Influence of pKa on solvent performance of MAPA promoted tertiary amines

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Influence of pKa on solvent performance of MAPA promoted tertiary amines

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Abstract

In the present work, absorption and desorption performance of ten single tertiary amines and their blends with MAPA was studied using a screening apparatus. Absorption experiments were conducted at 40 °C and up to 9.5 kPa partial pressure of CO_2, while desorption experiments were conducted at 80 °C and down to 1.0 kPa partial pressure of CO_2. In addition, the pKa value of the studied amines was measured at 25 °C.

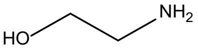
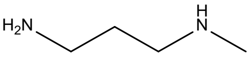
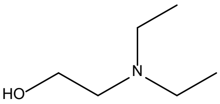
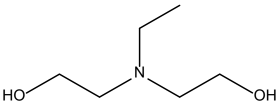
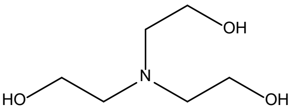
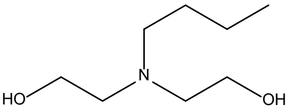
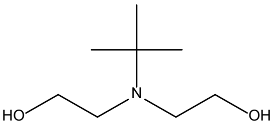
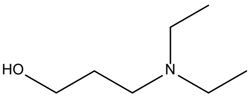
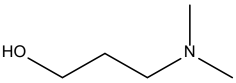
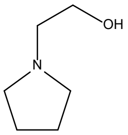
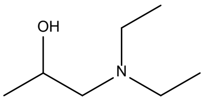
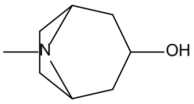
The results indicated that the optimal pKa of the tertiary amines, giving the highest absorption capacity and cyclic capacity, was in the range of 9.48 to 10.13. At a higher pKa value, the cyclic capacity was decreased. Further, addition of MAPA to the tertiary amines influenced the absorption performance by increasing the absorption capacity for tertiary amines with low pKa (7.79-9.03) and decreasing the absorption capacity for tertiary amines with high pKa (9.48-10.42). Also, the CO_2 absorption rate was significant enhanced by addition of MAPA.

1 Introduction

Amine-based chemical absorption is the most developed method to capture CO_2 from the flue gas of fossil fuel-fired power plants. However, a major obstacle for commercial application is the high capital cost and the high energy needed to regenerate the solvent (Liang et al., 2015). To minimise the cost and the energy penalty, it is important to continue developing new solvents. A solvent with fast reaction kinetics will reduce the size and operating cost of the absorber, and a solvent with high cyclic capacity will reduce the sensible heat loss and the size of the cross heat exchanger. A solvent system that has received great attention is blended amine solvents in which a primary or secondary amine is blended with a tertiary amine (Conway et al., 2015; Du et al., 2016). The blended amines can lead to considerable improvements in chemical absorption as they combine the advantages of the amines that are mixed. The carbamate forming primary/secondary amines enhance the reaction kinetics, while the bicarbonate promoting tertiary amines lower the heat of absorption and obtain high absorption capacity (Kohl and Nielsen, 1997). A well-studied blended amine system, that has shown potential to reduce the energy penalty, is 2-(Diethylamino)ethanol (DEEA)/ 3-(Methylamino)propylamine (MAPA) (Arshad et al., 2013; Knuutila and Nannestad, 2017; Monteiro et al., 2015; Pinto et al., 2014). DEEA is a tertiary amine and MAPA is a diamine, consisting of both a primary and a secondary amine. At a certain concentration of DEEA and MAPA, the blend forms two distinct liquid phases upon CO_2 loading; one CO_2-lean phase and one CO_2-rich phase. Pinto et al. (2014) tested the two phase system 5M DEEA + 2M MAPA in a pilot plant campaign and obtained a specific reboiler duty of less than 2.4 GJ/ton of CO_2. Thus, significant lower than 30wt% MEA. However, a disadvantage of the blended system is that it was found to be more volatile than MEA. Hartono et al. (2013), who conducted ebulliometric measurements, showed that in aqueous solution DEEA was more volatile than MAPA. Therefore, it is of interest to substitute DEEA with another tertiary amine.

This work investigates the CO_2 absorption capacity, cyclic capacity and the absorption rate of ten single tertiary amines and their blends with MAPA using a screening apparatus. The tertiary amines were selected based on molecular structure in which both the number of hydroxyl groups and number of carbons were varied (Table 1). Additionally, the pKa value is measured and the influence of the pKa value of the tertiary amine on the absorption/desorption performance is studied.

Table 1. Molecular structure of the studied amines

Chemical name	CAS-number	Molecular structure	Molar mass (g/mol)
Monoethanolamine (MEA)	141-43-5		61.08
3-(Methylamino)propylamine (MAPA)	6291-84-5		88.15
2-(Diethylamino)ethanol (DEEA)	100-37-8		117.19
N-Ethyldiethanolamine (EDEA)	139-87-7		133.19
Triethanolamine (TEA)	102-71-6		149.19
N-Butyldiethanolamine (BDEA)	102-79-4		161.24
N-*tert*-Butyldiethanolamine (t-BDEA)	2160-93-2		161.24
3-Diethylamino-1-propanol (3DEA1P)	622-93-5		131.22
3-Dimethylamino-1-propanol (3DMA1P)	3179-63-3		103.16
1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD)	2955-88-6		115.17
1-Diethylamino-2-propanol (1DEA2P)	4402-32-8		131.22
Tropine	120-29-6		141.21

2 Materials and Methods

2.1 Materials

Monoethanolamine (purity ≥ 99%), 3-(Methylamino)propylamine (purity ≥97%), 2-(Diethylamino)ethanol (purity ≥99.5%), N-Ethyldiethanolamine (purity 98%), Triethanolamine (purity ≥99.0%), N-Butyldiethanolamine (purity ≥98.6%), 3-dimethylamino-1-propanol (purity 99%), 3-Dimethylamino-1-propanol (purity 99%) and Tropine (purity ≥97%) were purchased from Sigma-Aldrich. N-tert-Butyldiethanolamine (purity >97%), 3-Diethylamino-1-propanol (purity >95%) and 1-Diethylamino-2-propanol (purity ≥98%) were purchased from TCI Europe, while 1-(2-Hydroxyethyl)pyrrolidine (purity 98%) was purchased from Chiron. The chemicals were used without further purification. Additionally, Carbon dioxide (CO_2) with purity 99.999% and Nitrogen (N_2) with purity 99.998% were purchased from AGA, and the antifoam Polyporpylene Glycol (CAS: 25322-69-4) was purchased from Nalco/Exxon Energy Chemicals L.P.

The aqueous amine solutions studied in this work (Table 2) were prepared by weighing the required amount of the amines using the Mettler Toledo MS6002S Scale, with an uncertainty of $\pm 10^{-5}$ kg. The solutions were made up to volume with deionised water. The total concentration of the blended MAPA systems was 4M and/or 2M solutions. A lower solvent concentration was used due to low solubility of Tropine and 1DEA2P. Further, foaming issues were observed for the solutions containing EDEA and BDEA. Therefore, 1000 ppm antifoam was added to these solutions prior the experiment.

