

A Review of potential amine solvents for CO₂ absorption process: Absorption capacity, cyclic capacity and pKa

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Abstract

Solvent selection is an important element to enable low energy requirement in post combustion CO₂ capture process by means of chemical absorption. In this paper, we investigated the CO₂ capture performance of 132 different aqueous amine solvents available in the literature. The properties studied were absorption capacity, cyclic capacity and the pKa – absorption capacity relationship. In addition, fast solvent screening was critically evaluated.

Based on published data, no single amine showed superior performance in terms of absorption capacity and cyclic capacity. However, most of the studied amine solvents showed a better performance than MEA. In some cases, amines studied using the different screening techniques showed results which contradicted with the equilibrium value; the screening work seemed to lead to results where the equilibrium value was exceeded. Further, it was indicated that a solvent with promising cyclic capacity with desorption at 70 °C or 80 °C, not necessarily show the same potential with desorption at 120 °C. Thus, the value of the screening experiments can be questioned. At last, it was found a linear relationship between the pKa value of an amine solvents and its absorption capacity.

Keywords

Review, CO₂ absorption, Amine solvents, Absorption capacity, Cyclic capacity, pKa

1 Introduction and background information

To avoid dangerous consequences of global warming, there is an urgent need to reduce greenhouse gas emissions. Among the options for CO₂ mitigation applied to large point sources, post combustion CO₂ capture based on chemical absorption is the most mature technology. In a typical chemical absorption process, a chemical solvent absorb CO₂ and releases the captured CO₂ upon heating. The absorption and regeneration section operates at around 40 °C and 120 °C, respectively. A huge barrier for implementing this technology is the high energy demand that is needed to regenerate the solvent. The regeneration energy demand is due to (1) the heat to overcome the sensible heat loss when the rich and lean solvent is heat exchanged, (2) the heat required to reverse the absorption reaction and (3) the heat required to produce stripping steam to overcome the overhead pressure drop in the stripper

(Svendsen et al., 2011). Therefore, to enable CO₂ capture with as low energy consumption as possible, there is a need to develop energy efficient solvents.

To reduce the sensible heat loss, the solvent should have high cyclic capacity. Cyclic capacity (typically gCO₂/kg solution) is defined as the difference between the CO₂ concentration in the rich and lean solution. That is:

$$\Delta\alpha = \alpha_{rich} - \alpha_{lean} \quad 1$$

A high cyclic capacity is achieved using a solvent with high absorption capacity and high ability to desorb CO₂ from the solution. A solvent with high cyclic capacity will also reduce the dimensions of the amine plant as it results in a smaller circulation flow rate (Liang et al., 2015b). To reduce the heat required to reverse the absorption reaction, a solvent with low heat of absorption could be beneficial. However, for the low CO₂ partial pressures encountered in the exhaust gas, low heat of absorption makes the equilibrium pressure of CO₂ less sensitive to temperature. Thus, a solvent with high heat of absorption might be more favourable, as it would reduce the stripping steam requirement (Svendsen et al., 2011). Several other factors need to be taken into account when selecting solvents. The solvent should be environmental friendly, resistant to degradation, non-toxic, non-corrosive, have low viscosity, fast reaction kinetic with CO₂ and preferably be non-expensive (Liang et al., 2015b).

The solvent system that traditionally have been the solvent of choice is aqueous amine solvents. Amines are divided into three groups based on the number of hydrogen attached to the nitrogen. The three groups are primary (two H atoms on nitrogen), secondary (one H atom on nitrogen) and tertiary (no H atom on nitrogen). Both primary and secondary amines act as a weak base and form carbamates when reacting with CO₂ (Versteeg and van Swaaij, 1988a). The net reaction is:



Based on the stoichiometry, where two amine molecules react with one CO₂ molecule, the maximum CO₂ loading is 0.5 mole CO₂/mole amine. Primary and secondary amines are known to have fast reaction rates and high heat of reaction (Svendsen et al., 2011).

When tertiary amines react with CO₂, they form bicarbonate through base catalysis of CO₂ hydration. The net reaction is as follows (Versteeg and van Swaaij, 1988b):



Since one amine molecule react with one CO₂ molecule, tertiary amines can theoretically achieve a loading of 1.0 mole CO₂/mole amine. This is twice the loading of primary and secondary amines. Tertiary amines are known to have a slow reaction rates for CO₂ absorption and low heat of absorption (Svendsen et al., 2011).

The amines can be further divided into multiamines and cyclic amines. Multiamines contain several primary, secondary or tertiary amine groups, or a mix of the groups, while cyclic amines are either secondary or tertiary amines that have one or more nitrogen atoms in the ring. The far most studied

amines are the primary amine Monoethanolamine (MEA), the secondary amine Diethanolamine (DEA) and the tertiary amine Methyldiethanolamine (MDEA) (Wang and Li, 2015).

Over the years, considerable effort has been devoted to the work in finding new amine solvents that have better performance than commercially used MEA. Instead of running time-consuming equilibrium measurements (Bougie and Iliuta, 2014; Conway et al., 2014; Derks et al., 2005; Liang et al., 2015a), potential candidates are often found after screening a large number of amines using a solvent screening apparatus. The screening experiments are performed by injecting a gas mixture of CO₂ and N₂ into a reactor containing an amine solution. A mass flow controller control the composition of the feed gas and a CO₂ analyser measures the CO₂ concentration of the outlet gas. Throughout the experiment, the solution is mixed at constant speed and fed with a constant gas flow rate. This procedure gives a fast and first-hand knowledge of the solvents absorption rate and absorption and desorption performance. In Table 1, experimental conditions used by different investigators are listed. They all uses the same methodology, but differ somewhat in how to determine the CO₂ concentration in the liquid phase and when to terminate the experiment. For instance, all, except El Hadri et al. (2017), measured the CO₂ concentration in the aqueous amine solution based on the difference between the concentration of CO₂ in the feed gas and the outlet gas using a CO₂ analyser. El Hadri et al. (2017) performed phosphoric acid titration of the liquid solution. Regarding termination of the experiments, RITE in Japan (Chowdhury et al., 2009; Chowdhury et al., 2011; Chowdhury et al., 2013; Goto et al., 2011) terminated the experiments after 60 minutes at each temperature. Masdar Institue in United Arab Emirates (El Hadri et al., 2017) and UT in Netherlands (Singh et al., 2011) terminated the experiments when equilibrium was reached i.e. when the CO₂ concentration of the outlet gas was equal the CO₂ concentration of the feed gas. NTNU, Norway (Aronu et al., 2011b; Hartono et al., 2017) specified the endpoint to be when the CO₂ concentration in the effluent reached 9.5 kPa and 1.0 kPa partial pressure of CO₂ in the absorption and desorption experiment, respectively. CSIRO, Australia (Puxty et al., 2009) used two different screening methods; (1) isothermal gravimetric analysis (IGA) and (2) macro-scale CO₂ absorption. The macro-scale method was regarded as more reliable as it was less influenced by evaporation and precipitation. IGA was terminated after six hours while the macro-scale method was terminated at equilibrium. Different conditions of termination makes comparison of obtained rich and lean CO₂ concentrations difficult between different studies. Additionally, when different CO₂ partial pressures and amine concentrations are used, it becomes even more demanding to compare.

Further, in most of the publications reporting screening data, a comparison between absorption rate and capacity is made (Aronu et al., 2011b; Chowdhury et al., 2013; Hartono et al., 2017). However, as absorption rates are only semi-quantitative it is not possible to compare this property between different publications. The screening absorption rate is semi-quantitative because there is no guarantee that the gas-liquid interfacial area and the bubble structure are the same in all experiments. Bubble size is mainly dependent on viscosity and surface tension (Chen and Rochelle, 2011).

Despite the fact that only approximate results are often obtained, screening has become an attractive method to use when searching for new amines. It is a rapid and simple method, but most importantly, it is believed to be reliable in suggesting solvents with the best absorption and desorption potential. Puxty et al. (2009) screened 76 different amines and identified seven outstanding candidates. Chowdhury et al. (2013) screened 24 and selected seven for further study, El Hadri et al. (2017) studied 30 amines and regarded six amines as good candidates, while Hartono et al. (2017) selected two solvents for further study, out of 15. As the number of available screening data are increasing, there is a need for a comprehensive evaluation of the published data. Also, a large amount of equilibrium data has been published by several groups (Chen et al., 2015; Li et al., 2014a; Li and Rochelle, 2014; Matin et al., 2013; Schäffer et al., 2012). Recently, Liang et al. (2015b) reviewed latest studies on solubility of CO₂ into amine solvents, while Rayer et al. (2012) provided an extensive database of VLE data of different amine systems. However, as these studies did not compare the different solvents to each other it is difficult to evaluate the potential of the solvents.

In this work, we compare 132 amines available in the literature with potential to be used in a post combustion chemical absorption process. The properties compared are absorption capacity data at 40 °C, cyclic capacity and pKa - absorption capacity relationship. In addition, we discuss the disadvantages of the fast solvent screening methods presented in the literature.

Table 1: Experimental conditions for different screening setups

Research group/country	Gas mixture	Total pressure	Temperature	Duration	Measurement of CO ₂ concentration	Reference
RITE, Japan	20 vol% CO ₂ and 80 vol% N ₂	1 atm	40 °C, 70 °C	60 min	CO ₂ gas analyzer	(Chowdhury et al., 2009; Chowdhury et al., 2011; Chowdhury et al., 2013; Goto et al., 2011)
NTNU, Norway	10 vol% CO ₂ and 90 vol% N ₂	1 atm	40 °C, 80 °C	9.5 kPaCO ₂ at 40 °C and 1.0 kPaCO ₂ at 80 °C	CO ₂ gas analyzer	(Aronu et al., 2011b; Hartono et al., 2017)
CSIRO, Australia	Method 1 (Isothermal Gravimetric analysis): 15 vol% CO ₂ and 85 vol% N ₂ Method2 (Macro-scale): 13 vol% CO ₂ and 87 vol% N ₂	1 atm	40 °C	Method 1: 6 hours Method 2: until equilibrium	Method 1: Seagram TG-DTA/DSC thermal gravimetric analyser Method 2: CO ₂ gas analyzer	(Puxty et al., 2009)
Republic of Korea	30 vol% CO ₂ and 70 vol% N ₂	112.78 kPa (Kim et al., 2014), 115 kPa (Kim et al., 2015)	40 °C, 60 °C, 80 °C	-	Gas Chromatography	(Kim et al., 2014; Kim et al., 2015)
Masdar Institute, United Arab Emirates	15 vol% CO ₂ and 85 vol% N ₂	1 bar	40 °C	Until equilibrium	Phosphoric acid titration (to determine CO ₂ loading in the amine solution)	(El Hadri et al., 2017)
UT and Procede Group BV, Netherlands	Pure CO ₂	1 atm	30 °C	200 min	Gas Burette	(Singh et al., 2007, 2009)
UT, Netherlands	10 kPaCO ₂ saturated with N ₂	1 atm	30 °C, 90 °C	Until equilibrium	Gas Chromatography	(Singh et al., 2011)

2 Methodology

The studied amines are presented in Table S1 to S5 (Supporting Information) where they are arranged in accordance to molecular weight and type of amine group. The studied amine groups were primary amines; secondary amines; tertiary amines; multiamines; and cyclic amines.

Data needed to study absorption capacity and cyclic capacity were collected from both equilibrium studies and screening experiments at various amine concentrations. The absorption capacity, defined in this work as rich CO₂ concentration (in gCO₂/kg solution or mole CO₂/mole amine), was collected at 15 kPa partial pressure of CO₂ when available. This was to resemble a flue gas from a coal-fired power plant where the CO₂ content varies between 10 to 15 vol % (Lackner et al., 2010). In some cases data had to be interpolated, while when data was not available the partial pressure used will be given. It was kept in mind that the solubility of CO₂ into the solvent increases with increasing equilibrium pressure of CO₂ (Kohl and Nielsen, 1997).

The results are presented as CO₂ loading versus aqueous amine concentration (Figure 1 to Figure 18). When only weight percent solution was given, it was assumed density equal to water. The absorption capacity is presented in unit of both mass basis (gCO₂/kg solution) and mole basis (mole CO₂/mole amine). Mass basis is useful from the industrial point of view as it tells how much mass of solvent that will be pumped from the absorption column to remove a specific amount of CO₂. Mole basis is useful for fundamental calculations.

3 Results

In this section, absorption capacity at 40 °C and cyclic capacity are studied for the conventional amine MEA, primary amines, secondary, tertiary amines, multiamines and cyclic amines. At the end, the relation between the pKa and the absorption capacity of the amines is investigated.

3.1 Monoethanolamine (MEA)

When new amine solvents are investigated, MEA is commonly used to validate the experimental setup and served as a reference solvent which amines are compared to. In Figure 1, the CO₂ loading in unit of gCO₂/kg solution, at different MEA concentrations, is given at 40 °C. Data are collected from 18 references, where 11 references are from equilibrium studies (black symbols), six are from screening experiments (coloured symbols), and one is from modelling studies (dashed line). Most of the collected data are at 15 kPa partial pressure of CO₂, but data from Idris et al. (2015), Chowdhury et al. (2014) and Goto et al. (2011), Aronu et al. (2011b) and Hartono et al. (2017), and Puxty et al. (2009) are given at 11.2 kPa, 20 kPa, 9.5 kPa and 13 kPa, respectively.

Comparison of the published data shows some scatter between values obtained from both equilibrium solubility studies and screening experiments. Of the equilibrium data, the greatest variation can be seen at 2.50 mol/L solution where the data range from 57.4 gCO₂/kg solution to 64.4 gCO₂/kg solution. This is a variation of 12 % when using the lowest value as a base (hereafter, percent variation will be

calculated similarly). Among them are Chang et al. (2013) and Nouacer et al. (2014) in agreement (~64.4 gCO₂/kg solution), while the other reported solubility data are scattered. It is therefore difficult to know which one to trust as they all reported small uncertainties in the measured data (T, P). At 4.91 mol/L solution, the reported equilibrium data range from 115.0 gCO₂/kg solution to 124.1 g/kg solution. This is a variation of 8 % that probably is due to the accuracy of the experimental work. In Figure 2, the CO₂ loading is given in unit of mole CO₂/mole amine and the same percent variation in reported data at 2.50 mol/L and 4.91 mol/L, as in Figure 1 discussed above, are present in this figure.

Among the screening data reported at 4.91 mol/L, most of them are within the range of the equilibrium values. However, Kim et al. (2014) reported a value that is considerably lower than the other reported values. As Kim et al. (2014) used a higher CO₂ content in the gas mixture (30 vol% CO₂ and 70 vol% N₂), one would expect the CO₂ loading to be higher. Puxty et al. (2009), who used two different methods to measure the absorption capacity, has reported two values for CO₂ loading at 4.91 mol/L, 105.9 gCO₂/kg solution and 121.1 gCO₂/kg solution. The former CO₂ loading was found using isothermal gravimetric analysis (IGA) at 15 kPaCO₂, while the latter was found using macro-scale CO₂ absorption (traditional screening technique) at 13 kPaCO₂. As discussed above, macro-scale absorption was regarded as more reliable. Singh et al. (2011), who conducted the screening experiment at 30 °C and 10 kPa partial pressure of CO₂, reported the CO₂ loading into MEA at 2.53 mol/L to be 57.9 gCO₂/kg solution (Figure 3). This is within the range of the equilibrium values at the same concentration discussed above.

