

High-capacity amine-imidazole solvent blends for CO₂ capture

Sigvart Evjen^a, Anne Fiksdahl^a, Hanna K. Knuutila^{b}*

a) Department of Chemistry, Norwegian University of Science and Technology, Høgskoleringen 5, 7034 Trondheim, Norway

b) Department of Chemical Engineering, Norwegian University of Science and Technology, Sem Sælands vei 6, 7034 Trondheim, Norway

The CO₂ absorption performance of aqueous solvent blends containing four imidazoles (2-MeIm, 2-Et-4-MeIm, 2,4,5-MeIm and 1,2,4,5-MeIm) and four promoters (MEA, DEA, PZ and MAPA) were investigated using a small-scale screening apparatus. Exceptionally high absorption capacity of 14 wt% and 16 wt% was obtained for 2,4,5-MeIm/PZ and 2,4,5-MeIm/MAPA solutions, respectively. Cyclic capacities as high as 12 wt% were obtained for 3 M 2,4,5-MeIm + 1 M PZ solutions between 40 and 80 °C at 10 kPa CO₂. The outstanding performance is the result of selective precipitation of 2,4,5-MeImH⁺ bicarbonate, allowing the formation of a highly loaded slurry solution. 2,4,5-MeIm/diamine solutions are proposed as a novel type of absorption blends for CO₂ capture.

1. Introduction

With the continuing rise of the atmospheric CO₂ concentration, the need to capture CO₂ is becoming increasingly more important in order to achieve the goal of the Paris Agreement. Chemical absorption with alkanolamines has served as the dominant technology for CO₂ capture. Unfortunately, alkanolamine systems require significant energy for solvent regeneration.¹ There are currently several other types of chemical absorption systems which have been and are investigated for carbon dioxide removal from flue gases, including piperazine (PZ),²⁻⁴ *N*-methylaminopropylamine (MAPA),⁵ ionic liquid^{6, 7} and amino acid^{8, 9} solvents. Such solutions attempt to address shortcomings of alkanolamine absorbents. Recently, increased attention has been given to imidazole-based systems.¹⁰ Imidazoles are commonly used as precursors for imidazolium ionic liquids as physical absorbents for CO₂ capture. We have recently reported that some imidazoles, especially 2,4,5-trimethylimidazole (2,4,5-MeIm), are potential chemical CO₂ absorbents.¹¹ Imidazoles exhibit low vapor pressure,¹² are thermally¹³ and oxidatively¹⁴ stable and have low heat of absorption¹¹. A hurdle for the utilization of imidazoles as absorbents for CO₂ capture is their low absorption rates. To improve absorption rates, imidazoles can be blended with a primary or secondary amine.^{15, 16} For amine blends, the chemical absorption is enhanced by combining the high absorption rate of the primary/secondary amine with the higher cyclic capacity of the imidazole/tertiary amine.¹⁷ Typically, alkanolamines have been the preferred tertiary amines for amine blends. An optimum p*K*_a of the tertiary amine of 9.1¹⁶ or 9.48–10.13¹⁸ in solution with PZ or MAPA, respectively, has been proposed to achieve the highest CO₂ absorption capacity and cyclic capacity. In our previous studies on imidazole, we tested new imidazoles with p*K*_a values in the range of 7-9.1.¹¹

In this study, the absorption capacity and cyclic capacity of four imidazoles (2-MeIm, 2-Et-4-MeIm, 2,4,5-MeIm and 1,2,4,5-MeIm) with different degree of alkylation were studied in amine

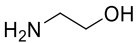
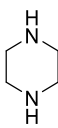
blends with MEA, PZ, MAPA and DEA by the use of a small-scale screening apparatus. The effect on the absorption capacity by changing imidazole and promoter concentration was investigated, and 2,4,5-MeIm was identified as a promising absorbent in blends with both PZ and MAPA, providing both high absorption capacity and large cyclic capacity in mixed amine solvents.