Table 2. Aqueous molar concentration

Amine	Molar concentration (mol/L)
Single amines	
TEA*, EDEA*, BDEA*, t-BDEA*, DEEA*, 3DMA1P, 3DEA1P, 1-(2HE)PRLD	3 M
DEEA, 1DEA2P, 3DEA1P, Tropine	1.5 M
Blended amines	
TEA*, EDEA*, BDEA*, t-BDEA*, DEEA*, 3DMA1P, 3DEA1P, 1-(2HE)PRLD	3M tertiary + 1M MAPA
TEA, EDEA, BDEA, t-BDEA, DEEA, 3DMA1P, 3DEA1P, 1-(2HE)PRLD	2M tertiary + 2M MAPA
DEEA, 1DEA2P, 3DEA1P, Tropine	1.5M tertiary + 0.5M MAPA
DEEA, 1DEA2P, 3DEA1P, Tropine	1M tertiary + 1M MAPA

*(Bernhardsen et al., 2017)

2.2 Screening Apparatus

A comparison of the different solvents absorption and desorption performance was obtained using a screening apparatus (Fig. 1). The apparatus, previously used by Hartono et al. (2017b), is designed for atmospheric pressure and can operate at temperatures up to 80 °C. It consists of a jacketed glass reactor (~200 cm^3), Bronkhors® High-Tech mass flow controllers (MFC) and a Fisher–Rosemount BINOS® 100 NDIR CO_2 analyser from Emerson Process Management. The obtained data gave information of the solvents CO_2 absorption rate, absorption capacity and CO_2 cyclic capacity. It should be noted that the obtained absorption rate is only semi-quantitative as it is not possible to ensure that the gas-liquid interfacial area and the bubble structure is the same in each experiment (Ma'mun et al., 2007). However, at 0.1 mol CO_2/mole amine 0.4 mol CO_2/mole amine, the rate data for 30wt% MEA deviated 5% and 14%, respectively, from the rate date reported by Hartono et al. (2017b)

Before the experiment started, the jacketed glass reactor was filled with about 124 g aqueous solution and a gas mixture, containing 10 vol% CO_2 and 90 vol% N_2, was circulated through a bypass valve to calibrate the CO_2 analyser. When the calibration was completed, the bypass valve closed automatically and the absorption experiment started. During the absorption, the gas mixture, with a maximum flow of 1 NL/min, passed through the aqueous solution with a temperature of 40 °C. To ensure good mixing, a magnet stirrer at 450 rpm was used. The gas phase leaving the reactor was cooled by passing through two condensers. The first condenser returned the possible condensate back to the reactor while the second condenser collected the condensate in a separator funnel. After the gas phase was cooled, the CO_2 analyser determined the CO_2 content in the gas phase. The absorption experiment terminated when the outlet gas reached 9.5 vol%CO_2, representing about 9.5 kPa partial pressure of CO_2. This endpoint was chosen to resemble an absorption process where 95% of the CO_2 is captured. Similar approach has been used by several investigators (Aronu et al., 2011b; Hoff et al., 2013).

The desorption experiment started by heating the same solution from 40 °C to 80 °C. When the temperature reached 80 °C, pure N_2 gas (1 NL/min) was introduced into the aqueous solution to enhance the CO_2 removal. Again, the gas phase leaving the reactor was cooled and the CO_2 analyser determined the CO_2 content in the gas phase. The desorption terminated when the outlet gas reached 1.0 vol%CO_2, representing about 1.0 kPa partial pressure of CO_2.

After both the absorption and the desorption experiment, a liquid sample was collected for CO_2 analysis using the precipitation-titration method described in Ma'mun et al. (2006). Briefly, CO_2 precipitated as $BaCO_3$ and excess HCl, which had not been used to dissolve $BaCO_3$, was titrated with 0.1 mol/L NaOH. The automatic titrator (Methrom 809 Titrando equipped with a carrousel) titrated until it reached the endpoint of pH 5.2. Further, due to possible solvent loss during the absorption and desorption experiment, the amine concentration was determined by titration (Ma'mun et al., 2006). A liquid sample of 200 µL was diluted with 50 cm^3 deionised water and titrated with 0.2 mol/L H_2SO_4 using the Mettler Toledo G20 compact titrator. The titrator titrated until it reached the endpoint of pH 2.5. On average, the amine concentration after the absorption experiments was found to deviate 2.5% from the initial concentration, while the amine concentration after the desorption experiments was found to deviate 3.4%. Thus, owing to the higher temperature during desorption, the amine concentration after desorption deviated most from the initial concentration due to some solvent loss during the experiment. The obtained amine concentration was used to establish the CO_2 loading of the collected liquid samples. Both, the CO_2 and the amine analysis were repeated two times with a deviation of less than 3%.

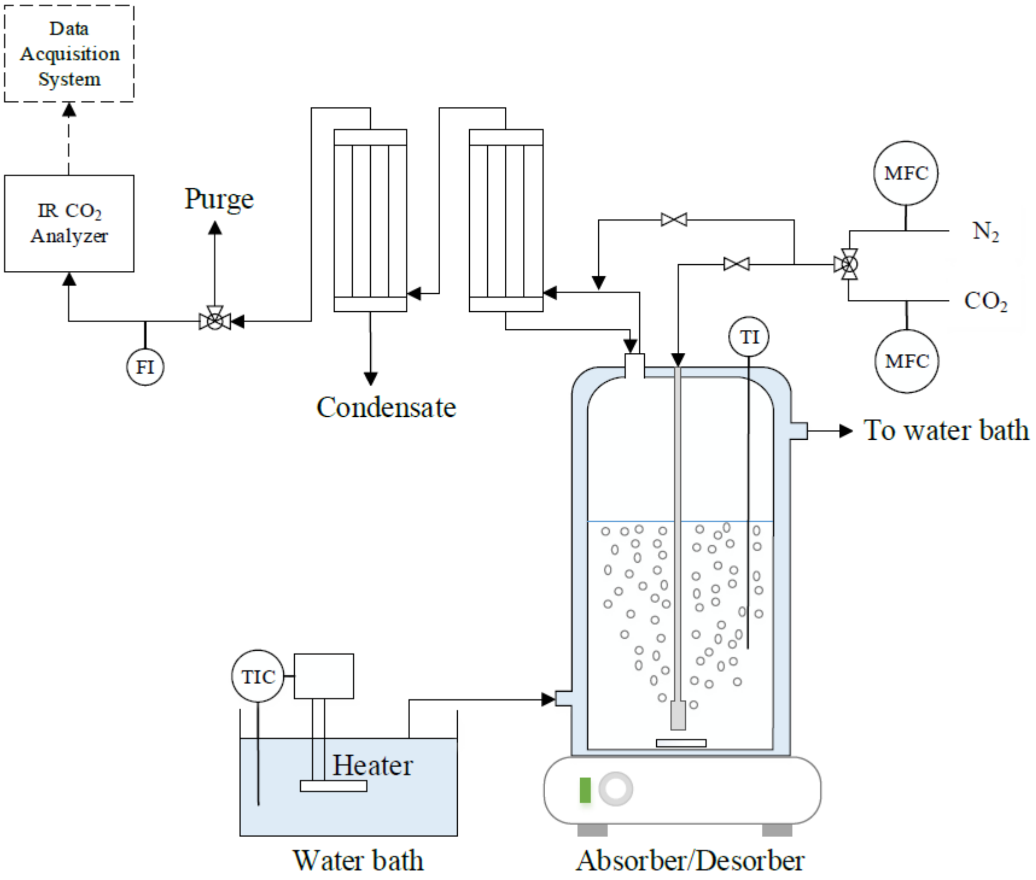


Fig. 1 Simplified flow diagram of the screening apparatus

2.2.1 Absorption - desorption calculations

During the screening experiments, the amount of CO_2 absorbed and desorbed were logged as a function of time by the following formula:

$$Q_{CO_2}\left[\frac{\text{mole CO}_2}{\text{s}}\right] = n_{CO_2}^{in} - \frac{x_{CO_2}^{out} n_{N_2}^{in}}{1\text{-}x_{CO_2}^{out}} \quad (1)$$

Where $n_{CO_2}^{in}$ and $n_{N_2}^{in}$ are the mole flow of CO_2 and N_2 fed into the reactor per seconds, respectively, and $x_{CO_2}^{out}$ is the volume fraction of CO_2 in the gas phase leaving the reactor.