It can be seen that most of the screening data are below the equilibrium solubility data. This is expected as equilibrium data represent the maximum amount of CO₂ that is possible to dissolve at a given temperature and pressure. Only El Hadri et al. (2017), with a value of 125.4 gCO₂/kg solution at 4.91 mol/L, is slightly above the value from Jou et al. (1995) (124.2 gCO₂/kg solution) at the same concentration. However, the difference of 1 % is so small that it can be neglected.

The extended UNIQUAC model framework developed by Aronu et al. (2011a) was applied to obtain solubility data of CO₂ in MEA concentrations ranging from 1.02 mol/L to 4.91 mol/L. The model seems to give a good representation of the experimental data reported by Maneeintr et al. (2009) at 2.0 mol/L, Chang et al. (2013) and Nouacer et al. (2014) at 2.50 mol/L and Yamada et al. (2013) at 4.91 mol/L (Figure 1). From the modelled data, it is noticeable that when the molar concentration increases, the CO₂ absorption capacity of MEA increases from 29.3 gCO₂/kg solution to 115.0 gCO₂/kg solution. The same trend can be seen from the screening work conducted by Aronu et al. (2011b) where the absorption capacity was measured from 1.0 mol/L to 5.0 mol/L at 9.5 kPaCO₂. In Figure 2, in which the CO₂ loading is in unit of mole CO₂/mole MEA, the CO₂ concentration decreases with increasing MEA concentration. Thus, when the molar concentration from the modelled data increases from 1.02 mol/L to 4.91 mol/L, the CO₂ concentration decreases from 0.66 mole CO₂/mol MEA to 0.53 mole CO₂/mol MEA.

In conclusion, most of the MEA data obtained from screening at 4.91 mol/L solution seems to agree quite well with the equilibrium data. This indicates that we can expect similar agreement when it comes to other amines. For Kim et al. (2014), where the absorption capacity is much lower, we would expect the absorption capacity of other amines from this publication to be lower than similar amines from other publications.

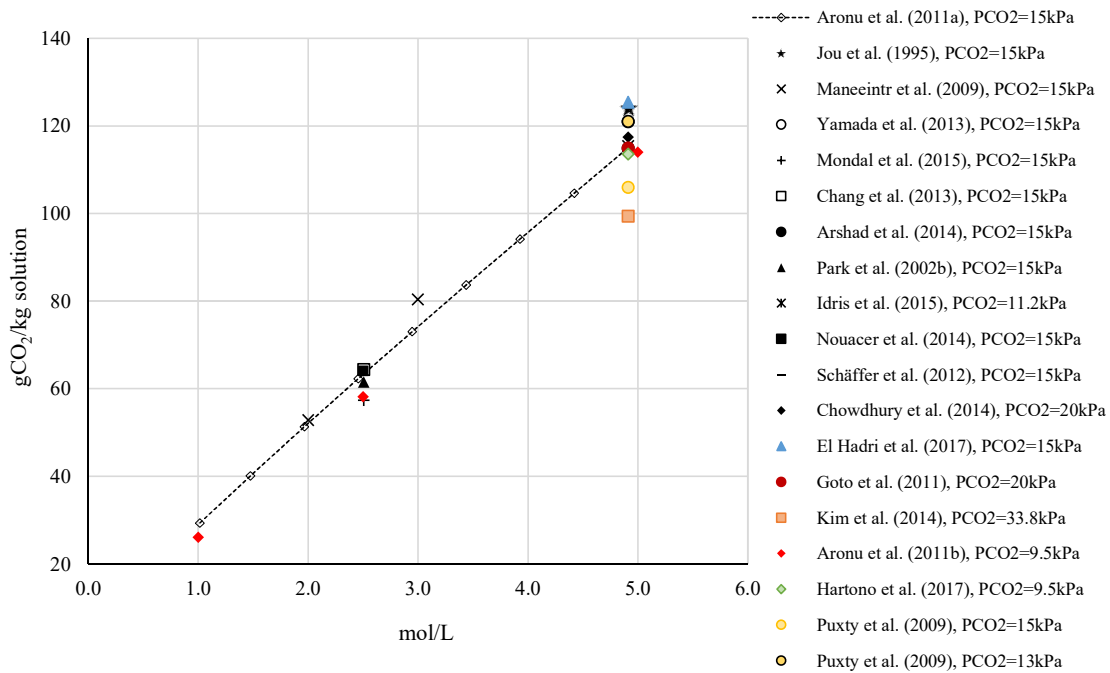


Figure 1: Absorption capacity (gCO₂/kg solution) of MEA at various molar concentrations at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

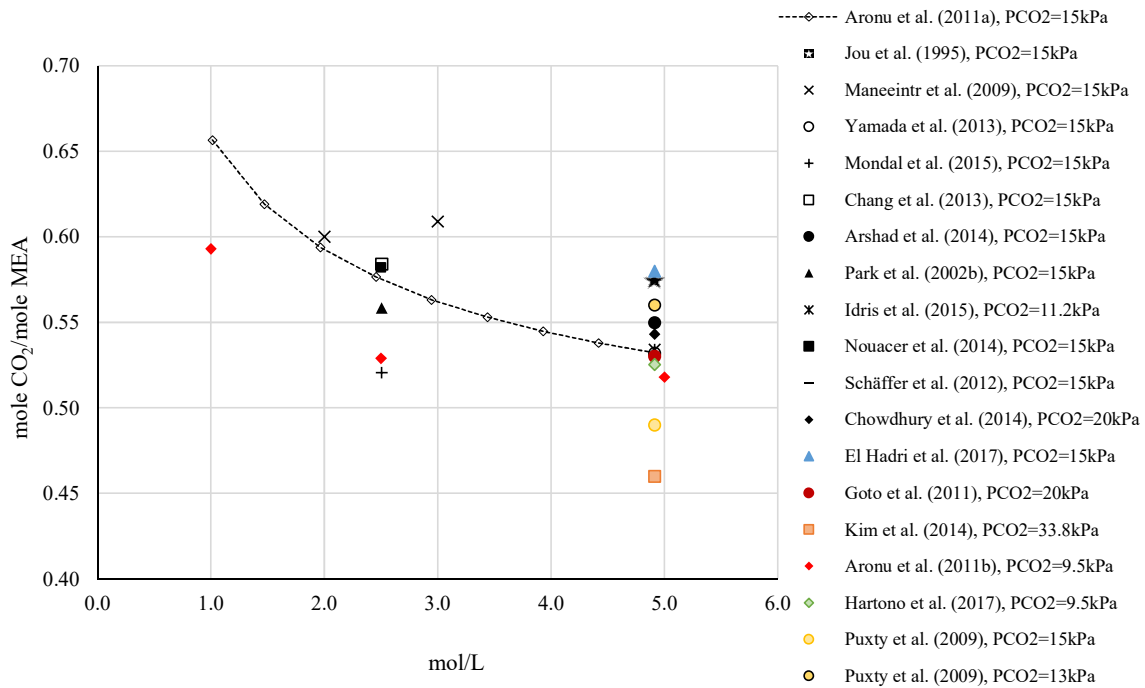


Figure 2: Absorption capacity (mole CO₂/mole MEA) of MEA at various molar concentrations at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

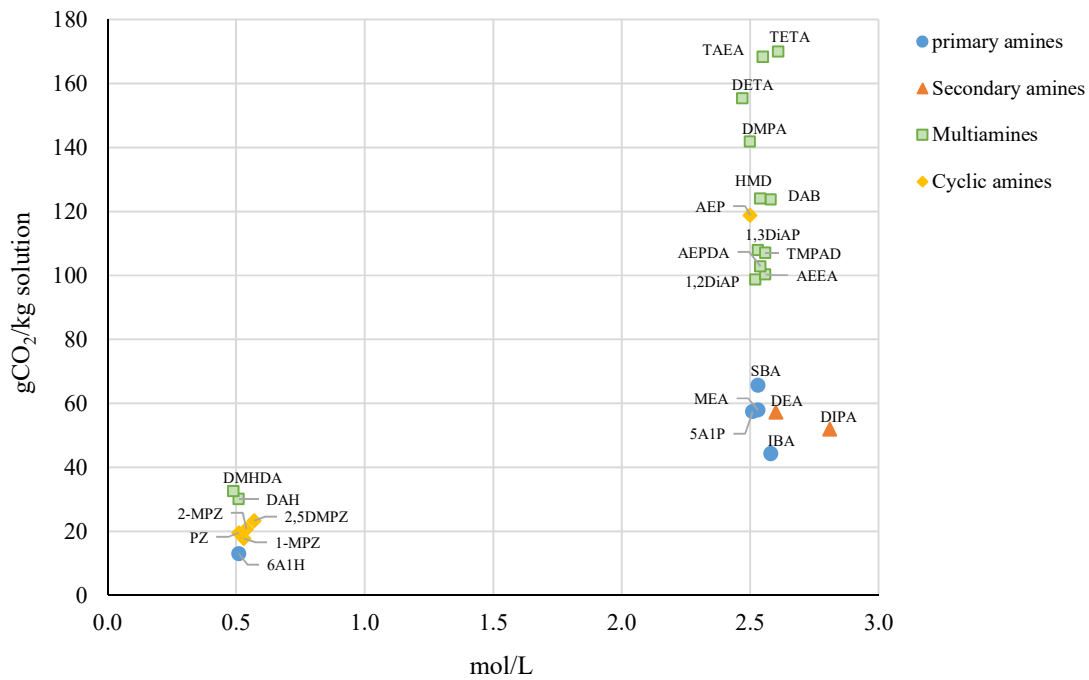


Figure 3: Absorption capacity in unit of gCO₂/kg solution reported by Singh et al. (2011) at 30 °C and 10 kPa partial pressure of CO₂

3.2 Absorption capacity of primary amine solvents at 40 °C

In Figure 4, the absorption capacity of 19 different primary amines is presented in unit of gCO₂/kg solution. Most of the amines are given at 15 kPa partial pressure of CO₂, but data from Idris et al. (2015), Park et al. (2002a) and Park et al. (2002b), Aronu et al. (2011b), Goto et al. (2011) and Puxty et al. (2009) are given at 1 kPa, 25 kPa, 9.5 kPa, 20 kPa and 13 kPa, respectively.

Among the studied primary amines, most of them are concentrated in the range from 60 gCO₂/kg solution to 120 gCO₂/kg solution, and 13 of the amines show a higher absorption capacity than MEA. The amine that has the highest absorption capacity is Isopropylamine (IPA) at 5.08 mol/L with a value of 149.7 gCO₂/kg solution. However, due to its high vapour pressure, 810.6 hPa at 25 °C (SciFinder Scholar™, 2016), IPA would require nonconventional process conditions like low temperatures in the absorber, similar to the chilled ammonia process (Han et al., 2013), and/or additional process units to minimize the loss of IPA.

In Figure 5, in which the CO₂ concentration is given in unit of mole CO₂/mole amine, the primary amines are mostly concentrated in the range of 0.5 mole CO₂/mole amine to 0.7 mole CO₂/mole amine. The amine with the highest CO₂ loading seems to be 2-Amino-2-methyl-1-propanol (AMP) at 3.36 mol/L with a value of 0.80 mole CO₂/mole amine. AMP is able to reach a high CO₂ loading due to the steric hindrance which lowers the carbamate stability and makes the behaviour of AMP more similar to the tertiary amines (Sartori and Savage, 1983). However, the values reported for AMP are not consistent. Four researchers reported the absorption capacity of AMP, and depending on the source, the absorption capacity varies from 0.59 mole CO₂/mole amine to 0.80 mole CO₂/mole amine. This is a variation of 36 % where some data obtained from the screening experiments are above and some below the equilibrium solubility data. The equilibrium data for AMP reported by Tong et al. (2012) is consistent with data at 40 °C from Kundu et al. (2003) and most of the data from Seo and Hong (1996). Puxty et al. (2009) reported a value for AMP that is lower than equilibrium at the same concentration, while El Hadri et al. (2017) reported a value that is 25 % higher than the equilibrium value. When solubility data at 40 °C from Tong et al. (2012) (equilibrium data available from 6.0 kPa to 265.8 kPa) and Seo and Hong (1996) (equilibrium data available from 3.9 kPa and 182.4 kPa) were interpolated to 20 kPaCO₂, it is also clear that Goto et al. (2011) reported a value that is higher than equilibrium. However, for 1-Amino-2-propanol (1A2P) at 4.0 mol/L it is the other way around; El Hadri et al. (2017) reported a value that is 5 % lower than the equilibrium value (Rebolledo-Morales et al., 2011), while Puxty et al. (2009) reported a value that is 5 % higher. As seen in Figure 2, both El Hadri et al. (2017) and Puxty et al. (2009) are consistent with values for MEA found in the literature. Therefore, one would also expect the reported values for AMP and 1A2P to be consistent with literature values. The discussion above clearly indicates that several screening methods used in the literature are inaccurate. The inaccuracy seems, in some cases, to lead to results indicating exceeding equilibrium and not reaching equilibrium in the same publication work. This makes it difficult to evaluate the real potential of the tested solvents.

Furthermore, as seen from Figure 5, few amine solvents investigated by the same researcher have been studied at the same concentration. This is because amines are in many cases studied using the same weight percent, typically 30 wt%, when a comparative study is being conducted (Chowdhury et al., 2013; El Hadri et al., 2017; Hartono et al., 2017; Puxty et al., 2009). Consequently, due to differences in density, molecular weight and solubility, the molar concentration will not be the same in all cases. An amine with high molecular weight will have less moles of absorbent present in the solution, thus a lower molar concentration compared to an amine with low molecular weight. Therefore, as discussed above, one should be aware that an amine with a higher molar concentration generally would have a higher gravimetric absorption capacity. For instance, if the concentration of 2-Amino-2-(hydroxymethyl)-1,3-propanediol (AHPD) or 2-Amino-2-ethyl-1,3-propanediol (AEPD), shown in Figure 4, was increased from 0.84 mol/L to 5.0 mol/L, would possibly the gravimetric capacity increased as well. However, a higher concentration is not always an advantage as it might lead to higher viscosity, foaming issues and causing solvation problems (Aronu et al., 2011b).

Singh et al. (2007) studied the effect of increasing chain length of the alkanolamines: MEA, 3-Amino-1-propanol (3A1P), 4-amino-1-butanol (4A1B) and 5-Amino-1-pentanol (5A1P) using a molar concentration of 2.50 mol/L at 30 °C and pure CO₂. In the study, it was found that the CO₂ loading in unit of both mole CO₂/mole amine and gCO₂/kg solution slightly increases from two to three carbon chain length, and then stays approximately the same. This is in agreement when comparing the values reported by Idris et al. (2015) where the solubility of CO₂ was studied using 5.0 mol/L.

Moreover, Singh et al. (2011) studied the primary amines Sec-butylamine (SBA) at 2.53 mol/L and Isobutylamine (IBA) at 2.58 mol/L at 30 °C and 10 kPaCO₂ (Figure 6). The investigation showed the same trend of increasing absorption capacity as reported by El Hadri et al. (2017) for SBA at 4.10 mol/L and IBA at 4.10 mol/L (Figure 4).