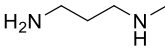
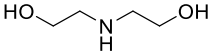

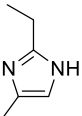
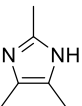
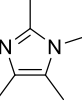
2. Experimental Section

2.1 Materials

An overview of the tested compounds is presented in Table 1. Monoethanolamine (MEA), piperazine (PZ), (3-methylamino)propylamine (MAPA), diethanolamine (DEA), 2-methylimidazole (2-MeIm), 2-ethyl-4-methylimidazole (2-Et-4-MeIm) were obtained from Sigma-Aldrich Merck. 1,2,4,5-Tetramethylimidazole (1,2,4,5-MeIm) was obtained from TCI Europe. CO₂ was supplied by AGA. Commercial compounds were used without further purification. 2,4,5-Trimethylimidazole (2,4,5-MeIm) was readily prepared by a one-step procedure in our laboratory from 2,3-butanedione, acetaldehyde and ammonium sulfate as detailed in another work.¹⁹ Samples were prepared using MilliQ water (18.2 Ω). An overview of the compounds is given in Table 1.

Table 1: Compounds studied in this work

Name	CAS	%Purity	Supplier	Structure
Monoethanolamine (MEA)	141-43-5	≥99.5%	Sigma-Aldrich	
Piperazine (PZ)	110-85-0	99%	Sigma-Aldrich	

(3-Methylamino)propylamine (MAPA)	6291-84-5	≥97%	Sigma-Aldrich	
Diethanolamine (DEA)	111-42-2	99%	Sigma-Aldrich	
2-Methylimidazole (2-MeIm)	693-98-1	99%	Sigma-Aldrich	
2-Ethyl-4-methylimidazole (2-Et-4-MeIm)	931-36-2	95%	Sigma-Aldrich	
2,4,5-Trimethylimidazole (2,4,5-MeIm)	822-90-2	98%	Synthesis ¹⁹	
1,2,4,5-Tetramethylimidazole (1,2,4,5-MeIm)	1739-83-9	98%	TCI-Europe	
Carbon dioxide (CO ₂)	124-38-9	99.999%	AGA	

2.2 CO₂ absorption capacity screening experiments

CO₂ absorption capacity screening experiments of the amine blends were carried out in a 300 mL reactor (Figure 1) previously used to study the absorption of non-promoted imidazole.¹¹ A certain amount of amine solution (1.5 mL at 40 °C and 8 mL at 80 °C) was added to the liquid well. The liquid was stirred slowly and the reactor was closed. The reactor was degassed under vacuum at 20 °C before the experiment was started at <5 kPa pressure.