The accumulated amount of CO_2 absorbed/desorbed was obtained by integration using Equation 2.

$$N_{CO_2}\left[\text{mole CO}_2\right] = \int_0^t Q_{CO_2}\,dt \quad (2)$$

The unit of CO_2 loading used in this work, mole CO_2/mole amine group and mole CO_2/kg solution, was obtained using equation 3 and 4, respectively. In equation 3, the accumulated amount of CO_2 is divided by the number of amine groups, $no_{\text{amine group}}$, and in equation 4, the accumulated amount of CO_2 is divided by the mass of solution, m_{solution}, added to the reactor.

$$\alpha_{\text{screening}}\left[\frac{\text{mole CO}_2}{\text{mole amine group}}\right] = \frac{N_{CO_2}}{no_{\text{amine group}}} \quad (3)$$

$$\alpha_{\text{screening}}\left[\frac{\text{mole CO}_2}{\text{kg solution}}\right] = \frac{N_{CO_2}}{m_{\text{solution}}} \quad (4)$$

The CO_2 loading obtained from the liquid analysis was regarded as a more accurate method to determine the CO_2 loading in the liquid phase and was therefore used in all calculations. It was used to correct the screening CO_2 loading and to calculate the screening cyclic capacity. The screening CO_2 loading was corrected by multiplying with a correction factor as following:

$$\alpha_{\text{corrected}}\left[\frac{\text{mole CO}_2}{\text{mole amine group}}\right] = \text{CF} \times \alpha_{\text{screening}} \quad (5)$$

where the correction factor (CF) is given as:

$$\text{Correction Factor (CF) [-]} = \frac{\alpha_{\text{liquid sample}}}{\alpha_{\text{screening,final loading}}} \quad (6)$$

A typical value for the correction factor was 0.94, indicating that the screening apparatus obtained slightly higher rich loadings than the one determined using liquid analysis.

The screening cyclic capacity was calculated by subtracting the CO_2 loading at desorption from the CO_2 loading at absorption:

$$\text{Screening cyclic capacity}\left[\frac{\text{mole CO}_2}{\text{mole amine group}}\right]=\alpha_{\text{abs, liquid sample}}\left(T=40\ ^\circ\text{C}\right)-\alpha_{\text{des, liquid sample}}\left(T=80\ ^\circ\text{C}\right) \qquad 7$$

Further, the CO_2 absorption rate was calculated by the following equation:

$$\text{Abs. rate}\left[\frac{\text{mole CO}_2}{\text{kg solution}\times\text{s}}\right]=\frac{1}{m_{\text{solution}}}\times Q_{CO_2} \qquad 8$$

2.3 pKa measurements

The acid dissociation constant (pKa) of the amines studied in this work was determined using the potentiometric titration method at 25 °C. The measurements were carried out in the same apparatus as applied in Kim et al. (2011) which consisted of a Mettler Toledo G20 compact titrator equipped with a pH-electrode DGi115-SC (uncertainty ± 0.02 pH) and a temperature sensor DT100 (uncertainty ± 0.1 °C). The titration was conducted in a jacketed glass reactor (100 mL volume) where the temperature was controlled using a Julabo M4 heating circulator (temperature stability ± 0.1 °C). The pH electrode was calibrated using technical buffer solutions at pH 4.01, 7.00, 9.21 and 11.00 from Mettler Toledo.

Approximately 35 g of amine solution (0.01 mole amine/kg H_2O) was titrated against 0.1 mol/L HCl solution until the endpoint of pH 2.5. The data were continuously logged using the LabX 3.1 software provided by Mettler Toledo, and the pKa values were calculated as the pH at half equivalence. Each experiment was performed in duplicate and the average was reported as the pKa-value. The difference in pKa value, between the two runs, was less than 0.1%.

3 Results and discussion

3.1 Repeatability and accuracy of the screening experiments

To obtain knowledge about the repeatability of the absorption and desorption screening experiments, selected amine solutions were repeated (see Table 3). For all solutions, the absorption experiments showed a higher repeatability as compared to the desorption experiments. For instance, the relative standard deviation of the absorption and desorption experiment for 30wt% MEA was 1.0 % and 6.4 %, respectively. This difference is believed to be related to the low partial pressure of CO_2 used as a stop criteria during the desorption experiment (1 vol% CO_2). Even small absolute changes in PCO_2 can have an influence on the liquid loading.

Moreover, a significant higher repeatability of the absorption experiments was obtained for the relatively fast reacting amine solutions, 30wt% MEA and blended MAPA solutions, compared to the slower reacting amines, 3M DEEA and 3M 3DEA1P. The fast reacting amine solutions typically finished the absorption experiment after 96-213 min, while the slower reacting amine solutions finished the experiment after 380-441 min. The difference in repeatability can be explained by Fig. 2 which shows the logged CO_2 content in the gas phase, leaving the reactor, as a function of the CO_2 loading for 30wt% MEA and 3M DEEA solutions. Due to this difference in absorption rate, they have a different slope and shape of the curve. 30wt% MEA has a fairly steep slope, while 3M DEEA has a flat slope over the entire CO_2 loading range. Thus, a small change in the slope for DEEA will have a greater impact on the CO_2 loading than for MEA. This is likely the reason for the low repeatability of the single tertiary amines as it made the endpoint slightly different each time.

Further, the high relative standard deviation of the desorption experiment, when using 3M DEEA (52.9 %) and 3M 3DEA1P (14.3 %) solution, is related to the low absolute capacity obtained, like 0.03 mole CO_2/mole amine group.

In conclusion, high repeatability is expected for blended MAPA systems, while a lower repeatability is expected for single tertiary amine solutions.

Table 3. Calculated standard deviation of screening experiments

Solution	Repeated runs	Lowest CO_2 loading obtained (mole CO_2/mole amine group)	Standard deviation (mole CO_2/mole amine group	Relative standard deviation (%)	Average experimental time [min]
30wt % MEA absorption	5	0.51	0.0050	1.0	123
30wt % MEA desorption	5	0.22	0.0160	6.4	99
3M DEEA absorption	5	0.56	0.0400	6.8	441
3M DEEA desorption	5	0.03	0.0240	52.9	82
3M 3DEA1P absorption	2	0.55	0.0350	6.0	380
3M 3DEA1P desorption	2	0.03	0.0050	14.3	93
3M DEEA + 1M MAPA absorption	2	0.53	0.0010	0.2	213
3M DEEA + 1M MAPA desorption	2	0.12	0.0050	4.1	115
2M DEEA + 1M MAPA absorption	2	0.53	0.0003	0.1	185
2M DEEA + 1M MAPA desorption	2	0.21	0.0080	3.7	113
1.5M DEEA + 0.5M MAPA absorption	2	0.64	0.0010	0.2	96

1.5M DEEA + 0.5M MAPA desorption	2	0.14	0.0080	5.2	92

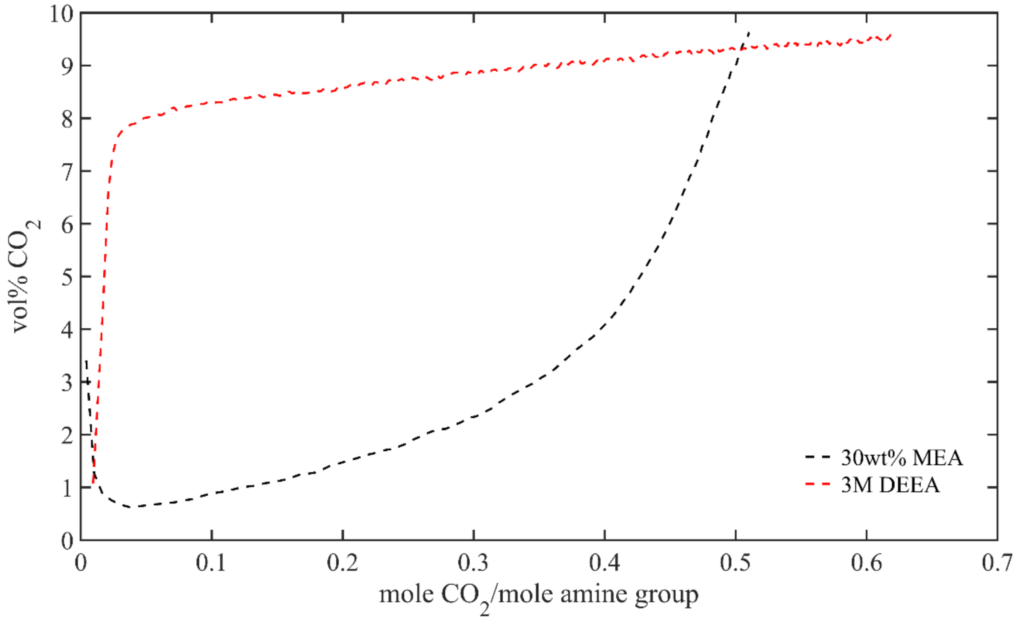


Fig. 2 Relationship between the vol%CO_2 in the gas phase, leaving the reactor, and the CO_2 loading in the absorption experiment using 30wt% MEA and 3M DEEA solution.