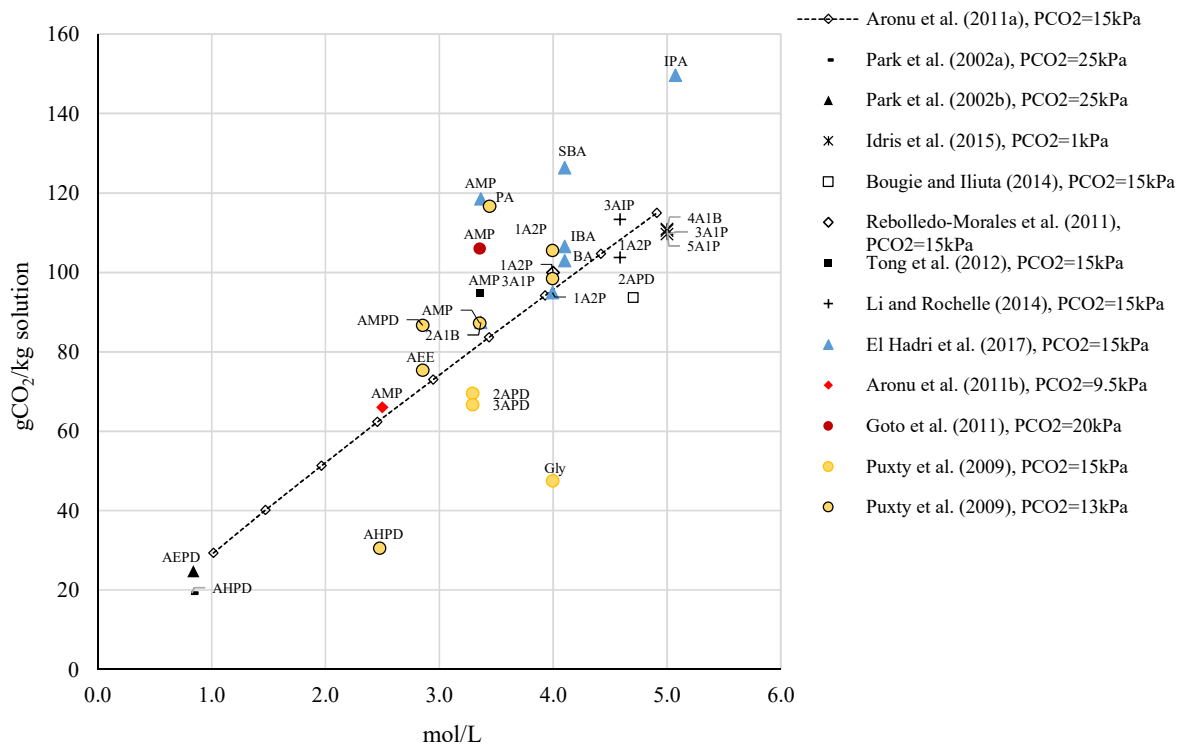


Figure 4: Absorption capacity (gCO₂/kg solution) of different primary amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

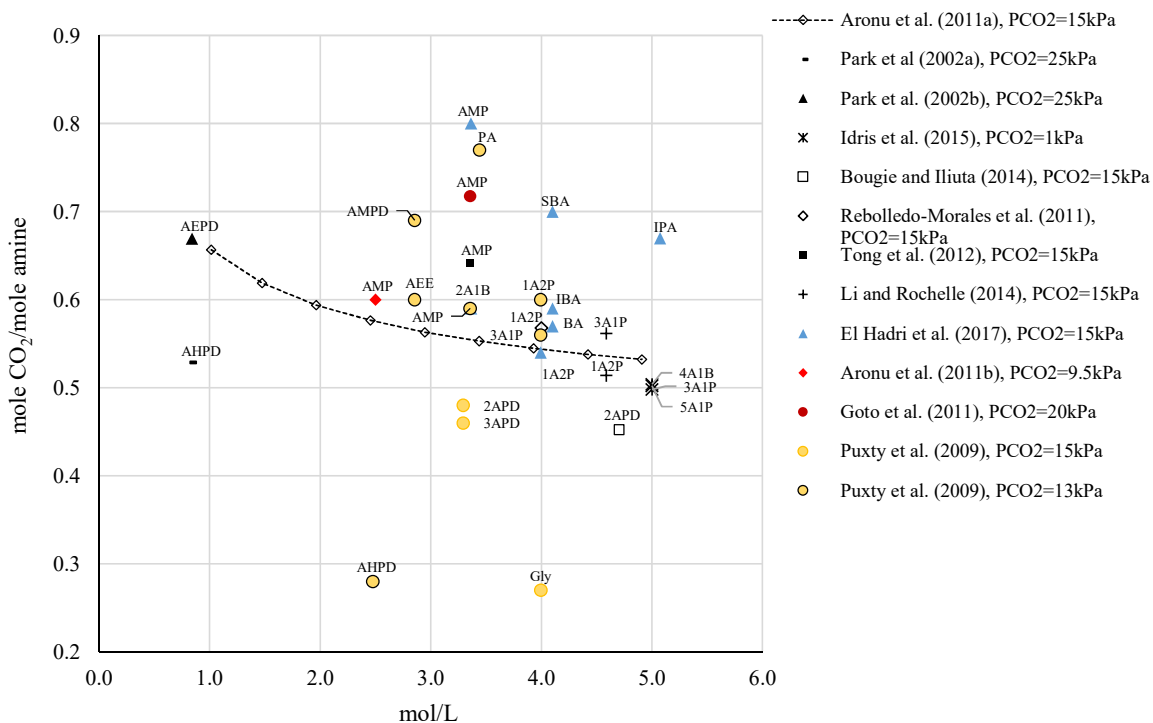


Figure 5: Absorption capacity (mole CO₂/mole amine) of different primary amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

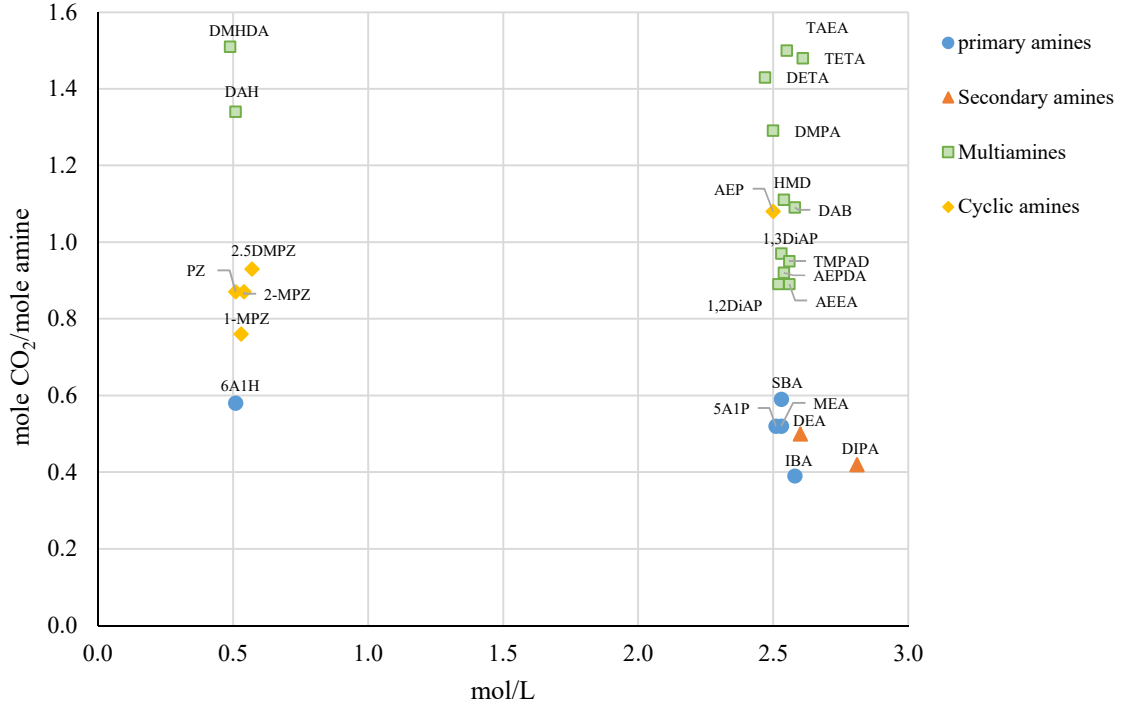


Figure 6: Absorption capacity in unit of mole CO₂/mole amine reported by Singh et al. (2011) at 30 °C and 10 kPa partial pressure of CO₂

3.3 Cyclic capacity of primary amine solvents

When new amines are screened, solvents with high cyclic capacity are chosen over solvents with low cyclic capacity. As discussed above, high cyclic capacity reduces the sensible heat loss and the size of the amine plant due to reduced solvent circulation flow rate.

For the primary amines, the cyclic capacity of five amines (MEA, 2-Amino-1,3-propanediol (2APD), 1-Amino-2-propanol (1A2P), AMP and 3A1P) was calculated from available literature data. Since different researchers use different conditions of temperature and pressure when evaluating the solvents absorption and desorption performance, the cyclic capacity was calculated using equation 4, 5 and/or 6 and is presented in Figure 7, Figure 8 and Figure 9, respectively. For comparison, the cyclic capacity of MEA at different concentrations, found using the VLE model by Aronu et al. (2011a), is given in each figure.

$$\Delta\alpha^{Fig.7} = \alpha_{40^{\circ}\text{C}, 20\text{kPaCO}_2} - \alpha_{70^{\circ}\text{C}, 20\text{kPaCO}_2} \quad 4$$

$$\Delta\alpha^{Fig.8} = \alpha_{40^{\circ}\text{C}, 15\text{kPaCO}_2} - \alpha_{80^{\circ}\text{C}, 15\text{kPaCO}_2} \quad 5$$

$$\Delta\alpha^{Fig.9} = \alpha_{40^{\circ}\text{C}, 15\text{kPaCO}_2} - \alpha_{120^{\circ}\text{C}, 100\text{kPaCO}_2} \quad 6$$

In Figure 7, in which desorption temperature is 70 °C, the cyclic capacity of 2APD at 4.70 mol/L is 91 % higher than 4.91 mol/L MEA. Although 2APD showed lower absorption capacity than MEA at 40 °C (Figure 5), it seems to be more easily regenerated. The same behaviour can be seen for 1A2P at 4.59 mol/L in Figure 8 where the desorption temperature is 80 °C. 1A2P at 4.59 mol/L showed a lower

absorption performance than MEA at 4.91 mol/L and 3A1P at 4.59 mol/L (Figure 5), but a higher cyclic capacity. The cyclic capacity of 1A2P at 4.59 mol/L is 12 % and 52 % higher than MEA at 4.91 mol/L and 3A1P at 4.49 mol/L, respectively. Thus, absorption capacity should not be used as the only parameter when searching for potential amines. An amine with low absorption capacity can have high cyclic capacity and vice versa. Moreover, data at 40 °C might not give a realistic picture of the performance of the solvent system in a real absorption tower with higher temperatures. However, all screening experiments are conducted at 40 °C.

Looking at Figure 9, in which desorption temperature is 120 °C, 1A2P at 4.0 mol/L shows a similar performance as the cyclic capacity of MEA at 3.93 mol/L and hence, seems less promising. This indicates that one should be cautious to conclude based on the performance at 80 °C since this differs from the performance at 120 °C. Thus, desorption performance should be tested under realistic desorption temperature, which is dependent on the type of solvent, to get a more realistic picture of the solvent performance. Given this, screening methods that perform desorption experiments at 80 °C, or lower, should not be used to identify few promising solvents from a large group of solvent candidates. Screening cyclic capacities should only be treated as a good indication whether the amine is able to release CO₂.

Another solvent showing a promising performance is AMP. At concentration of 3.36 mol/L it has a cyclic capacity that is 120 % higher than MEA at 3.92 mol/L (Figure 8). This is expected since AMP is known to have high cyclic capacity (Tong et al., 2012). However, the absorption rate is low so AMP is always used with a promoter like MEA and DEA (Adeosun and Abu-Zahra, 2013; Conway et al., 2015; Mandal and Bandyopadhyay, 2005).

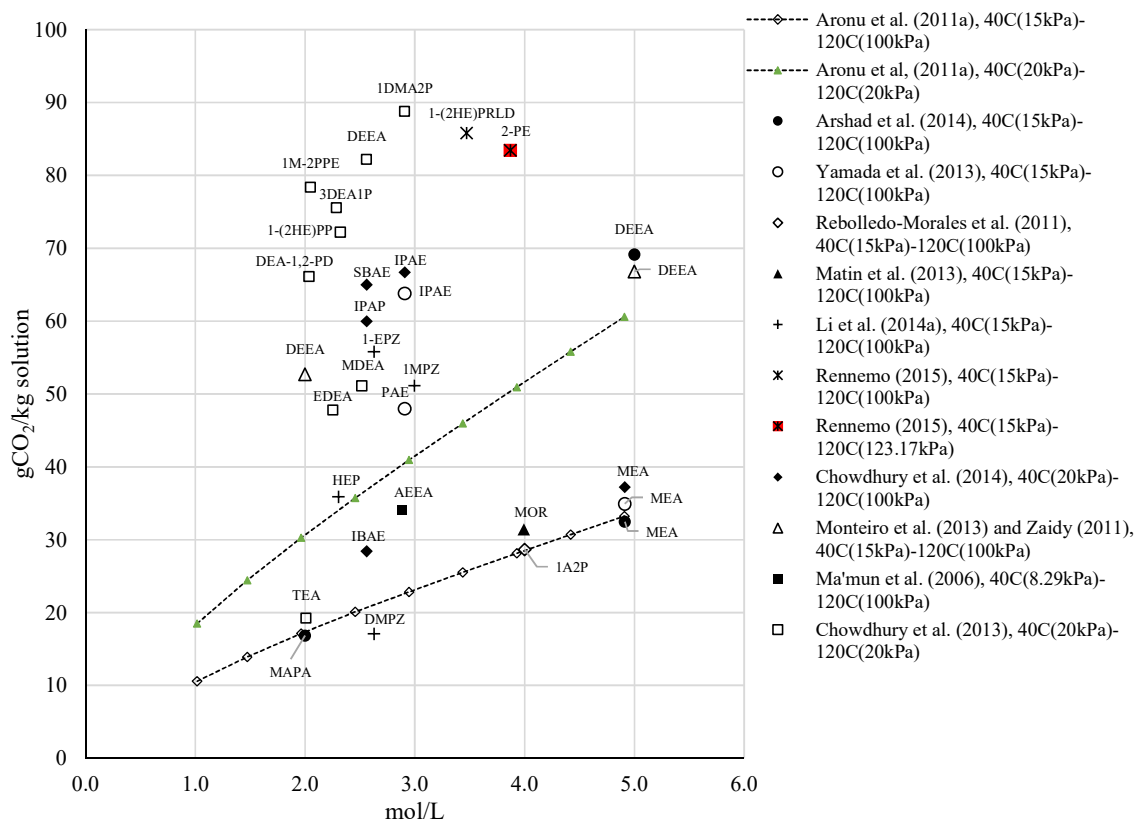


Figure 9: Cyclic capacity of different amines, calculated using data available at 40 °C and 120 °C (Equation 6). The dashed line represent model predictions of MEA.

3.4 Absorption capacity of secondary amine solvents at 40 °C

In Figure 10, the absorption capacity of 18 different secondary amines is presented in unit of gCO_2/kg solution. Again, most of the collected data is at 15 kPa partial pressure of CO_2 , but data from Haghtalab et al. (2014), Li (2015), Chowdhury et al. (2014) and Goto et al. (2011), Kim et al. (2014), Hartono et al. (2017) and Puxty et al. (2009) are given at 107 kPa, 6.9kPa, 20 kPa, 33.8 kPa, 9.5 kPa and 13 kPa, respectively.