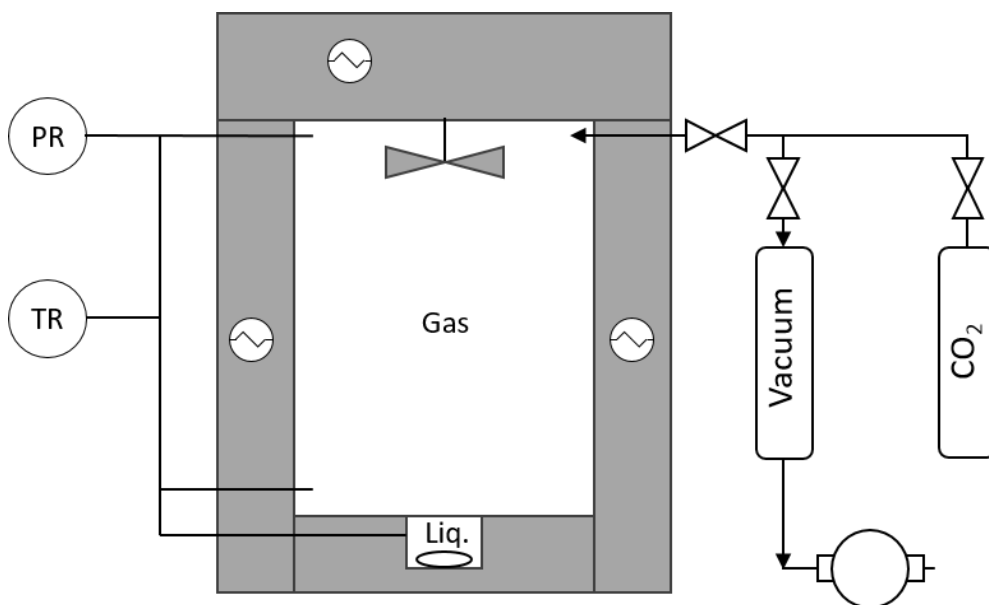


Figure 1: Small-scale reactor for CO₂ absorption measurements.

The reactor was heated with current carrying metal rods in the four corners of the apparatus and two on the lid of the apparatus. The temperature in the medium was measured in three points: in the liquid solution, at the bottom of the gas phase and at the top of the gas phase. Temperature control was performed using Labview 2016 and experiments were run at 40 ± 0.2 °C or 80 ± 0.2 °C.

CO₂ was at 40 °C added in twelve sequential injections of CO₂ with one hour interval, from a storage cylinder (1000 mL) with recorded temperature and pressure. CO₂ was added in to injections for measurements at 80 °C. The amount of CO₂ added to the reactor was calculated from the change in pressure in the storage cylinder, and the amount that remained in the gas phase was calculated from the final and initial pressures. The vapor pressures of solvent and amine were considered constant throughout the experiment, independent of CO₂-loading. The pressure was recorded with Keller LEO5 relative pressure gauge (-1-3 barg, accuracy 0.05% FS) in the reactor and Keller LEO5 pressure gauge (0-11 bara, accuracy 0.05% FS) in the storage cylinder.

3. Results and discussion

3.1 Repeatability and accuracy

To assess the repeatability of the results obtained from the screening apparatus, three CO₂ absorption experiments were performed for 3 M 2-MeIm + 1 M MEA at 40 °C, Figure 2. Furthermore, to estimate the accuracy of the measurements, an experiment with 30 wt% MEA was performed and the results were compared to a published VLE model.²⁰ as shown in Figure 3. . Good repeatability was obtained for 3 M 2-MeIm + 1 M MEA solutions with most measurements being within 3% of the median value. The largest difference was observed at low CO₂ pressures due to the accuracy of the pressure gauges used in the set-up. At low pressures, the pressure in the storage cylinder changed very little, giving high uncertainties. The absorption performance of 30 wt% MEA was within 3% of the VLE model²⁰ at CO₂ loadings of 0.46 mol/mol amine, and shows that good accuracy is obtained with the apparatus even when using only 1.5 mL of solvent. At lower pressures, <1 kPa, measurement uncertainties are greater than CO₂ equilibrium partial pressures. However, as mentioned above, results are consistent for parallel measurements. For comparing the absorption performance of imidazole/promoter systems, the current set-up works well and allows for fast comparison of the systems using small amounts of solvent.