The accuracy of the obtained screening absorption and desorption data was evaluated by comparing to available literature equilibrium data at same conditions (T, P). A summary is shown in Table 4. In general, when taking the different concentrations into account, the obtained screening absorption capacities showed a good agreement with the literature. The high deviation for 1M MAPA (7.0-8.6%) might be because the partial pressure of CO_2 in Arshad et al. (2014) was calculated by simply subtracting the saturation pressure of the solution from the total pressure, and not measured. Further, screening desorption data for 3M tertiary amines showed a significant relative deviation from the literature values. It seems that we do not come as close to the equilibrium as we manage with the MEA and MAPA. However, it should be noted that the CO_2 partial pressure from Nouacer et al. (2014) was 5.448 kPa (80 °C) and that the concentrations in the literature were slightly different. Nevertheless, taking into account the different concentrations, between the solutions tested in this work and the equilibrium data found in the literature, and low loadings after the desorption experiments (0.06 to 0.15 mole CO_2/mole amine group) for DEEA, 1-(2HE)PRLD and 3DEA1P, the accuracy of the performed screening experiments is acceptable.

Table 4. Comparison with literature data

Solvent	kPaCO$_2$	T [°C]	Literature			This work		%Error
			mol/L	loading	Ref.	mol/L	loading	
Monoethanolamine (MEA)	9.5	40	4.91	0.52	(Aronu et al., 2011a)	4.91	0.51	0.7
	1.0	80		0.26			0.26	0.7
3-(Methylamino)propylamine (MAPA)	9.5	40	1	0.60	(Arshad et al., 2014)	1	0.55	8.6
	1.3	80		0.39			0.36	7.0
1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD)	9.5	40	3.47	0.66	(Hartono et al., 2017a)	3	0.58	12.2
	1.0	80		0.04			0.09	-130.4
N,N-Diethylethanolamine (DEEA)	9.5	40	2	0.78	(Monteiro et al., 2013)	1.5	0.73	6.1
	1.0	80		0.09			0.15	-53.8
3-Dimethylamino-1-propanol (3DMA1P)	9.5	40	2.5	0.56	(Nouacer et al., 2014)	3	0.54	4.5
	5.448 /1.0	80		0.17			0.06	63.4

3.2 pKa

Table 5 presents the measured pKa values at 25 °C and the corresponding pKa values available in the literature. The measured pKa values generally showed good agreement with values from the literature. Particularly, when compared to the values reported in Rayer et al. (2014) who used same temperature and amine concentration. Hartono et al. (2017b) also used same temperature and amine concentration and, except for 3DEA1P, it showed good agreement. 3DEA1P showed a significant lower pKa value (9.67) than the value found in this work (10.13) and the other listed values.

Further, from Table 1 and Table 5 it can be seen that the pKa value decreases with an increase of number of hydroxyl groups on the tertiary amine. This is because hydroxyl group acts as an electron withdrawer which lowers the electron density on the nitrogen in the amine and therefore also the base strength.

Table 5. Experimental pKa values

Solvent	pKa	
	This work, (25 °C, 0.01 mol/kg H$_2$O)	Literature
Monoethanolamine (MEA)	9.51	9.45, c = 0.01 mol/L, T = 25 °C (Rayer et al., 2014), 9.50, I = 0.02-0.08, T = 25 °C (Perrin, 1972) 9.50, c = 0.01 mol/L, T = 25 °C (Hartono et al., 2017b)
3-(Methylamino)propylamine (MAPA)	pKa1: 10.59 pKa2: 8.60	pKa1: 10.77, pKa2: 8.89, c = 0.01 mol/L, T= 20 °C (Aronu, 2011)
Triethanolamine (TEA)	7.79	7.73, c = 0.01 mol/L, T = 25 °C (Rayer et al., 2014),

		7.92, c = n/a, T = 25 °C (Perrin, 1972) 7.85, c = n/a , T = 23-26 °C (Chowdhury et al., 2013)
N-Ethyldiethanolamine (EDEA)	8.83	8.80, c = 0.01 mol/L, T = 25 °C (Rayer et al., 2014), 8.92, c = n/a, T= 25 °C (Perrin, 1972) 8.86, c = n/a, T = 23-26 °C (Chowdhury et al., 2013), 9.08, c = 2×10^{-4} mol/L, T = rt (Hayashi et al., 2014)
N-Butyldiethanolamine (BDEA)	8.86	8.90, c = 0.01 mol/L, T = 25 °C (Rayer et al., 2014) 8.89, I = 0-0.1, T = 25 °C (Perrin, 1972)
N-*tert*-Butyldiethanolamine (t-BDEA)	9.03	9.03, c = 0.01 mol/L, T = 25 °C (Rayer et al., 2014), 9.06, c = n/a, T = 23-26 °C (Chowdhury et al., 2013)
3-Dimethylamino-1-propanol (3DMA1P)	9.48	9.54, c = n/a, T = 23-26 °C (Chowdhury et al., 2013)
1-(2-Hydroxyethyl)pyrrolidine (1-2HE)PRLD	9.78	9.86, c = n/a, T = 23-26 °C (Chowdhury et al., 2013), 9.80, c = 0.01 mol/L, T = 25 °C (Hartono et al., 2017b)
2-(Diethylamino)ethanol (DEEA)	9.84	9.73, c = 0.01 mol/L, T = 25 °C (Rayer et al., 2014), 9.75 and 9.82, c = n/a, T = 25 °C (Perrin, 1972) 10.01, c = n/a, T = 23-26 °C (Chowdhury et al., 2013), 9.94, c = 2×10^{-4} mol/L, T = rt (Hayashi et al., 2014), 9.75, c = 0.01 mol/L, T = 25 °C (Hartono et al., 2017b)
1-Diethylamino-1-propanol (1DEA2P)	10.11	10.18, c = n/a, T= 23-26 °C (Chowdhury et al., 2013) 10.14, c = 2×10^{-4} mol/L, T = rt (Hayashi et al., 2014),
3-Diethylamino-1-propanol (3DEA1P)	10.13	10.29, c = n/a, T = 23-26 °C (Chowdhury et al., 2013), 10.17, c = 2×10^{-4} mol/L, T = rt (Hayashi et al., 2014), 9.67, c = 0.01 mol/L, T = 25 °C (Hartono et al., 2017b)
Tropine	10.42	10.48, c = n/a, T = 25 °C (Xu et al., 1993)

$I = \frac{1}{2}\sum c_i z_i^2$ = ionic strength, c = concentration in mol/L, n/a = not available, rt = room temperature