The majority of the studied secondary amines are concentrated in the same range as the primary amines, and 14 of the secondary amines have higher absorption capacity than MEA. The amine with the highest absorption capacity is Diethylamine (DA) at 4.10 mol/L with a value of 149.8 gCO_2/kg solution. It performs similar to the primary amine IPA at 5.08 mol/L. Also in Figure 10, there seems to be increase of absorbed CO_2 with increasing amine concentration.

On mole basis, most of the secondary amines are concentrated at a slightly higher CO_2 loading compared to the primary amines (Figure 11). The CO_2 loading is in the range of 0.5 mole CO_2/mole amine to 0.8 mole CO_2/mole amine compared to 0.5 mole CO_2/mole amine to 0.7 mole CO_2/mole amine for the primary amines. The higher performance is likely related to the many secondary amines that are sterically hindered, such as 3-(Isopropylamino)propanol (IPAP) at 2.56 mol/L, 4-(Isopropylamino)-2-

butanol (4IP2B) at 3.0 mol/L and 2-(Isopropylamino)ethanol (IPAE) at 2.91 mol/L. IPAP shows the highest CO₂ loading with a value of 0.90 mole CO₂/mole amine.

When studying the secondary amine DEA reported by Benamor and Aroua (2005) at 2.0 mol/L and 4.0 mol/L and Seo and Hong (1996) at 2.85 mol/L, it is noticeable that the absorption capacity gives an almost linear increase in unit of gCO₂/kg solution (Figure 10). On mole basis, this causes the capacity to be independent of the DEA concentration (Figure 11).

Moreover, five different researchers have reported the absorption capacity of DEA at 2.85 mol/L solution using the screening technique. The reported values range from 59.0 gCO₂/kg solution to 75.4 gCO₂/kg solution, which gives a variation of 28 % (Figure 10). Compared to the equilibrium value reported by Seo and Hong (1996) (65.6 gCO₂/kg solution), El Hadri et al. (2017) and Puxty et al. (2009) exceeds the equilibrium value with 2 % and 15 %, respectively, while Goto et al. (2011), Hartono et al. (2017) and Kim et al. (2014) are below the equilibrium value. Kim et al. (2014), who under predicted the value of MEA at 4.91 mole CO₂/mole amine, as discussed in Chapter 3.1, also under predict the value of DEA. In addition, variation of reported values from screening experiments are also evident for the amines 2-(Methylamino)ethanol (MAE) at 4.0 mol/L, IPAE at 2.91 mol/L, 2-(tert-Butylamino)ethanol (tBAE) at 2.56 mol/L and N-Ethylethanolamine (EEA) at 3.37 mol/L (Figure 10). Screening data reported for MAE at 4.0 mol/L, by Puxty et al. (2009) and El Hadri et al. (2017), varies with 13%. Puxty et al. (2009) is close to the equilibrium value at 4.59 mol/L (within 1%), while El Hadri et al. (2017) is 13% below the equilibrium value. However, it should be noted that the screening and equilibrium concentrations of MAE are different. Regarding IPAE at 2.91 mol/L, four researchers have reported the absorption capacity. Those are Goto et al. (2011), Chowdhury et al. (2014), Hartono et al. (2017) and Yamada et al. (2013). Goto et al. (2011) reported a value that is 7 % above the equilibrium value reported by Chowdhury et al. (2014) at the same partial pressure, whereas data reported by Hartono et al. (2017) agree well with equilibrium reported by Yamada et al. (2013) (within 1 %). Consequently, as was the case for the primary amines, the inaccuracy of the screening experiment seems every now and then to lead into results where the equilibrium value is exceeded. This clearly indicates problems with the analytical methods used. It is critical that the analytical methods are accurate to confirm the CO₂ concentration in the liquid phase and, when possible, deviations from literature values should be reported alongside the data.

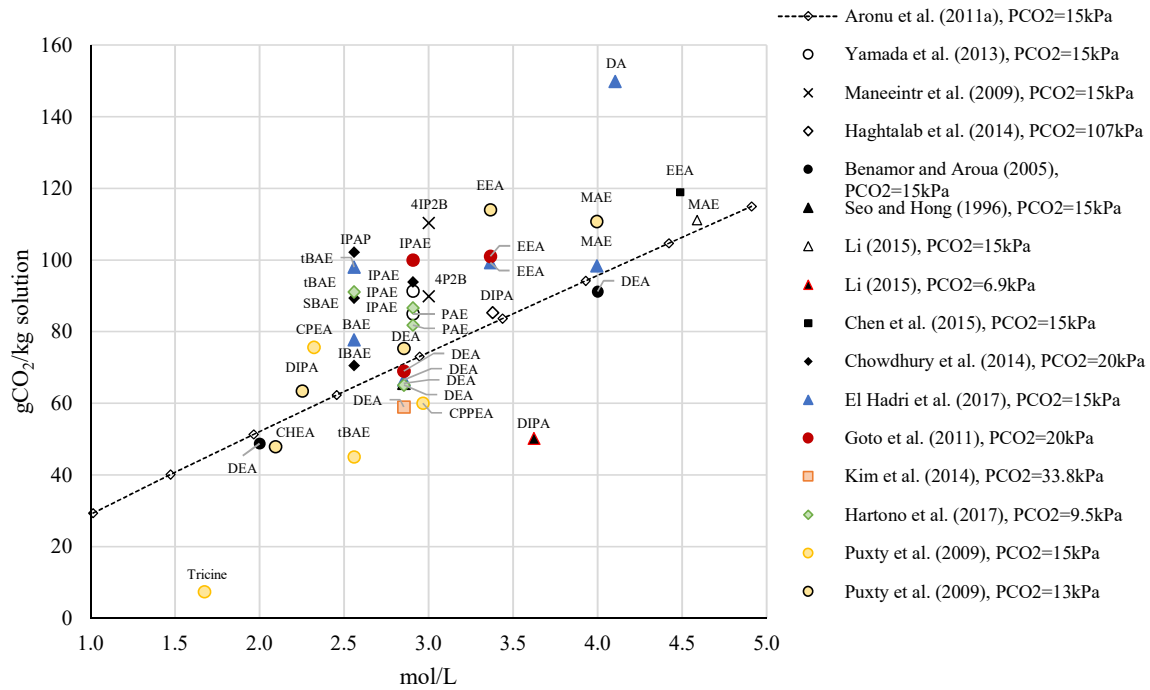


Figure 10: Absorption capacity (gCO₂/kg solution) of different secondary amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

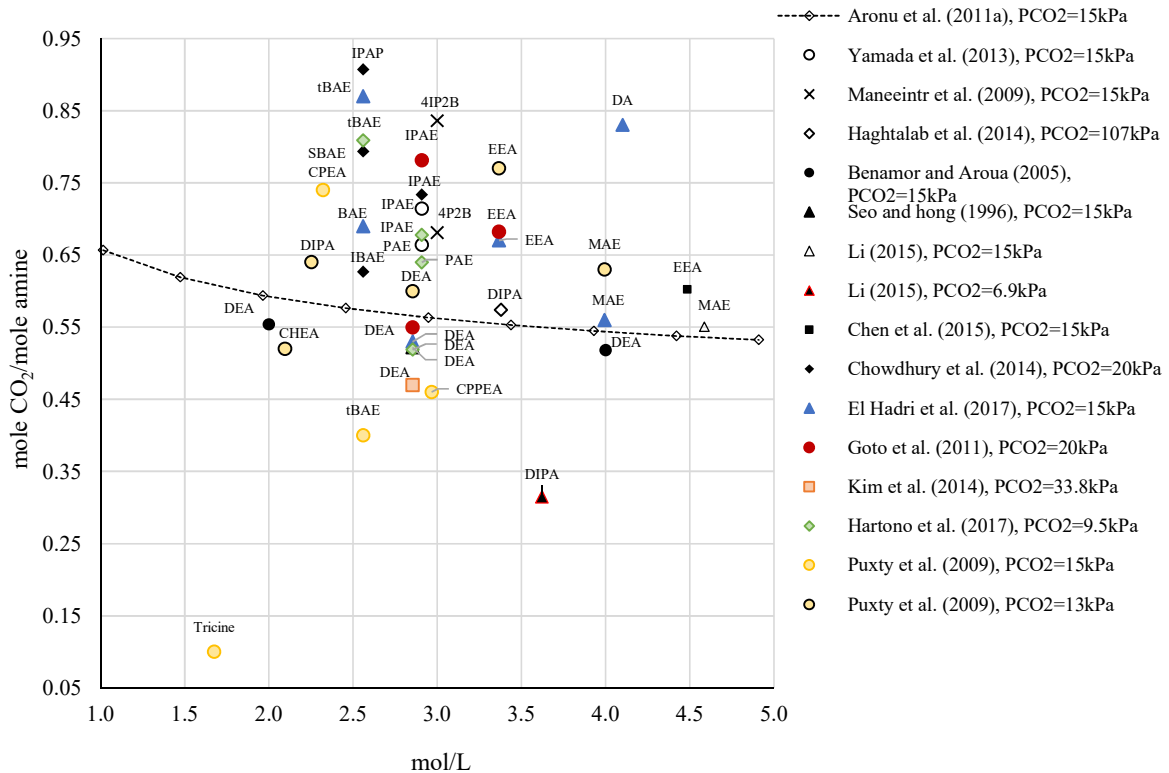


Figure 11: Absorption capacity (mole CO₂/mole amine) of different secondary amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

3.5 Cyclic capacity of secondary amine solvents

Cyclic capacity of eleven different secondary amines using equation 5, 6 and/or 7 (given below), is presented in Figure 8, Figure 9 and Figure 12, respectively.

$$\Delta\alpha^{Fig.12} = \alpha_{40^{\circ}C, 9.5kPaCO_2} - \alpha_{80^{\circ}C, 1.0kPaCO_2} \quad 7$$

Cyclic capacity reported by Chowdhury et al. (2014) slightly deviate from equation 6 as the partial pressure of CO₂ at 40 °C is 20 kPa and not 15 kPa (Figure 9). Further, the cyclic capacity reported by Li (2015) deviate from equation 7 as the CO₂ partial pressure at 40 °C is 6.9kPa and 0.1kPa at 80 °C (Figure 12).

In Figure 8, the secondary amines 4-Propylamino-2-butanol (4P2B) and 4IP2B at 3.0 mol/L reported by Maneeintr et al. (2009) shows a higher cyclic capacity than MEA. However, Figure 8 shows that Maneeintr et al. (2009) reported a significant higher cyclic capacity for 3.0 mol/L MEA than predicted by the VLE model. This high cyclic capacity for MEA reported by Maneeintr et al. (2009) made them to conclude that 2.0 mol/L 4IP2B had lower cyclic capacity than MEA. This type of uncertainties illustrates why different published studies find different novel amines promising.

Three different researchers have reported the cyclic capacity of IPAE at 2.91 mol/L. Equilibrium cyclic capacity, reported by Yamada et al. (2013) and Chowdhury et al. (2014), is given in Figure 9 with a value of 63.8 gCO₂/kg solution and 66.7 gCO₂/kg solution, respectively, and screening cyclic capacity, reported by Hartono et al. (2017), is given in Figure 12 with a value of 44.0 gCO₂/kg solution. In all cases, IPAE shows a higher cyclic capacity than MEA. However, between the equilibrium and screening cyclic capacity there is a noticeable difference in how much better IPAE performs at 2.91 mol/L than the modelled MEA at 2.95 mol/L. For instance, Yamada et al. (2013) shows a cyclic capacity that is 179 % higher than MEA, while Hartono et al. (2017) only shows a cyclic capacity that is 24 % higher. The reason is likely related to the experimental inaccuracies and to the difference in desorption temperature and CO₂ partial pressure. This difference in performance can also be seen for the tertiary amine N,N-Diethylethanolamine (DEEA) and the cyclic amine 1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD) which will be discussed in Chapter 3.7 and 3.11, respectively. The cyclic capacity of MEA at 4.91 mol/L reported by Hartono et al. (2017) is in agreement with the modelled MEA at the same concentration (Figure 12).

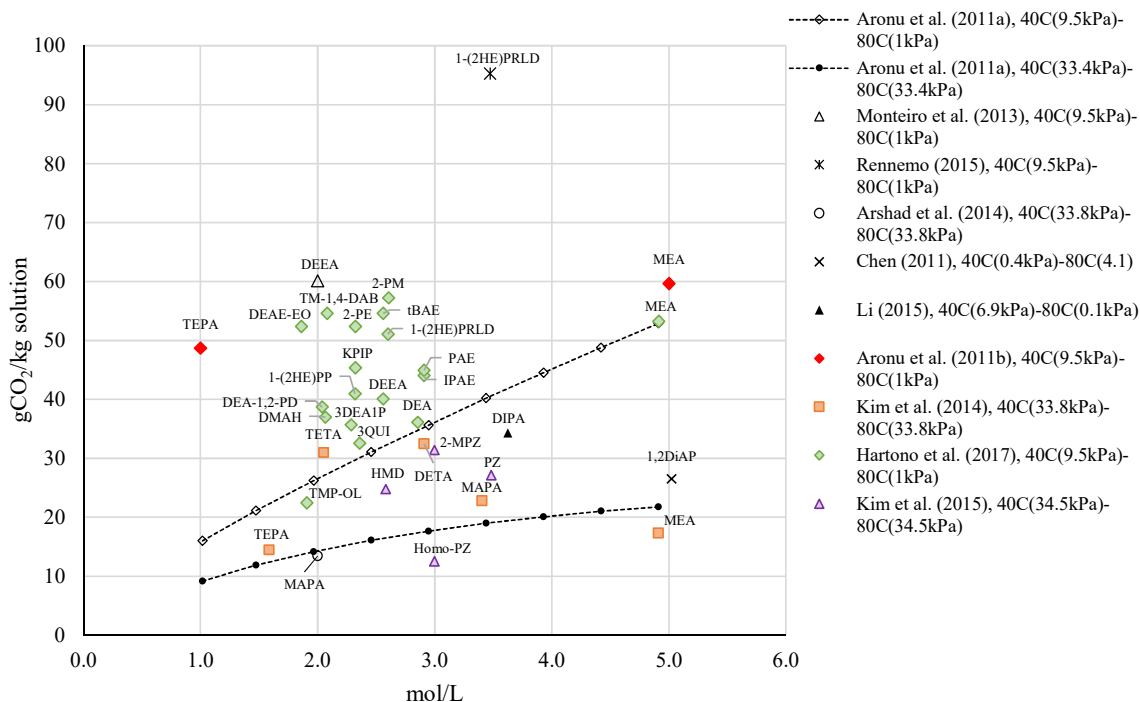


Figure 12: Cyclic capacity of different amines calculated using data available at 40 °C and 80 °C (Equation 7). The dashed lines represent model predictions of MEA. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

3.6 Absorption capacity of tertiary amine solvents at 40 °C

Absorption capacity at 40 °C in unit of gCO₂/kg solution for 21 different tertiary amines is plotted in Figure 13. Literature data was mainly collected at 15 kPa partial pressure of CO₂, but data from Chowdhury et al. (2013), Hartono et al. (2017) and Puxty et al. (2009) were collected at 20 kPa, 9.5 kPa and 13 kPa, respectively.