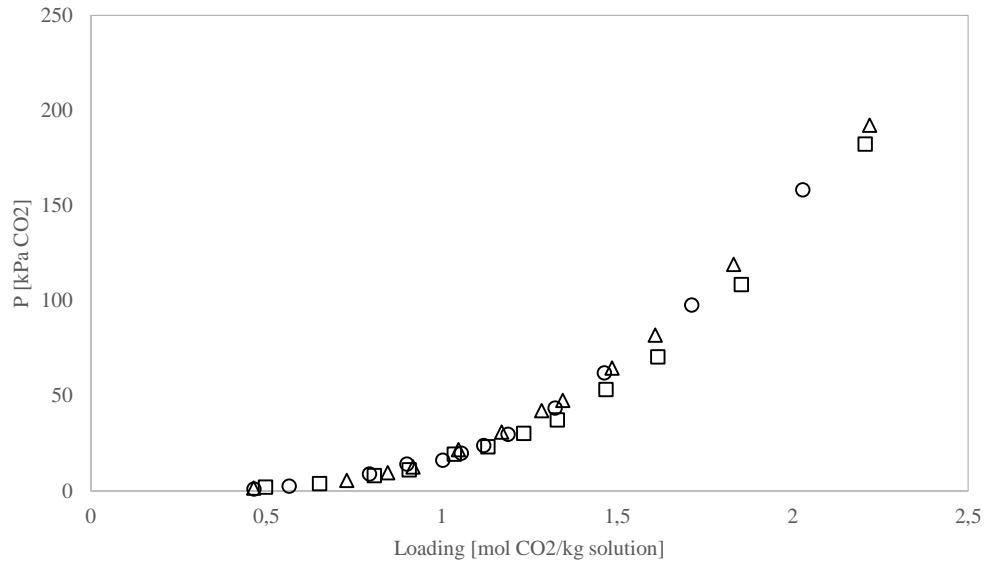


Figure 2: CO₂ absorption profile for 3 M 2-MeIm + 1 M MEA at 40 °C for three runs (□, ○ and △).

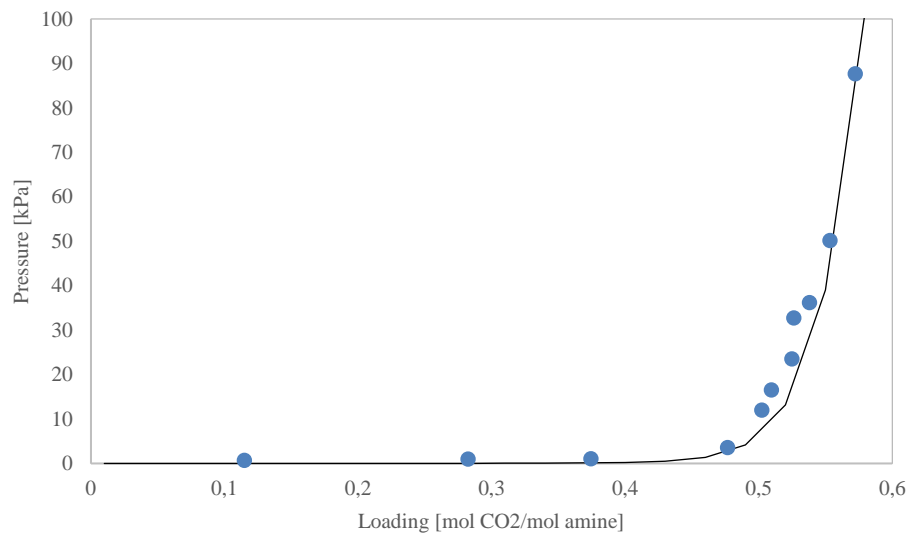


Figure 3: Comparison of 30 wt% MEA CO₂ absorption performance (●) with MEA-CO₂ equilibria model by Bruder et al.²⁰ (solid line).

3.2 The effect of imidazole and promotor concentration on CO₂ loading

To assess the effects of concentrations of imidazole and promoter on the loading capacities of their blends, 2-methylimidazole (1-4 M) and MEA (0.5-2 M) mixtures were screened for CO₂ absorption. The partial pressure of CO₂ as a function of CO₂ loading of 2-methylimidazole/MEA blends are shown in Figure 4. The absorption capacities at 10 kPa of the different 2-methylimidazole/MEA blends are compared in Figure 5.