3.3 CO_2 absorption capacity VS pKa

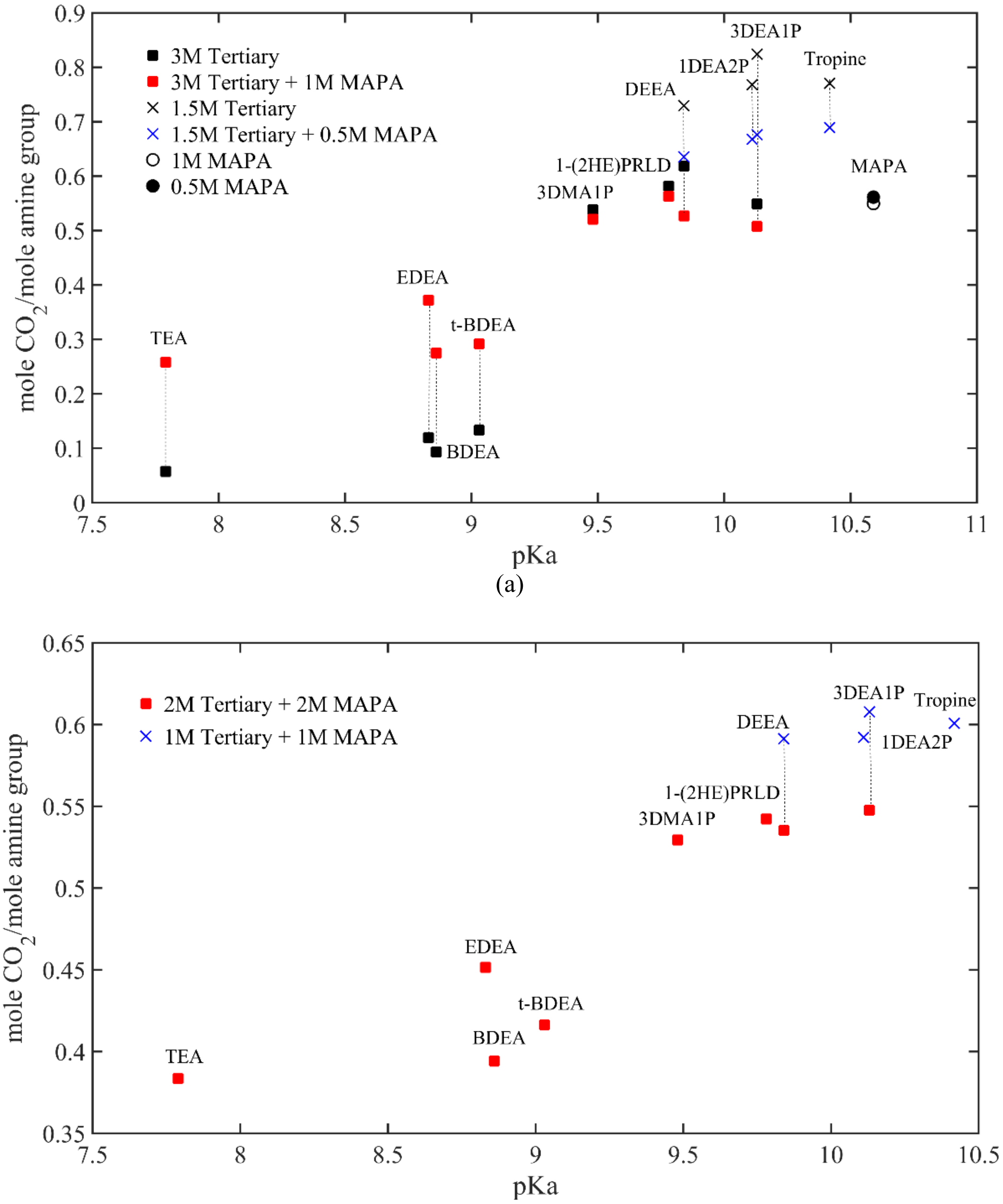
In Fig. 3(a-b) and Fig. 4(a-b), the CO_2 absorption capacity at 40 °C of the studied solvent systems in unit of mole CO_2/mole amine group and mole CO_2/kg solution, respectively, is given as a function of the pKa value of the tertiary amine. Among the tertiary amines with the largest difference in pKa value, i.e. different number of hydroxyl groups, the CO_2 absorption capacity, of both the single and the blended MAPA systems in both units, increased with increasing pKa value. For instance, at increasing pKa and decreasing number of ethanolamine groups on the tertiary amine (DEEA→EDEA→TEA), the absorption capacity increased. Thus, the reactivity of the nitrogen atom of the amine in the CO_2 absorption environment was reduced when the number of hydroxyl groups were increased. In the NMR study performed by Perinu et al. (2017), it was reported that at increasing pKa of the tertiary amine, the activity of the MAPA species to further react with CO_2 increased, leading to an increase of the absorption capacity.

Among the tertiary amines with the same number of hydroxyl groups, the absorption capacity, of the single and blended MAPA systems in both units, was practically the same. Solutions containing EDEA, t-BDEA and BDEA (two hydroxyl groups) obtained a similar absorption capacity, and also solutions containing 1-(2HE)PRLD, DEEA, 3DEA1P, 3DMA1P, 1DEA2P and Tropine (one hydroxyl group).

Further, depending on the unit used to analyse the absorption performance, the outcome of which molar ratio and total concentration that showed the highest absorption capacity changed. In unit of mole CO_2/mole amine group (Fig. 3), the blended MAPA systems with a total concentration of 4M showed a higher absorption capacity in molar ratio 1:1 (2M 3^{ary} amine : 2M MAPA) than in ratio 3:1 (3M 3^{ary} amine : 1M MAPA). Whereas, the opposite was true for the blended MAPA system with a total concentration of 2M. Also, in the same unit a total concentration of 2M obtained a higher rich loading than at 4M. In unit of mole CO_2/kg solution (Fig. 4), molar ratio 1:1 obtained a higher absorption capacity than ratio 3:1 when using both a total concentration of 4M and 2M. In the same unit, a total concentration of 2M showed a lower absorption capacity than at 4M.

Furthermore, when comparing the CO_2 absorption capacity of the single tertiary amines and the corresponding blended MAPA systems in unit of mole CO_2/mole amine group (Fig. 3a), there is a noticeable difference between the tertiary amines with low pKa (7.79-9.03) and high pKa (9.48-10.42). For the tertiary amines with pKa $\leq$ 9.03, the absorption capacity was improved with addition of 1M MAPA compared to the single 3M tertiary amine solutions. For instance, the absorption capacity of the single 3M TEA solution was improved from 0.06 mol CO_2/mole amine group to 0.26 mol CO_2/mole amine group with addition of 1M MAPA. This indicates that MAPA is the main driving force when the tertiary amine has a low pKa value. When the tertiary amine had a pKa $\geq$ 9.03, the absorption capacity was reduced when 1M or 0.5M MAPA solution was added to the tertiary amines. For instance, the absorption capacity of single 3M DEEA solution was reduced from 0.62 mol CO_2/mole amine group to 0.53 mol CO_2/mole amine group with addition of 1M MAPA. Thus, MAPA is influencing these tertiary amines by increasing the absorption rate (discussed in Chapter 3.5) on the expense of the absorption capacity on mole basis. Nevertheless, in unit of mole CO_2/kg solution, all blended MAPA solutions showed a higher absorption capacity than the single tertiary amines (Fig. 4a). This is because the total amine concentration is increased when 1M or 0.5M MAPA solution is added to the tertiary amines.

