $0.95\ \alpha_{rich}$, due to a higher amine concentration. The methylated picolylamines reacted faster with CO_2 than the unsubstituted

picolylamines. Over the resembled industrial loading range, $\alpha = \alpha_{lean}$ to 0.95 α_{rich}, 2-MePic and 3-MePic exhibited higher absorption rates compared with MEA, whereas 3 M 3-Pic, 4-Pic and 4-MePic had slightly slower absorption rates, Figure 4. The average APIm and MEA absorption rates were substantially reduced when considering the cyclic loading range compared with the full range. The average absorption rate reduction for the picolylamines was smaller when considering cyclic range instead of full range, due to the lean loadings reached during the desorption step, $\alpha_{lean, MEA} > \alpha_{lean,Pic}$. Amines possessing high cyclic capacity and high absorption rate are desirable, as indicated with an arrow in Figure 4. Based on this consideration, the three methylated amines and two of the unsubstituted amines are promising amines for CO_2 capture with higher cyclic capacities and comparable absorption rates to that of MEA.
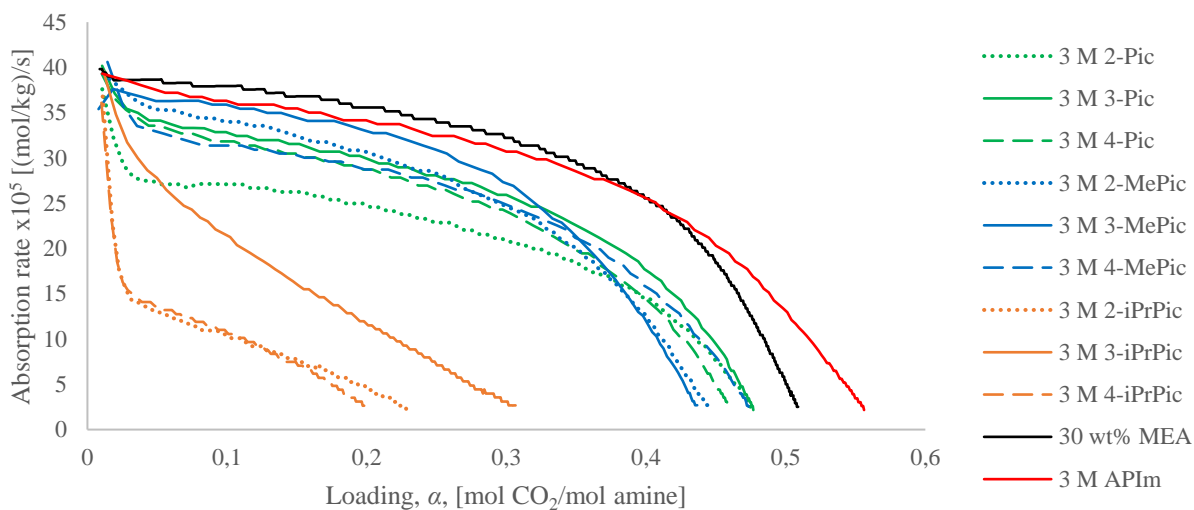
Figure 3. CO_2 absorption rate and absorption capacity at 40 °C of 3 M aminoalkyl-funcionalized heterocycles and 30 wt% MEA.
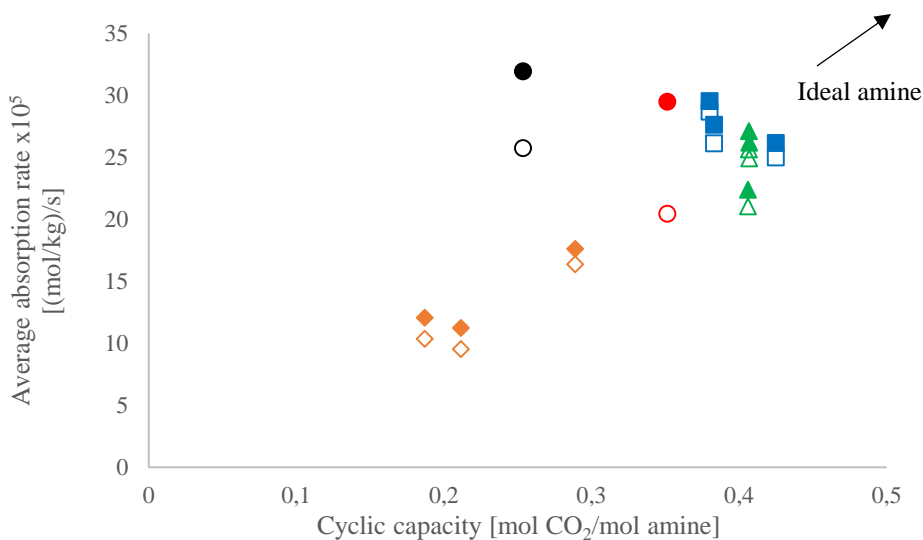
Figure 4. Average absorption rate given as cyclic capacity of different aqueous 3 M primary picolylamines (green triangle), methylated (blue square), isopropylated (orange diamond), 3 M APIm (red circle) and 30 wt% MEA (black circle), from loadings of $\alpha = 0.0$ to 0.95 to maximum absorption loading, α_{rich}, (filled markers) and from desorption loading to 0.95 maximum absorption loading (empty markers).