Solutions containing higher concentrations of 2-methylimidazole and MEA gave higher CO₂ loading than the leaner solutions. The effect by increasing the concentration of MEA is more profound (0.5 mol CO₂/kg solution for each mol MEA added) than the effect observed by increasing the amount of 2-methylimidazole (0.07-0.10 mol CO₂/kg solvent for each mol 2-MeIm added). Much of the CO₂ is absorbed into the solutions at pressures higher than 10 kPa, typical inlet flue gas concentration of CO₂. Consequently, mixtures of 2-methylimidazole/MEA are not promising for post-combustion removal of CO₂. These results are in agreement with results obtained in other studies.^{11, 16, 18}

Bernhardsen et al.¹⁸ investigated a number of tertiary alkanolamines with MAPA using solutions of 3 M tertiary amine and 1 M MAPA. To obtain comparable results, we chose to investigate blends of 3 M imidazole and 1 M promoter. The effects of altering the concentrations are expected to be comparable to observed effects for 2-methylimidazole/MEA solutions.

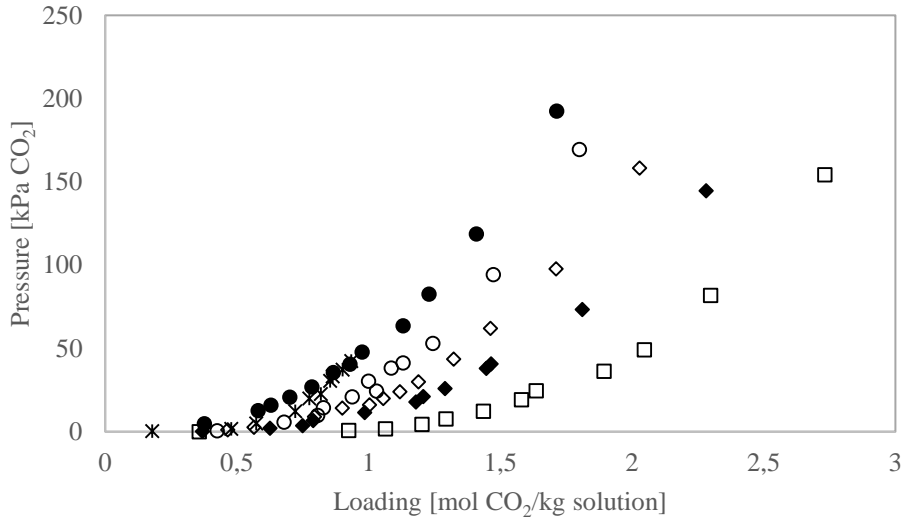


Figure 4: CO₂ loadings of aqueous 2-MeIm/MEA blends, 1 M + 1 M (*), 2 M + 1 M (O), 3 M + 1 M (◇), 4 M + 1 M (◆), 3 M + 0.5 M (●), 3 M + 2 M (□), at 40 °C.