Of the studied tertiary amines presented in Figure 13, 17 amines perform better than MEA. The gravimetric capacity is similar to most of the primary and secondary amines, but none of the tertiary amines have as high capacity as the best primary and secondary amine, IPA at 5.08 mol/L and DA at 4.10 mol/L, respectively. This is likely due to the higher molecular weight and lower molar concentration of the tertiary amines. On the contrary, when CO₂ loading is in unit of mole CO₂/mole amine most of the tertiary amines have, as expected, a higher absorption capacity (Figure 14). The tertiary amines are mostly concentrated in the area 0.6 mole CO₂/mole amine to 0.9 mole CO₂/mole amine. The tertiary amine with the highest CO₂ loading on mole basis is 2-(2-Diethylaminoethoxy)ethanol (DEAE-EO) at 1.86 mol/L with a value of 1.09 mole CO₂/mole amine.

It can be seen that DEEA at 2.0 mol/L and 5.0 mol/L reported by Monteiro et al. (2013) has the opposite behaviour of DEA; the gravimetric capacity for DEEA is almost independent of the concentration (Figure 13), while the capacity on mole basis decreases linearly with increase in concentration (Figure 14).

As already discussed for the primary and secondary amines, also here it appears that some of the published screening results show capacities exceeding equilibrium. For the tertiary amines, this is particularly evident for DEEA at 2.56 mol/L, N,N-Dimethylethanolamine (DMEA) at 3.37 mol/L and 3-Dimethylamino-1-propanol (3DMA1P) at 2.91 mol/L (Figure 13). For DEEA at 2.56 mol/L, two out of four researchers reported a value that is higher than the equilibrium value reported by Chowdhury et al. (2013). Those are Chowdhury et al. (2013) and El Hadri et al. (2017). Solvent screening result by Chowdhury et al. (2013) exceeds the equilibrium value reported in the same publication slightly, while El Hadri et al. (2017), who performed screening at a lower partial pressure of CO₂, reported a value that is 13 % above the equilibrium loading at 20 kPa. Further, the value reported by Hartono et al. (2017) seems to be too high since it is close to the equilibrium value of 20kPaCO₂. However, Hartono et al. (2017) is consistent with literature values for MEA given in Figure 1. For DMEA at 3.37 mol/L, El Hadri et al. (2017) and Puxty et al. (2009) exceeds the equilibrium value, reported by Tong (2012), by 33% and 68%, respectively, while Chowdhury et al. (2013) reported a value that is 11% lower. For the amine 3DMA1P at 2.91 mol/L, El Hadri et al. (2017) exceeds the equilibrium value, reported by Nouacer et al. (2014) at 2.50 mol/L, with 61 % while Puxty et al. (2009) and Chowdhury et al. (2013) reported a value that is below the equilibrium value.

Furthermore, there is a considerable spread in reported screening values for DEEA at 2.56 mol/L, 3DMA1P at 2.91 mol/L and DMEA at 3.37 mol/L (see Figure 13). The variation in reported data are 30 %, 536 % and 87 %, respectively, and the huge variation have affected the conclusion of the published studies. For instance, El Hadri et al. (2017) selected 3DMA1P at 2.91 mol/L for further study, while Puxty et al. (2009) and Chowdhury et al. (2013) did not consider the solvent to be further studied. In addition, El Hadri et al. (2017) and Puxty et al. (2009) regarded DMEA at 3.37 mol/L as a promising solvent while Chowdhury et al. (2013) did not.

Further, four researchers have reported the absorption capacity of MDEA at 2.52 mol/L (Figure 13). All, with exception of Puxty et al. (2009), seems to be in agreement. Puxty et al. (2009) reported a value that is 33 % lower than the equilibrium value reported by Shen and Li (1992). However, it should be remembered that screening experiments are often not designed to reach equilibrium.

Among the four researchers who have measured the absorption capacity of Triethanolamine (TEA) at 2.01 mol/L, there seems to be an agreement that TEA has a low absorption performance (Figure 13). The low CO₂ loading is due to the electron withdrawing effect of the three hydroxyl groups connected to the nitrogen in TEA (El Hadri et al., 2017).

At last, when comparing the screening and equilibrium work for the same amines conducted by Chowdhury et al. (2013), almost the same trend of increasing absorption capacity is obtained (see Figure 13). That is TEA at 2.01 mol/L < N-Ethyldiethanolamine (EDEA) at 2.25 mol/L < MDEA at 2.52 mol/L < 3-Diethylamino-1,2-propanediol (DEA-1,2-PD) at 2.01 mol/L < 3-Diethylamino-1-propanol (3DEA1P) at 2.29 mol/L < DEEA at 2.56 mol/L < 1DMA2P at 2.91 mol/L. The only difference is that DEEA at 2.56 mol/L, from the screening work, perform slightly better than 1DMA2P at 2.91 mol/L.

However, this is because the screening value for DEEA at 2.56 mol/L exceeded its equilibrium value as addressed above.

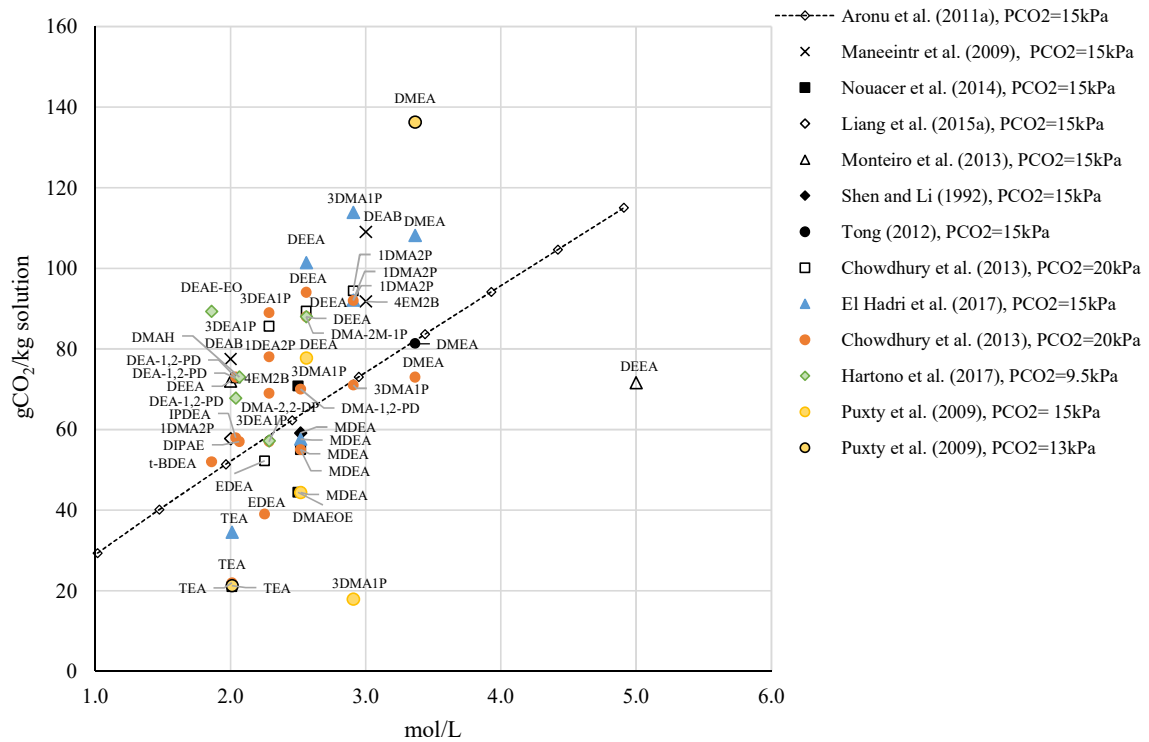


Figure 13: Absorption capacity (gCO₂/kg solution) of different tertiary amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

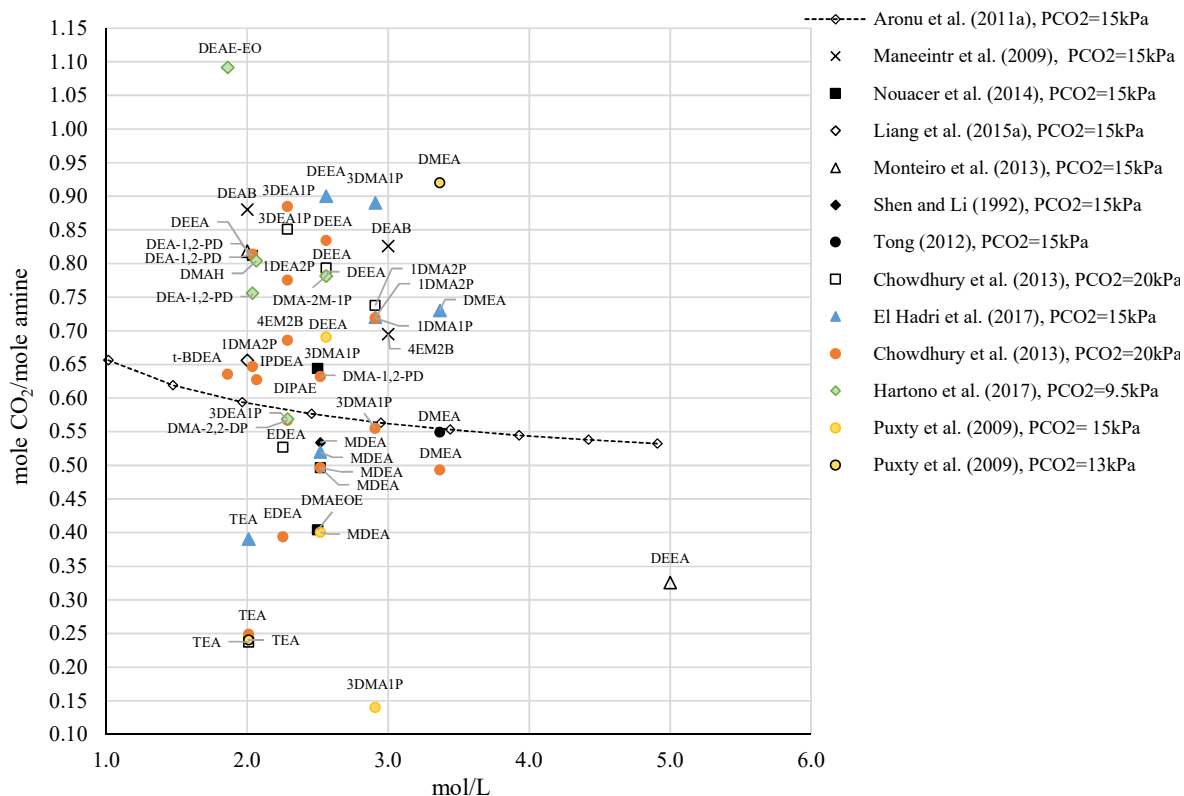


Figure 14: Absorption capacity (mole CO₂/mole amine) of different tertiary amines at 40 °C. Black symbols are experimental studies, coloured symbols are screening experiments and the dashed line represents model prediction of MEA.

3.7 Cyclic capacity of tertiary amine solvents

Cyclic capacity of 21 different tertiary amines using equation 4, 5, 6 and/or 7 is presented in Figure 7, Figure 8, Figure 9 and Figure 12, respectively. The screening and equilibrium cyclic capacity reported by Chowdhury et al. (2013) slightly deviate from equation 4 and 6, respectively. The former is given at an unknown partial pressure of CO₂ at 70 °C (Figure 7), while the latter is given at 20 kPaCO₂ for both 40 °C and 120 °C (Figure 9).

In Figure 7, in which desorption temperature is 70 °C, all tertiary amines shows a higher cyclic capacity than MEA. The tertiary amine with the highest cyclic capacity is 1-Dimethylamino-2-propanol (1DMA2P) at 2.91 mol/L. It is 270 % higher than MEA at 2.95 mol/L and 56 % higher than the primary amine 2APD at 4.70 mol/L presented in the same figure.

Ten of the amines reported by Chowdhury et al. (2013) in Figure 7 have both screening and equilibrium cyclic capacities. Chowdhury et al. (2013) compared the results from the equilibrium and screening experiments and stated that the cyclic capacity increases under equilibrium conditions compared to the screening experiments because equilibrium is not reached in the screening work. However, the screening and equilibrium cyclic capacities might not be directly comparable as it is unclear which partial pressure of CO₂ at 70 °C that is reached in the screening experiment. Further, it is noticeable that the order of increasing cyclic capacity between the screening and equilibrium data reported by Chowdhury et al. (2013) are not the same. In Figure 7, the screening study shows the

following trend: TEA at 2.01 mol/L < EDEA at 2.25 mol/L < MDEA at 2.52 mol/L < 3DEA1P at 2.29 mol/L < DEA-1,2-PD at 2.04 mol/L < 1DMA2P at 2.91 mol/L < DEEA at 2.56 mol/L, while the equilibrium study shows the following trend: TEA at 2.01 mol/L < 3DEA1P at 2.29 mol/L < DEA-1,2-PD at 2.04 mol/L < EDEA at 2.25 mol/L < MDEA at 2.52 mol/L < DEEA at 2.56 mol/L < 1DMA2P at 2.91 mol/L. Therefore, from the screening study one get for instance impression that DEEA at 2.56 mol/L has 3 % higher cyclic capacity than 1DMA2P at 2.91 mol/L, while the equilibrium study shows that 1DMA2P at 2.91 mol/L has 29 % higher cyclic capacity than DEEA at 2.56 mol/L. The reason might be because Chowdhury et al. (2013) terminated the desorption experiment after 60 minutes. When time is the endpoint criteria, it may lead to different approaches to equilibrium. Consequently, it can be questioned whether a time dependent screening experiment is able to give a reliable representation of the solvents potential.

Among the tertiary amines presented in Figure 9, in which desorption temperature is 120 °C, 1DMA2P at 2.91 mol/L still seems to have the highest cyclic capacity followed by DEEA at 2.56 mol/L. Compared to MEA at 2.95 mol/L, 1DMA2P at 2.91 mol/L and DEEA at 2.56 mol/L have 117 % and 101 % higher cyclic capacity, respectively. However, when comparing the equilibrium work conducted by Chowdhury et al. (2013), the order of increasing cyclic capacity differ from the equilibrium and screening work in Figure 7. In Figure 9 the trend is as following: TEA at 2.01 mol/L < EDEA at 2.25 mol/L < MDEA at 2.52 mol/L < DEA-1,2-PD at 2.04 mol/L < 3DEA1P at 2.29 mol/L < DEEA at 2.56 mol/L < 1DMA2P at 2.91 mol/L. Hence, EDEA at 2.25 mol/L shows a poorer performance than 3DEA1P at 2.29 mol/L, while it is the other way around for the equilibrium work in Figure 7. Therefore, as addressed in Chapter 3.3, one should be cautious to draw a conclusion at a lower temperature as it differ from the one found at 120 °C. A solvent that seems promising at 70 °C is not necessarily promising at 120 °C.

In Figure 8, in which desorption temperature is 80 °C, 4-(Ethyl-methyl-amino)-2-butanol (4EM2B) at 3.0 mol/L has a considerably higher cyclic capacity than the other presented tertiary amines. The cyclic capacity is 76.6 gCO₂/kg solution, which is 367 % higher than MEA at 2.95 mol/L and 81 % higher than AMP at 3.36 mol/L reported by Seo and Hong (1996). Compared to the tertiary amines 4-(Diethylamine)-2-butanol (DEAB) at 3.0 mol/L and DEEA at 5.0 mol/L, the cyclic capacity of 4EM2B at 3.0 mol/L is 49 % and 22 % higher, respectively.