In addition to the promising absorption rate and cyclic capacity results, the heterocyclic alkylamines have other characteristics highlighting the potential of this new class of solvents. The presence of an alkaline aromatic ring increases the aqueous solubility significantly compared with phenylamines, such as benzylamine and phenethylamine.[24] The isopropyl-functionalized amines were readily soluble as 3 M solutions, and no phase-change occurred for any of the amines during absorption. No precipitation was observed during storage of loaded aqueous solutions at 4 °C. Picolylcarbamate/picolyl ammonium crystals formed around the cap of the bottles over time.[10] Neat APIm, *N*-methyl and *N*-isopropylpicolylamines did not form CO_2 containing crystals within 3 months of storage. Picolylamines are less volatile (b. p. 3-Pic: 226 °C) and more hydrophilic than BZA (b. p. 185 °C), reducing the relative amine vapor pressure.[25] Amine degradation[3] and corrosion[26] rates are closely related to CO_2 concentration in solution. Thus, picolylamine solvents possessing very lean CO_2 loadings are promising aqueous absorbents for post combustion capture. Further investigation into picolylamines may potentially lead to a process with significantly reduced absorption costs.

4. Conclusion

Nine picolylamines and an aminoalkylimidazole were investigated as potential CO_2 absorbents. The picolylamines readily release CO_2 at 80 °C, affording improved stripping behavior compared with other primary and secondary amines. Both primary and methylated picolylamines showed absorption rates similar to those of MEA and up to 63% higher cyclic capacity. Improved absorption rate is obtained by methylation of picolylamines. The low picolylamine lean loadings may be explained by their low pK_a values and potentially the structural rigidity of the carbamate. A higher CO_2 capacity was obtained for APIm compared with MEA, but absorption rates were lower. Further work should focus on vapor-liquid equilibria, stability and corrosion studies to validate the potential of picolylamine based solvents. Eventually, aminoalkyl-functionalized pyridines may represent efficient CO_2 capture absorbents.

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Author Contributions
All authors have given approval to the final version of the manuscript.

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Supporting Information

Aminoalkyl-functionalized pyridines as high cyclic capacity CO_2 absorbents

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Table S1. CO_2 loadings as mol/kg solution and mol/mol amine after absorption and desorption, with corresponding cyclic capacity [mol/mol amine] for different aqueous 3 M heterocyclic alkyl amines and 30 wt% MEA.

Solution	CO_2 absorption loading		CO_2 desorption loading		Cyclic capacity
	[mol/kg]	[mol/mol amine]	[mol/kg]	[mol/mol amine]	[mol/mol amine]
3 M 2-Pic	1.35	0.48	0.21	0.07	0.41
3 M 3-Pic	1.35	0.48	0.21	0.07	0.41
3 M 4-Pic	1.30	0.46	0.15	0.05	0.41
3 M 2-MePic	1.08	0.44	0.16	0.06	0.38
3 M 3-MePic	1.06	0.44	0.14	0.06	0.38
3 M 4-MePic	1.06	0.47	0.12	0.05	0.42
3 M 2-iPrPic	0.64	0.23	0.048	0.02	0.21
3 M 3-iPrPic	0.82	0.31	0.049	0.02	0.29
3 M 4-iPrPic	0.56	0.20	0.040	0.01	0.19
3 M APIm	1.56	0.56	0.60	0.20	0.35
30 wt% MEA	2.26	0.51	1.16	0.25	0.26

^{1}H NMR were recorded on a Bruker Avance DPX 400 MHz spectrometer. Chemical shifts are expressed in ppm (δ) and referenced to tetramethylsilane (TMS). Multiplicity of the signals is reported as singlet (s), doubled (d), triplet (t), heptet (h), multiplet (m) or a combination of these. Solvent used for NMR was d_6-DMSO.

n-Methyl-1-(pyridin-2-yl)methanamine (2-MePic) ^{1}H NMR (400 MHz, DMSO) δ (ppm): 8.49-8.48 (1H, m), 7.76-7.72 (1H, m), 7.42-7.40 (1H, m), 7.24-7.21 (1H, m), 3.73 (2H, s), 2.29 (3H, s).[1]

n-Methyl-1-(pyridin-3-yl)methanamine (3-MePic) ^{1}H NMR (400 MHz, DMSO) δ (ppm): 8.52-8.51 (1H, m), 8.45-8.43 (1H, m), 7.73-7.70 (1H, m), 7.34-7.29 (1H, m), 3.64 (2H, s), 2.25 (3H, s).[2]

n-Methyl-1-(pyridin-4-yl)methanamine (4-MePic) ^{1}H NMR (400 MHz, DMSO) δ (ppm): 8.51-8.46 (2H, m), 7.34-7.30 (2H, m), 3.66 (2H, s), 2.26 (3H, s).[3]

n-(Pyridin-2-ylmethyl)propan-2-amine (2-iPrPic) ^{1}H NMR (400 MHz, DMSO) δ (ppm): 8.49-8.47 (1H, m), 7.74-7.70 (1H, m), 7.43-7.41 (1H, m), 7.22-7.19 (1H, m), 3.79 (2H, s), 2.72 (1H, h, $J = 6.3$ Hz), 1.01 (6H, d, $J = 6.3$ Hz).[4]

n-(Pyridin-3-ylmethyl)propan-2-amine (3-iPrPic) ^{1}H NMR (400 MHz, DMSO) δ (ppm): 8.53-8.52 (1H, m), 8.43-8.41 (1H, m), 7.75-7.73 (1H, m), 7.33-7.30 (1H, m), 3.70 (2H, s), 2.68 (1H, h, $J = 6.2$ Hz), 1.00 (6H, d, $J = 6,2$ Hz).[5]

n-(Pyridin-4-ylmethyl)propan-2-amine (4-iPrPic) ^{1}H NMR (400 MHz, DMSO) δ (ppm): 8.48-8.46 (2H, m), 7.35-7.34 (2H, m), 3.71 (2H, s), 2.66 (1H, h, $J = 6.3$ Hz), 0.99 (6H, d, $J = 6.3$ Hz).[6]

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