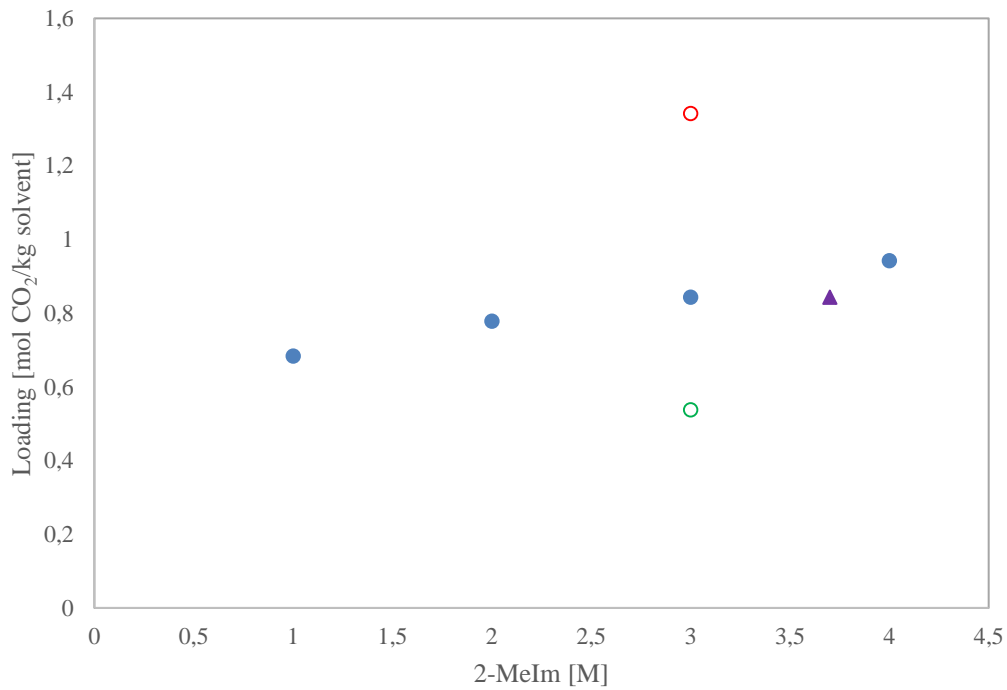


Figure 5: Absorption capacity of 30 wt% 2-MeIm (▲), 1-4 M 2-MeIm + 1 M MEA (●), 3 M 2-MeIm + 0.5 M MEA (○) and 3 M 2-MeIm + 2 M MEA (○) at 10 kPa, 40 °C.

3.3 CO₂ absorption into 3 M imidazole/1 M promoter systems

In our previous study on the absorption properties on aqueous imidazole solutions, we observed that a very high absorption capacity was obtained for 2,4,5-MeIm solutions.¹¹ Unfortunately, the CO₂ absorption rate of 2,4,5-MeIm and other imidazoles was low compared with tertiary amines. Therefore, we decided to investigate the absorption performance of imidazole-promoter blends. Two common alkanolamines, MEA and DEA, as well as two diamines, PZ and MAPA, were chosen as promoters for the imidazole solutions. MEA and DEA have seen extensive use as absorbents in CO₂ capture processes, whereas PZ and MAPA have high CO₂ absorption rates. Thus, mixed amine systems of 3 M imidazoles (2-MeIm, 2-Et-4-MeIm, 2,4,5-MeIm, 1,2,4,5-MeIm) and 1 M promoters (MEA, PZ, MAPA, DEA) were screened at 40 and 80 °C. The loadings obtained at each pressure for the different imidazoles are presented in Figures 6-9. The CO₂ absorption capacities of 3 M imidazole/1 M promoter blends at 10 kPa are given in Figure 10. Cyclic capacities between 10 kPa at 40 °C and 10 kPa 80 °C of 3 M imidazole/1 M promoter blends, calculated from the difference in loading at the two temperatures, are presented in Figure 11.

From the absorption performance experiments conducted at 40 °C, Figures 6-9, it is shown that the absorption capacity of the imidazole increases in the order 2-MeIm \approx 2-Et-4-MeIm<1,2,4,5-MeIm<2,4,5-MeIm for each promoter. These results are in accordance with results obtained in our previous study.¹¹ The order in which the promoters contribute to improving the CO₂ absorption capacity was DEA<MEA<PZ<MAPA.

Exceptional CO₂ absorption capacity was observed for 2,4,5-MeIm/PZ and 2,4,5-MeIm/MAPA blends at 40 °C and 10 kPa CO₂, being as high as 3.19 and 3.53 mol CO₂/kg solvent, respectively. These absorption capacities were significantly better than for 30 wt% MEA, at 2.46 mol CO₂/kg