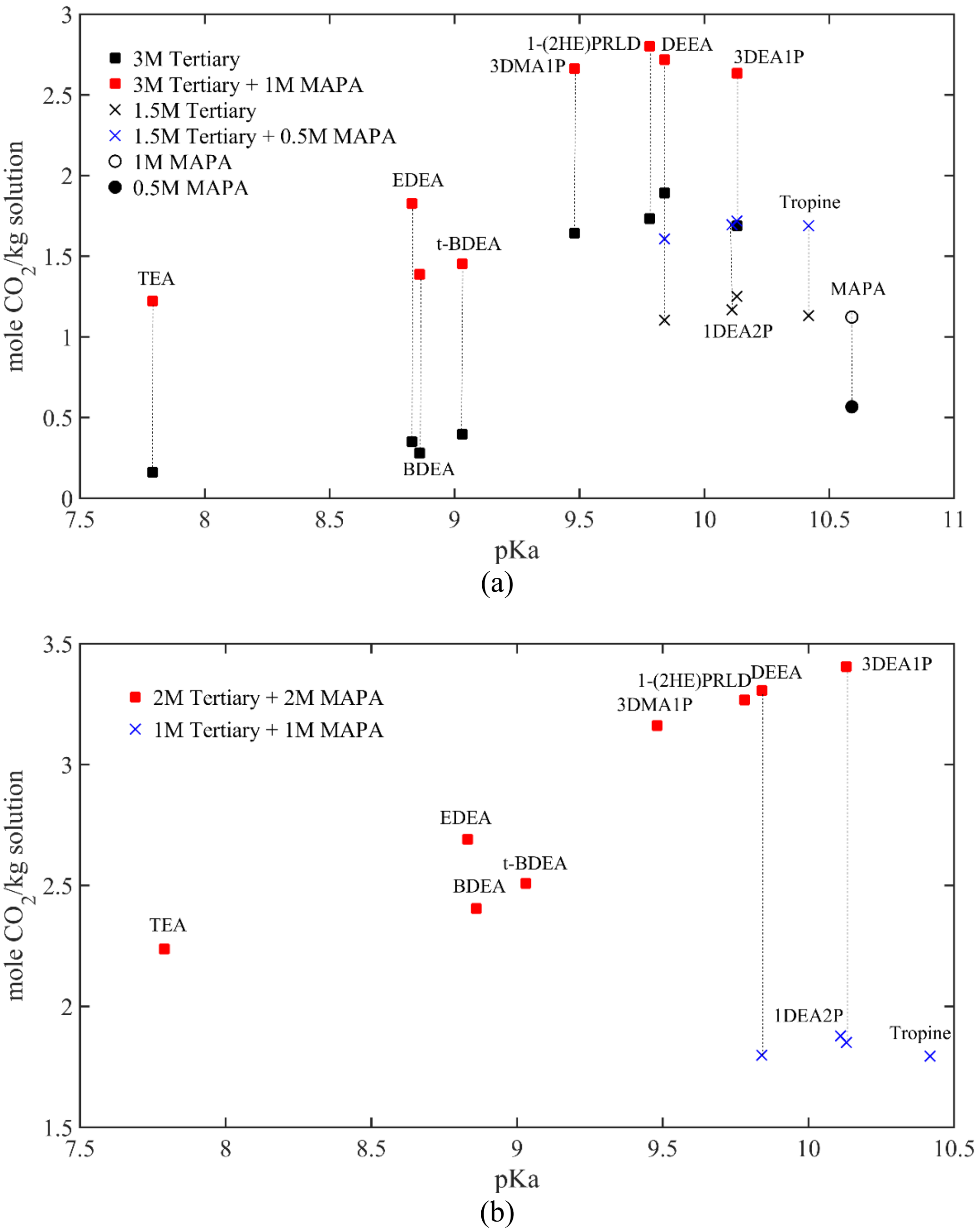
From Fig. 3a it can also be seen that the sum of the CO_2 absorption capacity of MAPA and the tertiary amines on their own are in all cases higher than the absorption capacity of the blended MAPA systems. For example, the sum of single 3M 3DEA1P (0.55 mol CO_2/mole amine group) and 1M MAPA solutions (0.55 mol CO_2/mole amine group) was 1.10 mol CO_2/mole amine group, while the absorption capacity of the blend 3M 3DEA1P + 1M MAPA was 0.51 mol CO_2/mole amine group. Thus, as the blends are not an additive composition of the constituent amines, when used as a single amine, it again indicates that there is some interaction between the amines that influences the absorption performance.



(a)

(b)

Fig. 3 CO_2 absorption capacity in unit of mole CO_2/mole amine group at 40 °C and pKa value of tertiary amines and MAPA; (a) single amine solvents and molar ratio, 3:1 (b) molar ratio 1:1



(a)

(b)

Fig. 4 CO_2 absorption capacity at 40 °C in unit of mole CO_2/kg solution and pKa value of tertiary amines and MAPA; (a) single amine solvents and molar ratio 3:1, (b) molar ratio 1:1

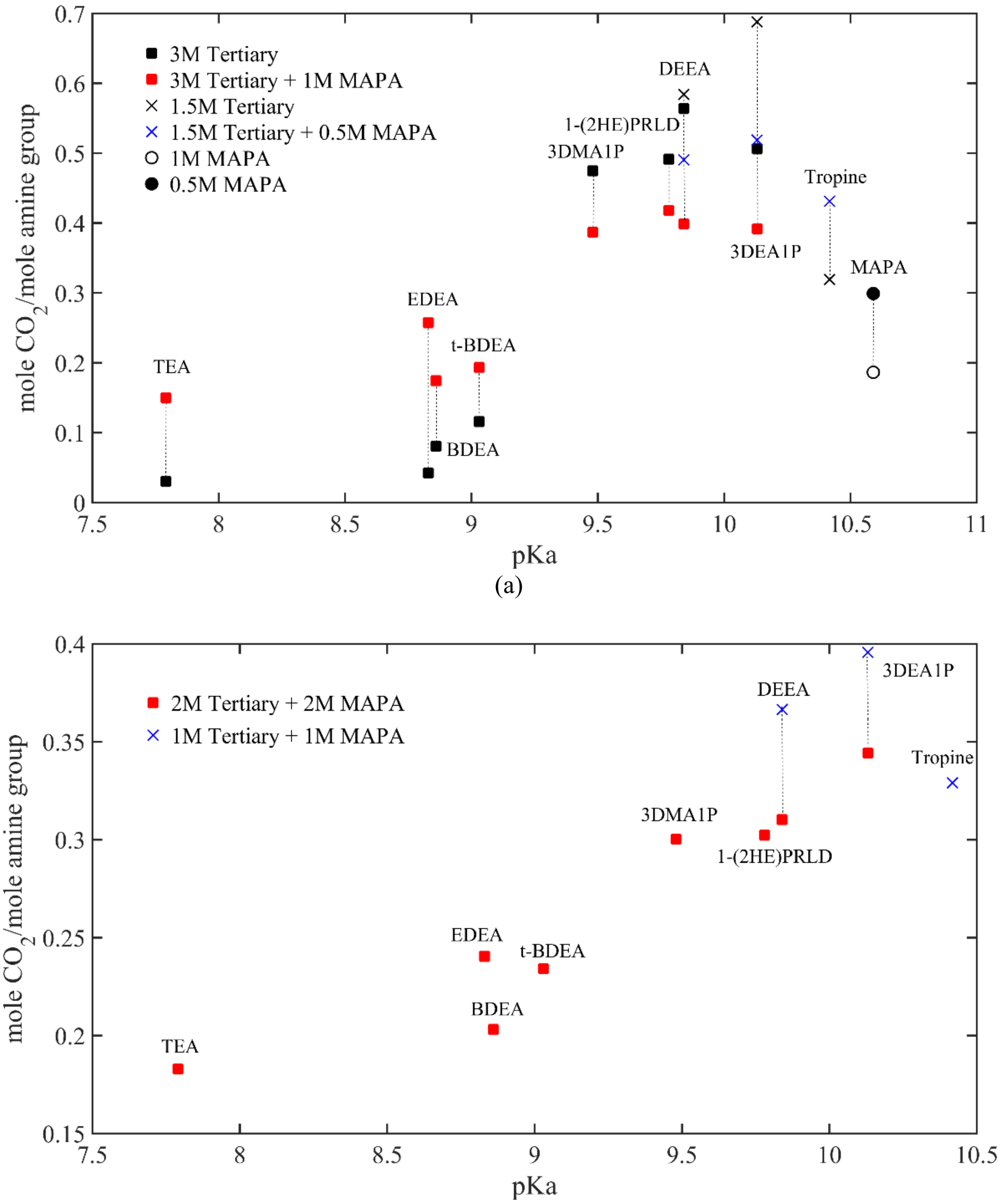
3.4 Screening CO_2 cyclic capacity

The screening CO_2 cyclic capacity of the studied solvent systems in unit of mole CO_2/mole amine group and mole CO_2/kg solution is shown in Fig. 5(a-b) and Fig. 6(a-b), respectively. Screening cyclic capacity of 1DEA2P solutions was not considered due to the observed two phases after the desorption experiment. As was the case for the absorption capacity, the screening cyclic capacity, in both units, also increased with decreasing number of hydroxyl groups and was approximately the same for amines with the same number of hydroxyl groups. However, with Tropine (pKa of 10.42), there was a drop in cyclic capacity. The drop might be due to the high pKa value of Tropine. If the pKa value of the tertiary amine is too high, less CO_2 may be released as the tendency to be deprotonated is lower.

Furthermore, similar to the absorption capacity in unit of mole CO_2/mole amine group, it can be seen from Fig. 5a that the single tertiary amine solutions with $pKa \leq 9.03$ have a screening cyclic capacity lower than the blended MAPA solutions. The single tertiary amine solutions with $pKa \geq 9.03$ have a cyclic capacity that is higher than the blended MAPA solutions. However, an exception is 1.5M Tropine which showed a lower screening cyclic capacity than the blended 1.5M Tropine + 0.5M MAPA solution. Thus, the removal of CO_2 from Tropine and from the tertiary amines at $pKa \leq 9.03$ was enhanced by addition of 0.5M MAPA solutions. However, in unit of mole CO_2/kg solution (Fig. 6a), all blended MAPA solutions obtained a higher screening cyclic capacity than the single tertiary amines.