In Figure 12, the tertiary amines studied by Hartono et al. (2017) shows a higher cyclic capacity than MEA. Among them, 2-(2-Diethylaminoethoxy)ethanol (DEAE-EO) at 1.86 mol/L has the highest cyclic capacity with a value of 52.4 gCO₂/kg solution. However, as addressed in Chapter 3.5, Hartono et al. (2017) seems to have reported a much lower difference between the amines and MEA. The difference in performance is particularly noticeable when comparing the equilibrium cyclic capacity of 2.0 mol/L DEEA, reported by Monteiro et al. (2013), to the screening cyclic capacity of 2.56 mol/L DEEA, reported by Hartono et al. (2017), at same conditions. Hartono et al. (2017) reported a value that is 50 % lower than the equilibrium value. Thus, this is again an example of the potential inaccuracies related

to solvent screening. Also, since the cyclic capacity reported by Hartono et al. (2017) agrees with the modelled MEA as mentioned above, it indicates that MEA should not be the only amine to validate the experimental setup. The experimental setup should also be validated by an amine with similar behaviour, such as absorption rate and heat of absorption, as those screened. For example, when screening tertiary amines, MDEA could be used as a control solvent.

3.8 Absorption capacity of multiamine solvents at 40 °C

In Figure 15, the absorption capacity at 40 °C for 38 different multiamines is compared at various molar concentrations. The partial pressure of CO₂ is mostly given at 15 kPa, but data from Ma'mun et al. (2006), Chen (2011), Aronu et al. (2011b) and Hartono et al. (2017), Kim et al. (2014), Kim et al. (2015) and Puxty et al. (2009) are given at 8.29 kPa, 0.41 kPa, 9.5 kPa, 33.8 kPa, 34.5 kPa and 13 kPa, respectively.

Among the studied multiamines, 35 amines seem to have a higher absorption capacity than MEA. The majority of the multiamines are concentrated in the range from 100 gCO₂/kg solution to 150 gCO₂/kg solution, which is a higher range than the primary, secondary and tertiary amines. Most of the multiamines also have a higher CO₂ loading in unit of mole CO₂/mole amine as they are concentrated in the area 0.9 mole CO₂/mole amine to 1.5 mole CO₂/mole amine (Figure 16). The reason for the high CO₂ loading is that multiamines have two or more amine groups available for the reaction with CO₂ (Singh et al., 2009).

The multiamine with the highest absorption capacity in unit of gCO₂/kg solution seems to be Diethylenetriamine (DETA) at 2.91 mol/L, reported by Puxty et al. (2009), with a value of 226.5 gCO₂/kg solution (Figure 15). However, this value is 76 % above the equilibrium value reported by Chang et al. (2013) at the same concentration. Therefore, as discussed above, one should be careful to draw conclusion based on screening data as some have a tendency to exceed equilibrium. Nevertheless, as DETA is highly corrosive it is not a suitable solvent for post combustion CO₂ capture by means of chemical absorption (Hayfron-Benjamin, 2013).

Three researchers have performed screening of Hexamethylenediamine (HMD) at 2.58 mol/L. Among them, El Hadri et al. (2017) exceeds the equilibrium reported by Mondal et al. (2015) with 18 %, whereas Puxty et al. (2009) and Kim et al. (2015) are below the equilibrium value. However, as Kim et al. (2015) used a higher CO₂ partial pressure one would expected the CO₂ loading to be higher.

It can be seen that both 1,8-*p*-Mentanediamine (MDA) at 0.63 mol/L and 1.25 mol/L, and HMD at 0.86 mol/L and 2.58 mol/L have a linear increase in the gravimetric capacity (Figure 15). On mole basis, MDA is independent of the concentration, while the capacity of HMD is decreasing linearly (Figure 16).

Singh et al. (2011) studied the effect on absorption capacity when increasing the number of amine groups at 10 kPaCO₂ and 30 °C. The studied amines were DETA (three amine groups) at 2.47 mol/L and Triethylenetetramine (TETA) (four amine groups) at 2.61 mol/L. The investigation showed that the

absorption capacity in unit of both gCO_2/kg solution and mole CO_2/mole amine increases with increasing number of amine groups (Figure 3 and Figure 6). Kim et al. (2014) who studied DETA at 2.91 mol/L and TETA at 2.05 mol/L shows the same trend in mole CO_2/mole amine, but the opposite trend in unit of gCO_2/kg solution; absorption capacity increases with decreasing number of amine groups. This is likely because Kim et al. (2014) studied DETA and TETA at different concentrations. Further, as Kim et al. (2014) under predicted the value for MEA discussed above, it is expected that also the reported values for DETA at 2.91 mol/L, TETA at 2.05 mol/L, TEPA at 1.58 mol/L and MAPA at 3.40 mol/L are under predicted. However, when comparing to the equilibrium value of DETA at 2.91 mol/L, Kim et al. (2014) reported a value that is 22 % above the equilibrium value.

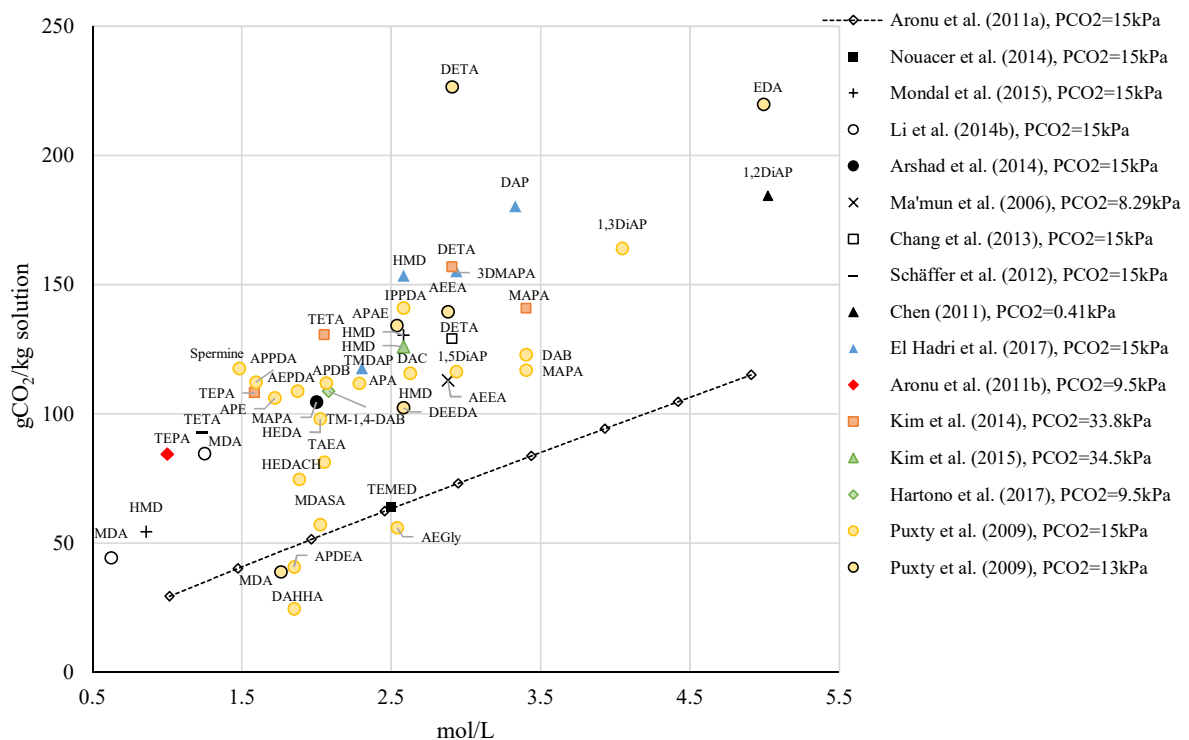


Figure 15: Absorption capacity (gCO_2/kg solution) of different multiamines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

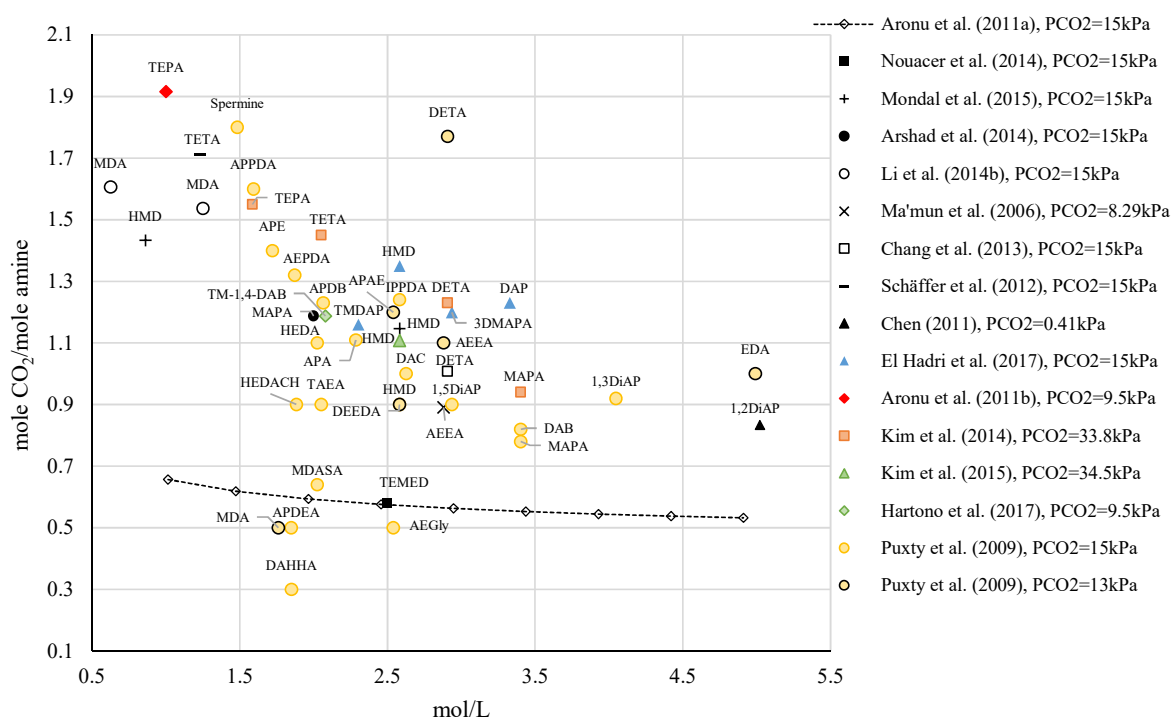


Figure 16: Absorption capacity (mole CO₂/mole amine) of different multiamines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

3.9 Cyclic capacity of multiamine solvents

From available literature data, cyclic capacity of ten multiamines using equation 5, 6, and/or 7 is presented in Figure 8, Figure 9 and Figure 12, respectively. The cyclic capacity reported by Nouacer et al. (2014) slightly deviate from equation 5 as the partial pressure of CO₂ is 25 kPa at both temperatures (Figure 8). Further, Ma'mun et al. (2006) slightly deviate from equation 6 as it is given at 8.29 kPaCO₂ at 40 °C and 100 kPaCO₂ at 120 °C (Figure 9). Chen (2011) slightly deviate from equation 7 as the partial pressure of CO₂ is 0.4 kPa at 40 °C and 4.1 kPa at 80 °C (Figure 12). Also, Kim et al. (2014) and Kim et al. (2015) deviate from equation 7 as they are given at 33.8 kPaCO₂ and 34.5kPaCO₂, respectively, for both temperatures.

In Figure 8, in which desorption temperature is 80 °C, MDA at 1.25 mol/L, reported by Li et al. (2014b), has a cyclic capacity that is 578 % higher than MEA at 1.02 mol/L. However, due to the low molar concentration, it is 25 % lower than the tertiary amine 4EM2B at 3.0 mol/L. Further, DETA at 2.91 mol/L, reported by Chang et al. (2013), has a cyclic capacity that is 41 % higher than MEA at 2.95 mol/L, while 70 % and 55 % lower than 4EM2B at 3.0 mol/L and the tertiary amine DEAB at 3.0 mol/L, respectively. Thus, DETA seems to have a lower potential to release CO₂ during regeneration than 4EM2B and DEAB.

In both Figure 8 and Figure 9, MAPA at 2.0 mol/L, reported by Arshad et al. (2014), are given. In Figure 8 the cyclic capacity is 15.3 gCO₂/kg solution (18 % higher than MEA at 1.96 mol/L), and in

Figure 9 the cyclic capacity is 16.9 gCO₂/kg solution (2 % lower than MEA at 1.96 mol/L). Thus, as the cyclic capacity of MAPA is approximately the same when using a desorption temperature of 80 °C and 120 °C, it indicates that MAPA is only slightly sensitive to temperature.

In Figure 12, TEPA at 1.0 mol/L has a cyclic capacity that is 204 % higher than MEA at 1.02 mol/L, while TM-1,4-DAB at 2.08 mol/L has a cyclic capacity that is 108 % higher than MEA at 1.96 mol/L. Compared to the tertiary amine DEAE-EO at 1.86 mol/L, the cyclic capacity of TEPA at 1.0 mol/L and TM-1,4-DAB at 2.08 mol/L are 7 % lower and 4 % higher, respectively. Further, among the amines studied by Kim et al. (2014), TETA at 2.08 mol/L and DETA at 2.91 mol/L shows the highest cyclic capacity. They have a cyclic capacity that is 118 % higher than MEA at 1.96 mol/L and 84 % higher than MEA at 2.95 mol/L, respectively. The percent increase in cyclic capacity of DETA compared to MEA is two times higher than what is seen for Chang et al. (2013) in Figure 8 discussed above. The reason is likely due to the difference in partial pressure and the inaccuracies related to the different ways the experimental work is performed. Further, MAPA at 3.40 mol/L, reported by Kim et al. (2014), and MAPA at 2.0 mol/L, reported by Arshad et al. (2014), shows similar cyclic capacities. As screening data reported by Kim et al. (2014) can be debated (see discussion on MEA, DEA and DETA), it is difficult to conclude that the cyclic capacity of MAPA is only slightly sensitive to changes in concentration.

3.10 Absorption capacity of cyclic amine solvents at 40 °C

Absorption capacity at 40 °C in unit of gCO₂/kg solution for 35 different cyclic amines is plotted in Figure 17. The partial pressure of CO₂ was in most cases collected at 15 kPa, but data from Nouacer et al. (2014), Chen and Rochelle (2011), Hilliard (2008), Chowdhury et al. (2013) and Goto et al. (2011), Kim et al. (2015) and Puxty et al. (2009) were collected at 30.5 kPa, 5.7 kPa, 5-4.7 kPa, 20 kPa, 34.5 kPa, and 13 kPa, respectively.

Among the studied cyclic amines, 21 amines perform better than MEA. The gravimetric capacity is similar to the primary, secondary and tertiary amines as most of the cyclic amines are concentrated in the range from 40 gCO₂/kg solution to 120 gCO₂/kg solution. The cyclic amines that seem to hold the highest absorption capacity are 1-(2-Aminoethyl)piperazine (AEP) at 3.38 mol/L and 2-Piperidineethanol (2-PE) at 3.87 mol/L, with a value of 150.6 gCO₂/kg solution and 137.1 gCO₂/kg solution, respectively. This is 60 % and 46 %, respectively, higher than MEA at 3.93 mol/L.