Overall, the results indicated that an optimum pKa value, giving the highest screening cyclic capacity and also the highest absorption capacity, can be identified and is in the range of 9.48 to 10.13. This behaviour is in line with Du et al. (2016) who studied 2.5m PZ/2.5m tertiary amine blends, and found an optimum pKa value of the tertiary amine, giving the greatest CO_2 cyclic capacity, to be around 9.1. At a higher pKa value, there was a decrease in cyclic capacity. Also, as the pKa values of PZ (pKa1 =9.71, pKa2 = 5.41 (Hamborg and Versteeg, 2009)) are lower than the one for MAPA (pKa1=10.59, pKa2=8.60), there seems to be an increase in the optimum pKa value of the tertiary amine with increasing pKa of the promoter.

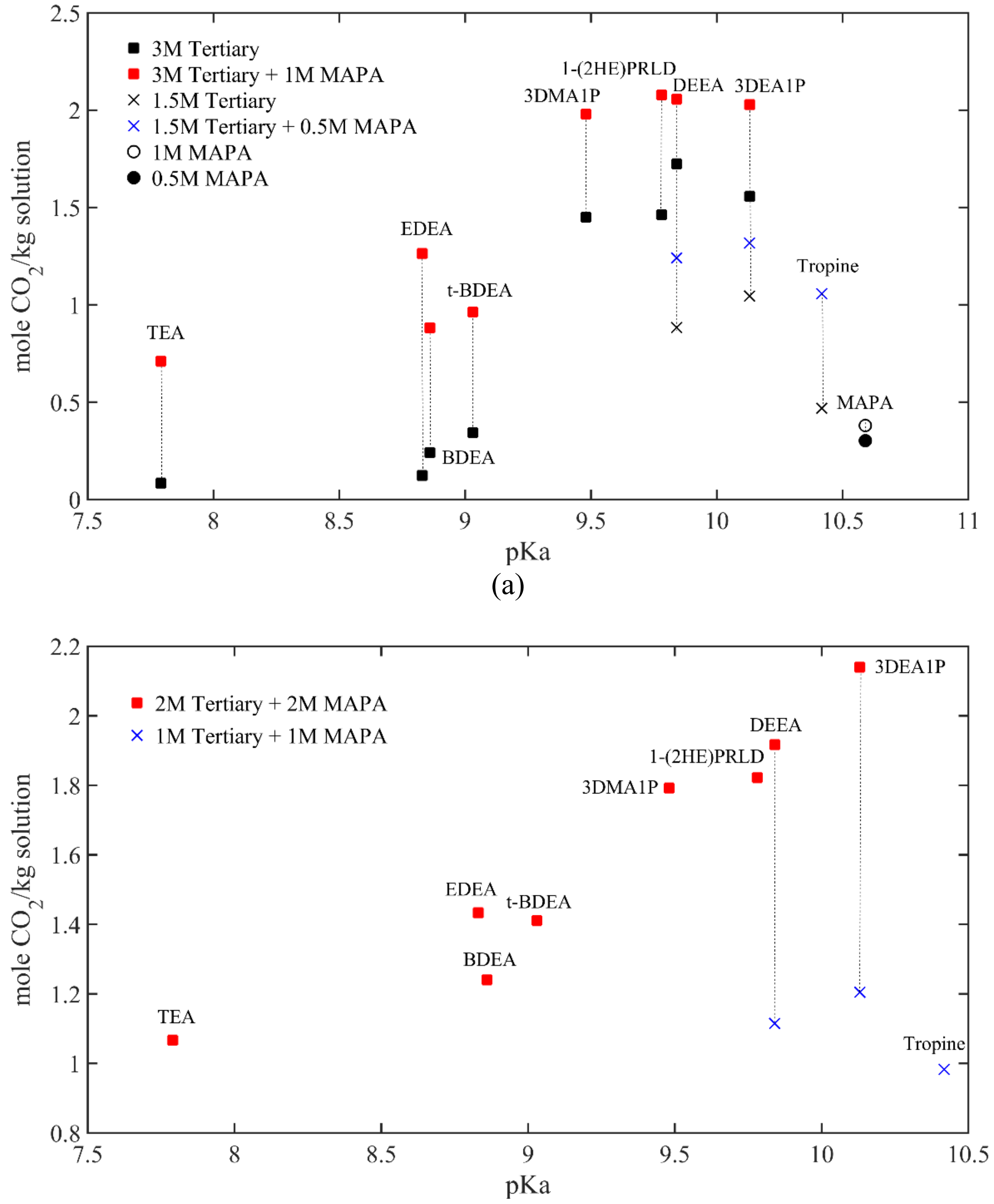
At last, it should be emphasized that the obtained screening cyclic capacity only gives an indication of the ability of the amine solutions to release CO_2. This is because the desorption temperature of 80 °C is lower than the more realistic desorption temperature of 120 °C (Bernhardsen and Knuutila, 2017).



(a)

(b)

Fig. 5 Screening cyclic capacity in unit of mole CO_2/mole amine group and pKa value of tertiary amines and MAPA; (a) single amine solvents and molar ratio 3:1, (b) molar ratio 1:1



(a)

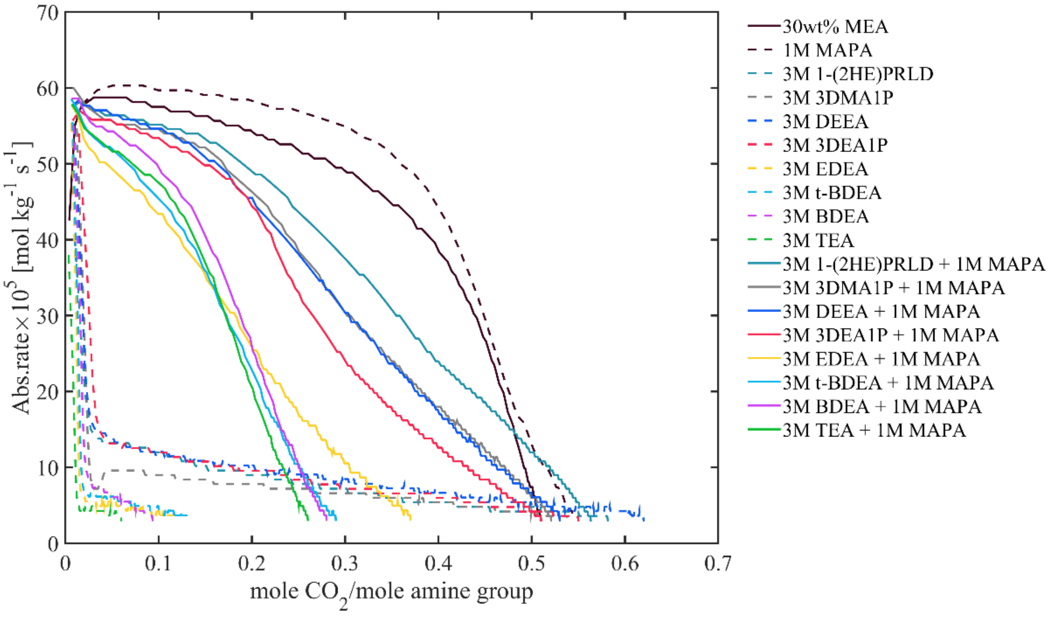
(b)

Fig. 6 Screening cyclic capacity in unit of mole CO_2/kg solution and pKa value of tertiary amines and MAPA; (a) single amine solvents and molar ratio 3:1, (b) molar ratio 1:1

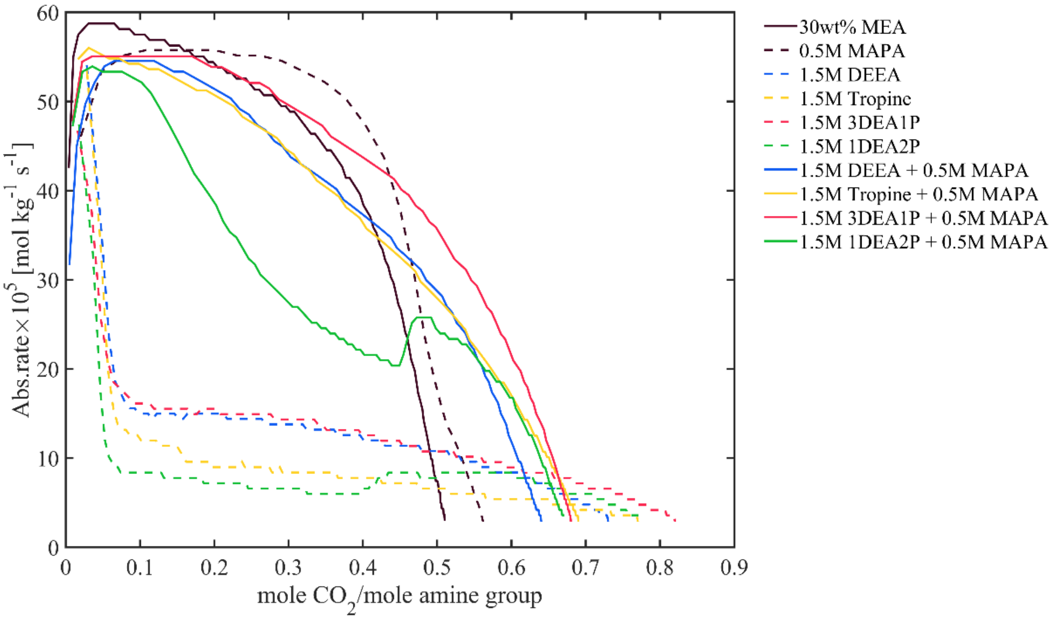
3.5 CO_2 absorption rate VS CO_2 absorption capacity

The change in CO_2 absorption rate versus CO_2 loading at 40 °C for the single tertiary amine solutions and the blended MAPA systems is presented in Fig. 7(a-b). As addressed in Chapter 2.2, the absorption rate data is only semi-quantitative but it is apparent that addition of 1M or 0.5M MAPA solutions to the single tertiary amines significantly enhanced the CO_2 absorption rate. This is expected as primary and secondary amines are known to have faster reaction rates as compared to the tertiary amines (Svendsen et al., 2011). In the whole CO_2 loading range, the single 3M and 1.5M tertiary amines showed an absorption rate lower than 20×10^{-5} mol kg^{-1} s^{-1} while the blended MAPA systems maintained a high absorption rate, even at high CO_2 loadings. For instance, all the blended MAPA systems with total concentration of 4M (Fig. 7a) showed an absorption rate above 40×10^{-5} mol kg^{-1} s^{-1} at CO_2 loading 0.12 mol CO_2/mole amine group. However, their absorption rate was lower than 1M MAPA and the commercially used 30wt% MEA. Among the blended MAPA systems with total concentration of 2M (Fig. 7b), the absorption rate was lower than the one for 0.5 MAPA and lower than the one for 30wt% MEA until a CO_2 loading of around 0.2 mol CO_2/mole amine group. At this loading the absorption rate of MEA started to decrease.

Further, the curves representing the single 1.5M 1DEA2P and the blended 1.5M 1DEA2P + 0.5M MAPA solutions show a sudden increase in absorption rate around loading of 0.4 - 0.5 mol CO_2/mole amine group (Fig. 7b). This increase in absorption rate was due to the phase change of the solvent. When the solutions were heated from room temperature to 40 °C, two phases were observed, but around loading of 0.4 - 0.5 the solutions became a single phase. When the same solutions were desorbed at 80 °C, two phases were present at the cut off. Thus, the formation of two phases seemed to be both dependent on temperature and CO_2 loading.



(a)



(b)

Fig. 7 Screening CO_2 absorption rate and CO_2 absorption capacity at 40 °C; (a) 30wt% MEA, 1M MAPA, 3M tertiary amines and their blends, (b) 30 wt% MEA, 0.5M MAPA, 1.5M tertiary amines and their blends

Fig. 8 illustrates the effect of the molar ratio between DEEA and MAPA on the CO_2 absorption rate. At a total concentration of both 4M and 2M, the highest average absorption rate was obtained when the molar ratio was 1:1. Thus, increasing the concentration of MAPA and decreasing the concentration of DEEA, while keeping the total concentration constant, increased the CO_2 absorption rate. However, increasing the concentration of MAPA affects the heat of absorption. Knuutila and Nannestad (2017) reported that the heat of absorption increases with increasing MAPA concentration. Thus, the energy needed to release the CO_2 from the amine solution is increased.

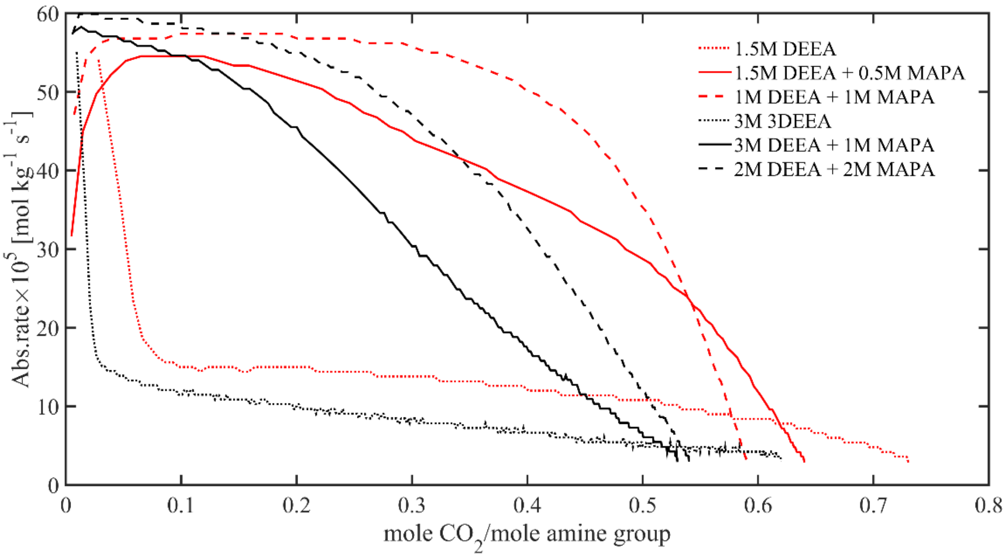


Fig. 8 Screening CO_2 absorption rate and CO_2 absorption capacity of single DEEA and DEEA/MAPA solutions

4 Conclusions

A comparison of the CO_2 absorption rate, CO_2 absorption capacity and cyclic capacity was carried out for ten single tertiary amines and their blends with MAPA. It was shown that the absorption capacity increases with increasing pKa on the tertiary amine and stays approximately the same for tertiary amines with the same number of hydroxyl groups. For the cyclic capacity, a similar trend was observed with exception of Tropine (pKa of 10.42), which showed a lower cyclic capacity. For this study, the optimal pKa range for the blended MAPA systems, giving the highest absorption capacity and CO_2 cyclic capacity, was found to be in the range of 9.48 to 10.13. This behaviour is in line with what was reported by Du et al. (2016) who also found an optimal pKa for blended PZ systems. Therefore, it is believed that there is a relationship between the pKa of the tertiary amine and the promoter.

Further, addition of MAPA to the tertiary amines influenced the absorption performance. For tertiary amines with low pKa (7.79-9.03), the absorption capacity of the tertiary amine in unit of mole CO_2/mole amine group was enhanced by addition of MAPA, while for tertiary amines with high pKa (9.48-10.42), the absorption capacity was reduced by addition of MAPA.

At last, addition of MAPA to the tertiary amines significantly enhanced the absorption rate of the tertiary amines.

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Nomenclature

α	CO_2 loading
c	Concentration [mol/L]
CF	Correction factor [-]
I	Ionic strength [mol/L]
n/a	Not available
$no_{amine\ groups}$	Number of amine groups [-]
n_i	Mole flow of component i [mole/s]
N_{CO2}	Accumulated amount of CO_2 [mole]
m	Mass [kg]
pKa	Dissociation constant [-]
rt	Room temperature
Q_{CO2}	CO_2 absorbed at a given time [mole/s]
x_i	Volume fraction of component i [-]

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