In unit of mole CO₂/mole amine, most of the cyclic amines are concentrated in the range of 0.4 mole CO₂/mole amine to 1.0 mole CO₂/mole amine (Figure 18). Thus, they perform slightly better than the tertiary amines.

Four researchers have reported the absorption capacity of Piperazine (PZ) at 3.48 mol/L. Depending on the source, the reported values varies from 118.8 gCO₂/kg solution to 168.6 gCO₂/kg solution (Figure 17). This is a variation of 42 %. El Hadri et al. (2017) and Kim et al. (2015) reported a value that is 1 % and 5 % lower than the equilibrium value, respectively, while Puxty et al. (2009) reported a value

that is 35 % higher. One would expect both El Hadri et al. (2017) and Kim et al. (2015) to report a higher value due to the higher partial pressure compared to the equilibrium value. However, as we have seen in the earlier chapters, screening experiments seem to lead to results that indicate lack of control of obtained data as some screening data are above the equilibrium limit.

Further, the screening value for 1-(2-hydroxyethyl)piperidine (1-(2HE)PP) at 2.32 mol/L reported by Chowdhury et al. (2013) slightly exceed the equilibrium value given in the same publication (within 5 %). However, for the amine 1-(2HE)PRLD at 2.60 mol/L both Chowdhury et al. (2013) and Hartono et al. (2017) are close to the equilibrium value reported by Rennemo (2015). The equilibrium value for 2-PE at 3.87 mol/L reported by Rennemo (2015) is consistent with data from Chen and Rochelle (2011).

For the amines Homopiperazine (HomoPZ) at 3.0 mol/L, 2-Piperidinemethanol (2-PM) at 2.60 mol/L and 3-Quinuclidinol (3QUI) at 2.36 mol/L, the reported screening values varies with 67 %, 30 % and 124 %, respectively. The reason for the huge differences are different CO₂ partial pressures and experimental inaccuracies.

Singh et al. (2011) studied AEP at 2.50 mol/L at 30 °C and 10 kPaCO₂ (Figure 3). The absorption capacity was reported to be 118.8 gCO₂/kg solution, which is 105 % higher than the capacity of MEA at the same concentration and condition.

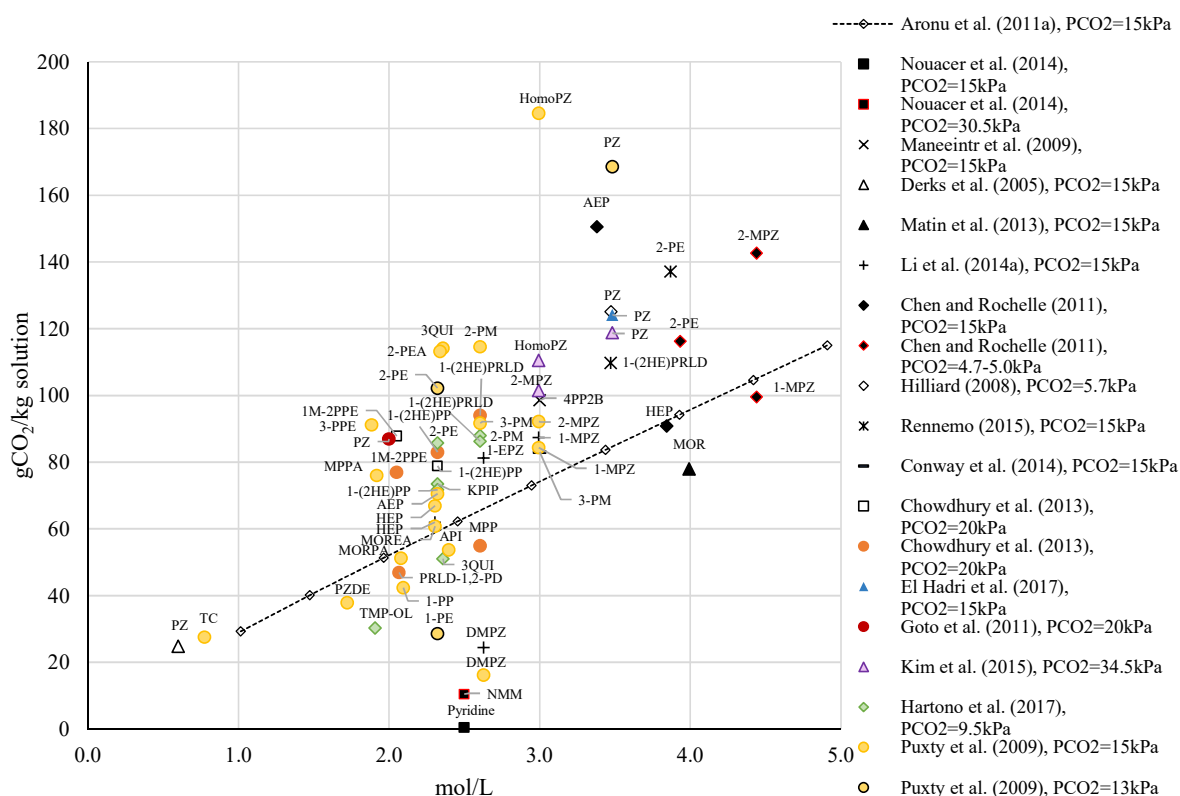


Figure 17: Absorption capacity (gCO₂/kg solution) of different cyclic amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

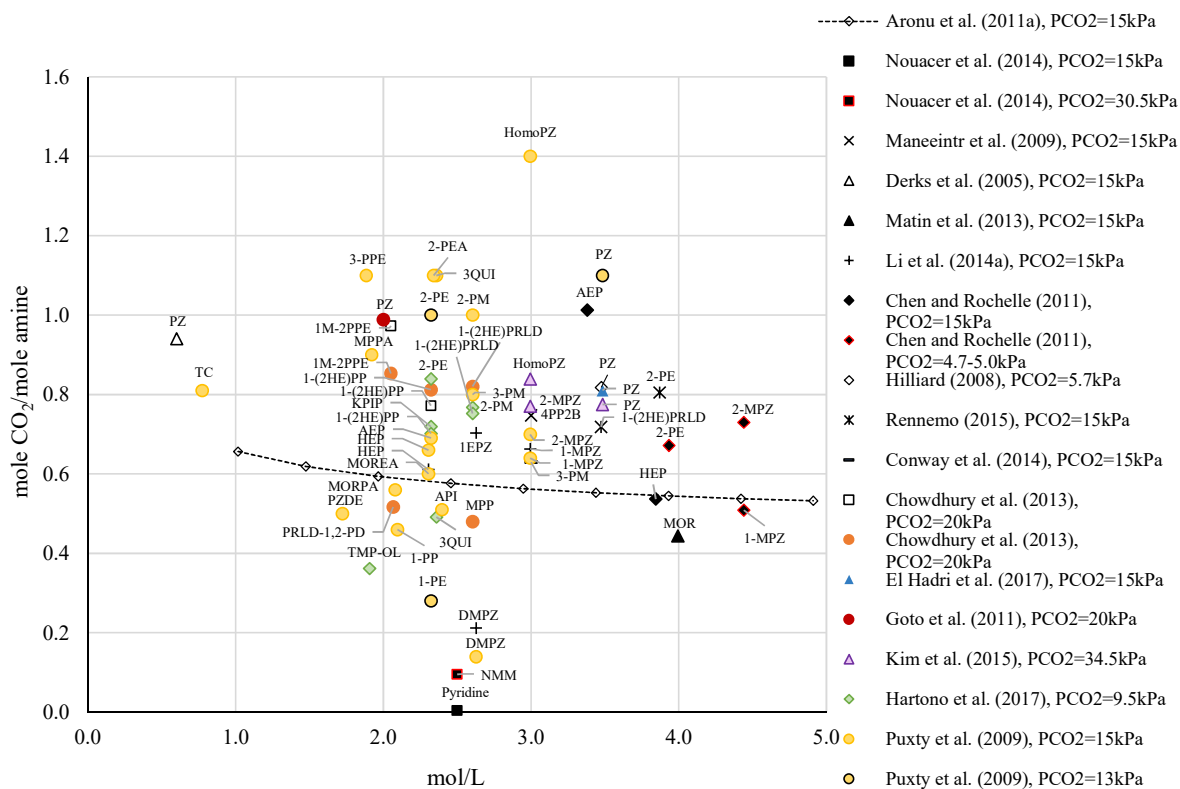


Figure 18: Absorption capacity (mole CO₂/mole amine) of different cyclic amines at 40 °C. Black symbols are from equilibrium studies, coloured symbols are from screening experiments and the dashed line represent model predictions of MEA.

3.11 Cyclic capacity of cyclic amine solvents

Cyclic capacity of 23 different cyclic amines using equation 4, 5, 6 and 7 is presented in Figure 7, Figure 8, Figure 9 and Figure 12, respectively. Again, the screening cyclic capacity reported by Chowdhury et al. (2013) slightly deviate from equation 4 as it is given at an unknown partial pressure of CO₂ at 70 °C (Figure 7). The cyclic capacity reported by Chen and Rochelle (2011) deviate from equation 5 as the CO₂ partial pressure is at 4.7-5 kPa (Figure 8). Further, cyclic capacity reported by Rennemo (2015) and Chowdhury et al. (2013) deviate from equation 6 as the former is given at 123.2 kPa at 120 °C and the latter is given at 20 kPa for both temperatures (Figure 9). Kim et al. (2015) deviate from equation 7 as it is given at 34.5 kPaCO₂ (Figure 12).

In Figure 7, in which desorption temperature is 70 °C, all cyclic amines perform better than MEA. The cyclic amine that has the highest cyclic capacity is 1-(2HE)PP at 2.32 mol/L. Its cyclic capacity is 42.2 gCO₂/kg solution, which is 247 % higher than MEA at 2.95 mol/L and 6 % lower than the tertiary amine 1DMA2P at 2.91 mol/L. Compared to the secondary amine 2APD at 4.70 mol/L, the equilibrium cyclic capacity of 1-(2HE)PP is 47 % higher. When comparing the screening and equilibrium values reported by Chowdhury et al. (2013) it is noticeable that also for the cyclic amines, as what was the case for the tertiary amines, the equilibrium values are higher than the screening values. However, unlike the tertiary amines, the trend of increasing cyclic capacity between the cyclic amines 1M-2PPE at 2.05 mol/L and 1-(2HE)PP 2.32 mol/L is the same in both the equilibrium and screening study. That

is 1M-2PPE < 1-(2HE)PP. On the contrary, in Figure 9, in which the desorption temperature is 120 °C, 1M-2PPE at 2.05 mol/L has 9 % higher cyclic capacity than 1-(2HE)PP at 2.32 mol/L. Thus, as discussed in Chapter 3.3, one should be careful to draw a conclusion of the best performing amine at low temperatures, as another conclusion may be drawn at a higher temperature.

Further, in Figure 8, in which desorption temperature is 80 °C, both 1-(2HE)PRLD and 2-PE shows a high cyclic capacity. The cyclic capacity of 1-(2HE)PRLD at 3.47 mol/L is 349 % higher than MEA at 3.44 mol/L, while 2-PE at 3.87 mol/L is 299 % higher than MEA at 3.93 mol/L. Further, 2-PE at 3.87 mol/L has a cyclic capacity that is comparable to the tertiary amine 4EM2B, while 1-(2HE)PRLD at 3.47 mol/L perform slightly better.

In Figure 9, in which the desorption temperature is 120 °C, 1-(2HE)PRLD at 3.47 mol/L and 2-PE at 3.87 mol/L shows similar cyclic capacity as the one in Figure 8. This indicates that they are only slightly sensitive to temperature. When comparing 1-(2HE)PRLD at 3.47 mol/L to DEEA at 5.0 mol/L, reported by Monteiro et al. (2013) and Zaidy (2011), and MEA at 3.44 mol/L, the cyclic capacity of 1-(2HE)PRLD is 28 % and 236 % higher, respectively. Further, 1,4-Dimethylpiperazine (DMPZ) at 2.63 mol/L, 1-Piperazineethanol (HEP) at 2.30 mol/L and Morpholine (MOR) at 4.0 mol/L, which showed a low absorption capacity in Figure 17, also shows low cyclic capacity.

In Figure 12, in which desorption temperature is 80 °C, 2-Piperidinemethanol (2-PM) at 2.60 mol/L has 9 % and 12 % higher cyclic capacity than 2-PE at 2.32 mol/L and 1-(2HE)PRLD 2.60 mol/L, respectively. However, also here it is evident that screening cyclic capacity reported by Hartono et al. (2017) is lower than the equilibrium cyclic capacity. Hartono et al. (2017) reported a cyclic capacity of 1-(2HE)PRLD at 2.60 mol/L that is 46 % lower than the cyclic capacity reported by Rennemo (2015) at 3.47 mol/L.

3.12 Correlation between pKa and the absorption capacity at 40 °C

The dissociation constant (pKa) is an important property to consider when searching for new amine solvents. The pKa value of an amine solvent has shown to be strongly correlated with the rate of CO₂ absorption where the reaction rate increases with pKa (da Silva and Svendsen, 2007; Versteeg et al., 1996). Additionally, several attempts have been made to correlate the pKa value of an amine solvent with the CO₂ absorption capacity (Chowdhury et al., 2013; da Silva, 2011; Mergler et al., 2011; Puxty et al., 2009). For instance, Puxty et al. (2009) plotted the pKa value as a function of CO₂ absorption capacity and showed that the tertiary amines were strongly correlated with pKa. The absorption capacity of the multiamines showed a slight dependence on pKa, while no correlation with pKa was seen for the primary and secondary amines.

To investigate the dependence on pKa of the studied amines in this work, the absorption capacity in unit of mole CO₂/mole amine was correlated to the pKa value. Due to the spread in reported screening data, only equilibrium data was considered. The pKa values at 25 °C are presented in Table S1 to S5 and where available the values were taken from the literature. For the values taken from Puxty et al.

(2009), only the pKa values with reference to NIST Critically Selected Stability Constants of Metal Complexes were extracted. The predicted pKa values were taken from SciFinder Scholar™ 2016 where they are calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs). Depending on the amine, the accuracy of the predicted pKa varied between ± 0.1 to ± 0.7 . For the diamines, the pKa value of the most basic amine group is listed.

Overall, the pKa values range from 5 to 11, and the general trend is that the absorption capacity increases with pKa. For the primary amines, the linear dependency is seen among the amines available at 15 kPaCO₂ (Figure 19). Data from Idris et al. (2015) shows low absorption capacity because the partial pressure of CO₂ are 1 kPaCO₂, and data from Park et al. (2002a) and Park et al. (2002b) shows high absorption capacity because the partial pressure of CO₂ is 25 kPaCO₂. For the secondary amines only a slight linear dependence can be seen (Figure 20), while a strong linear dependency is seen for the tertiary amines (Figure 21). For DEEA, the CO₂ loading is given at both 0.33 mole CO₂/mole amine and 0.82 mole CO₂/mole amine due to the difference in CO₂ concentration, 5.0 mol/L and 2.0 mol/L respectively. Thus, the difference in molar concentration also affects the relation between pKa and the absorption capacity. For the multiamines and the cyclic amines given in Figure 22 and Figure 23, respectively, a rough linear relationship can be seen. However, the trend seen for the multiamines might not be representative as there are few equilibrium data available. Puxty et al. (2009), as mentioned above, showed a slight dependence on pKa for the multiamines.

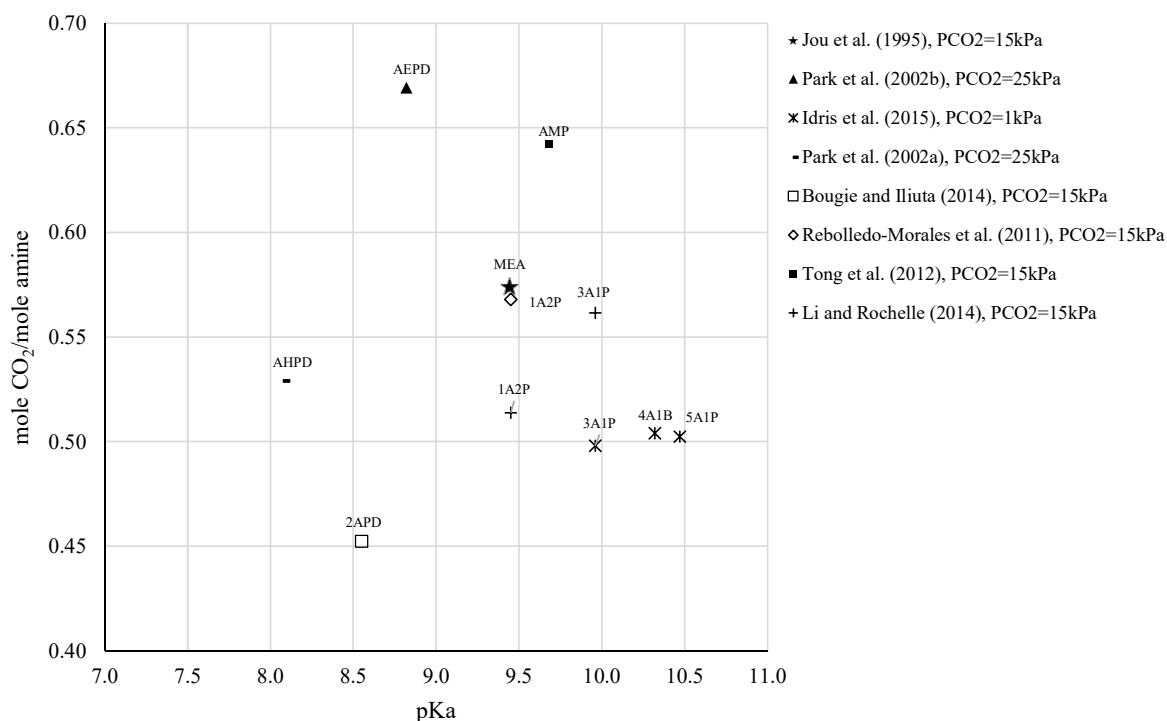


Figure 19: Correlation between pKa of primary amine solvents and their absorption capacity at 40 °C

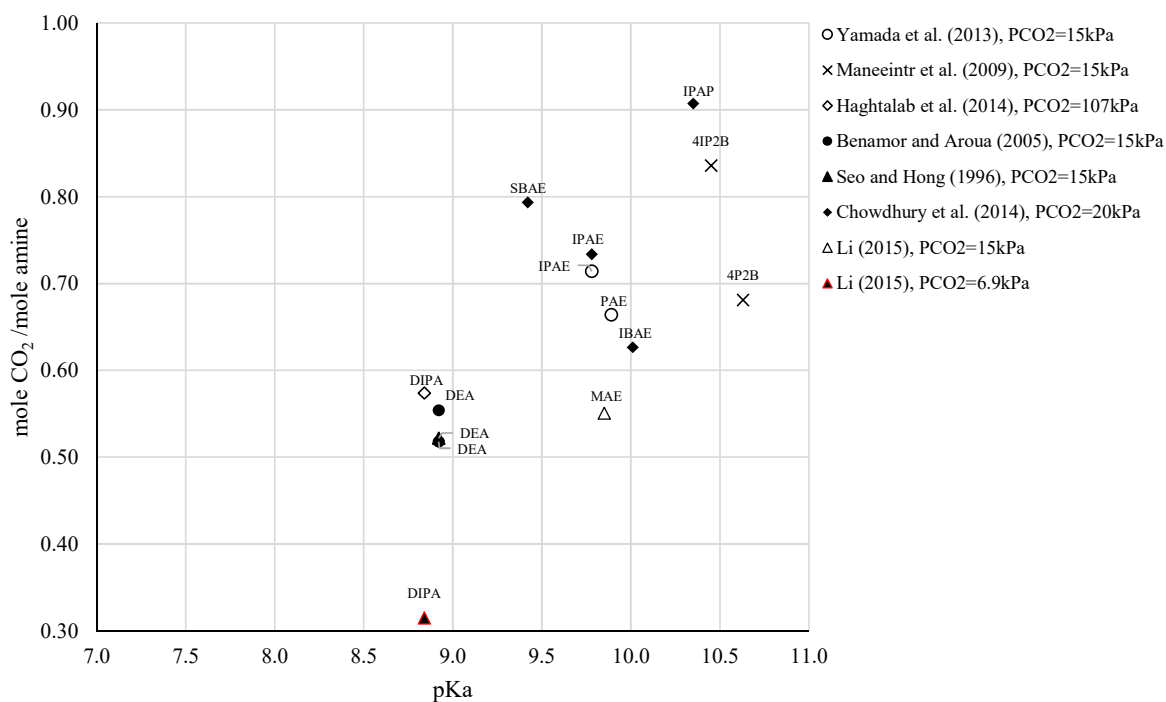


Figure 20: Correlation between pKa of secondary amine solvents and their absorption capacity at 40 °C

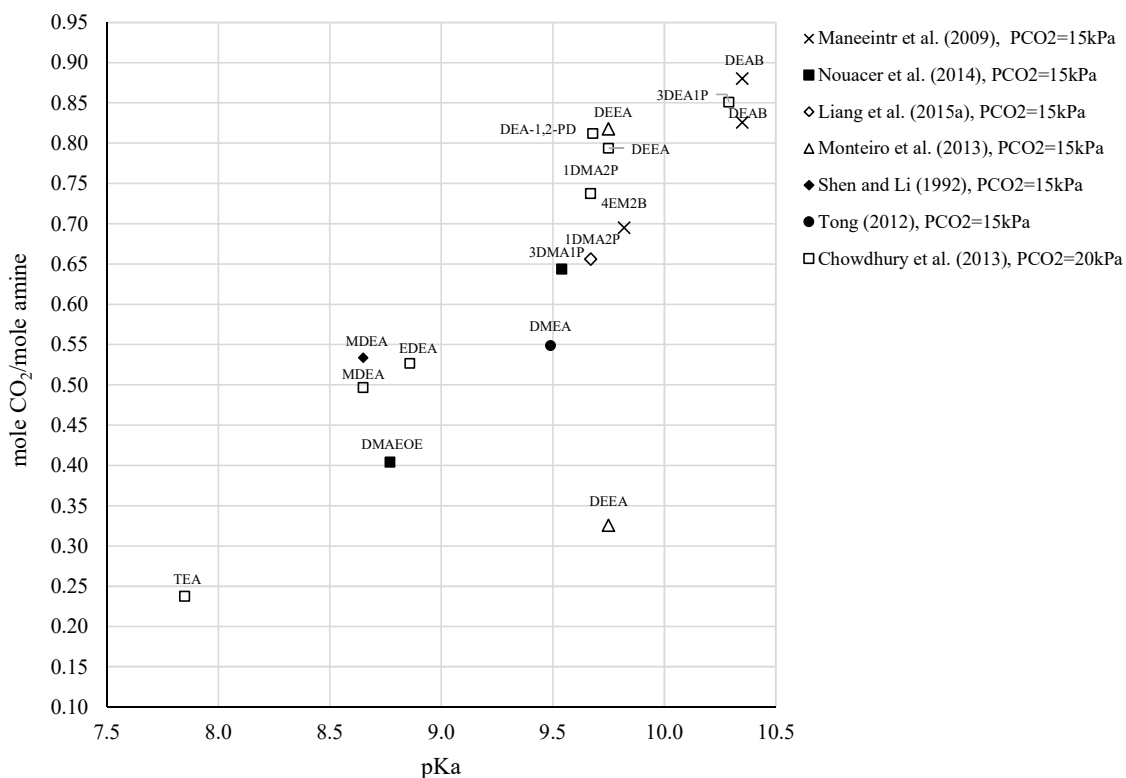


Figure 21: Correlation between pKa of tertiary amine solvents and their absorption capacity at 40 °C

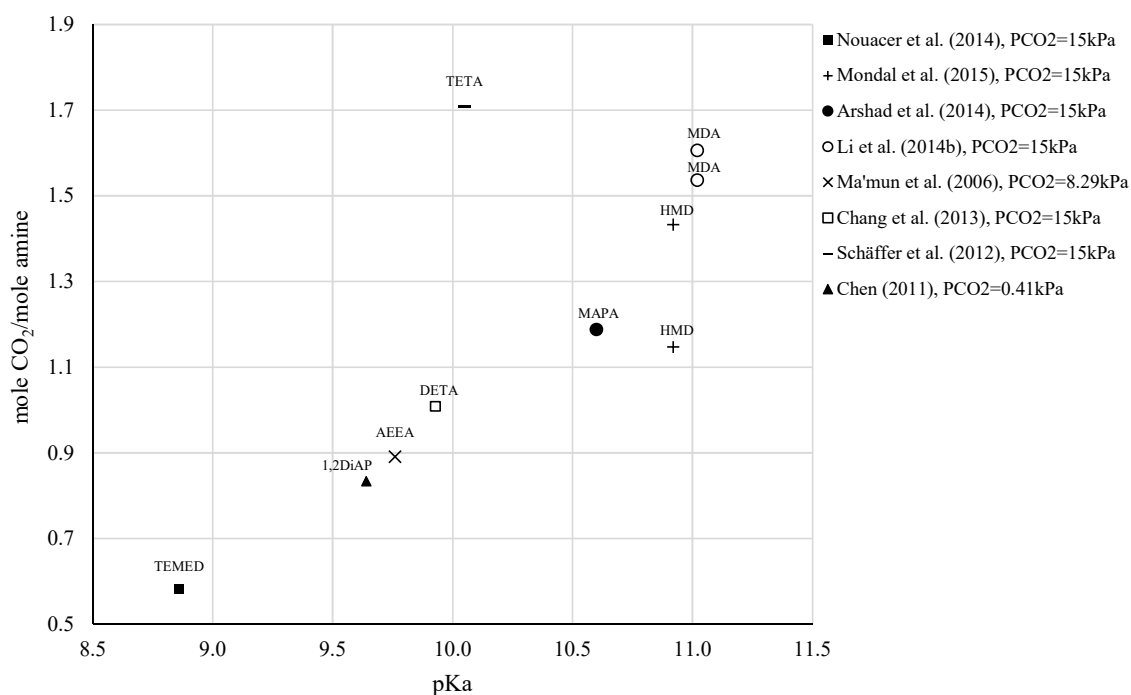


Figure 22: Correlation between pKa of multiamine solvents and their absorption capacity at 40 °C

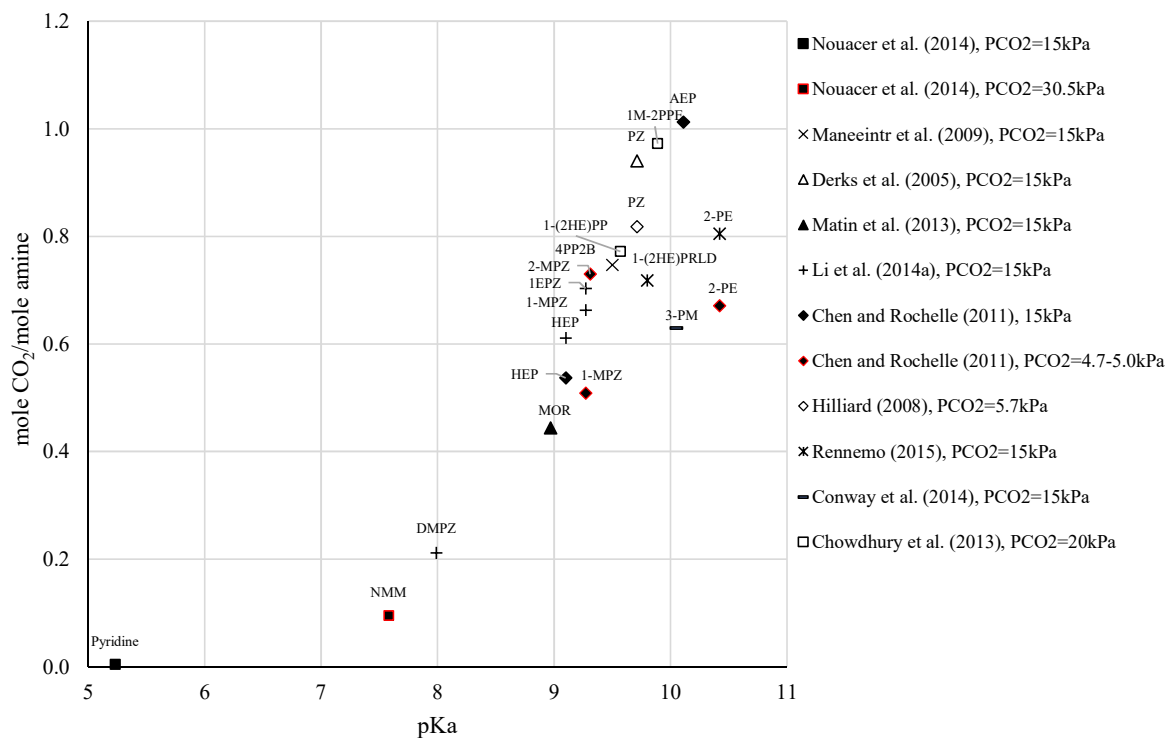


Figure 23: Correlation between pKa of cyclic amine solvents and their absorption capacity at 40 °C

4 Conclusion

In this work absorption capacity at 40 °C, cyclic capacity and the relation between pKa of the amine solvents and absorption capacity were studied. In total, 132 single aqueous amine solvents with potential to be used in a chemical absorption process were investigated.

Based on the published data, no single amine was identified to have superior absorption capacity and cyclic capacity performance. However, most of the amines spanned between slightly and significantly better performance than MEA. In some cases, the reported screening work led to results where the equilibrium value was exceeded. Additionally, sometimes a large spread in the reported values, for the same amine, was seen.

Further, a solvent that seemed promising in terms of cyclic capacity with desorption at 70 °C or 80 °C, did not always show the same potential with desorption at 120 °C. Consequently, cyclic capacities calculated from screening experiments can give an unrealistic picture of the cyclic capacity. It is therefore difficult to identify the most potential solvents based on the available screening data.

It is clear that analytical methods leading into correct determination of liquid loadings are crucial and that the screening experiments should not be terminated on a time criteria as it leads to different approaches to equilibrium. Furthermore, desorption tests should be performed under realistic process temperatures. Finally, uncertainties in measurements and calculated values should be reported alongside the data and the experimental setup should be validated by amines with similar properties as those screened.

Overall, screening is useful to identify amines that clearly performs poorly. If screening is performed using well validated and trustful methods using relevant temperatures, it can be used to identify a group of well performing amines.

At last, the absorption capacity seemed to be linearly dependent on the pKa value of the amine solvent.

Acknowledgements

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