solvent, as shown in Figure 8. The high absorption capacity for 2,4,5-MeIm solutions is the result of 2,4,5-MeImH⁺ bicarbonate precipitation. The high absorption capacity of 2,4,5-MeIm/PZ and 2,4,5-MeIm/MAPA blends show that the absorption capacity of 2,4,5-MeIm (0.9 mol CO₂/mol amine)¹¹ is almost completely retained also for binary amine solutions where diamines are present, due to precipitation. The proposed reaction pathways for precipitation of imidazolium bicarbonate in the 2,4,5-MeIm/PZ system is displayed in Scheme 1. The mechanism is further discussed in 3.4 *CO₂ absorption performance of 2,4,5-MeIm/PZ*. Interestingly, 2,4,5-MeIm/MEA showed no clear indication of precipitation, whereas for 2,4,5-MeIm/DEA, a solid layer was formed on top of the liquid, consequently drastically reducing the CO₂ absorption rate.

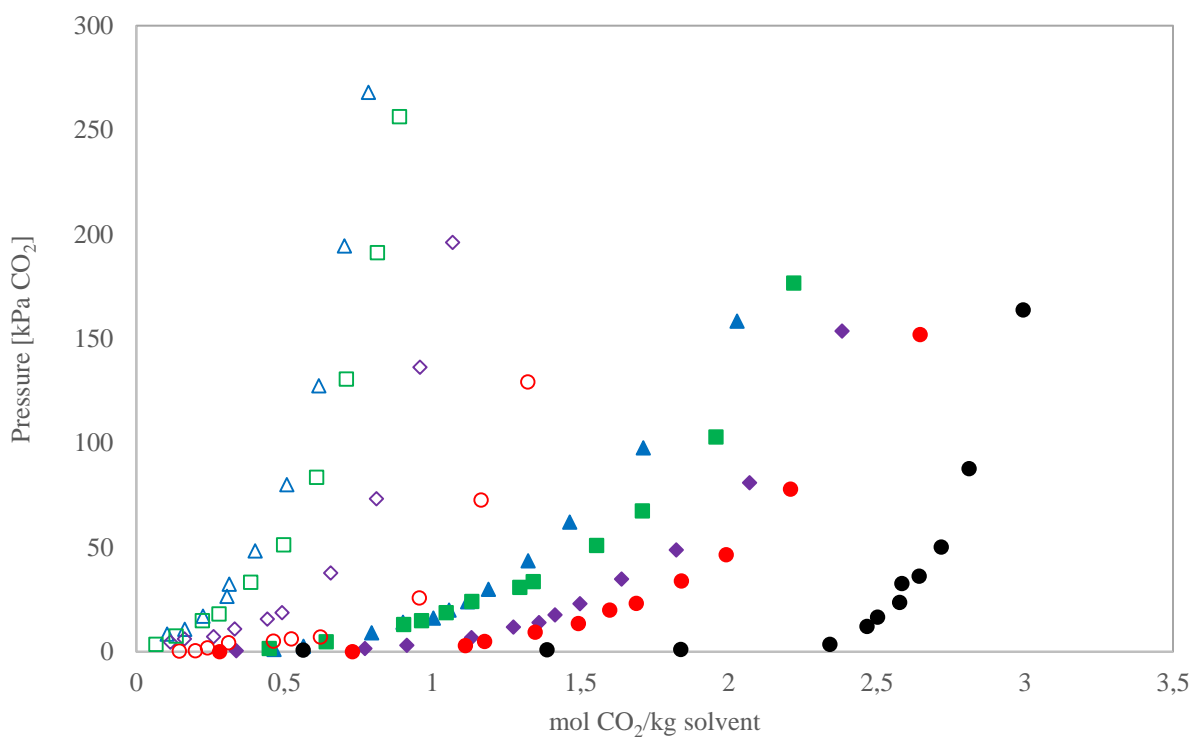


Figure 6: CO₂ loading vs CO₂ pressure for 3 M 2-MeIm with 1 M MEA (▲), PZ (◆), MAPA (●) and DEA (■) at 40 °C (filled markers) and 80 °C (hollow markers). MEA 30 wt% (●) at 40 °C used for comparison.

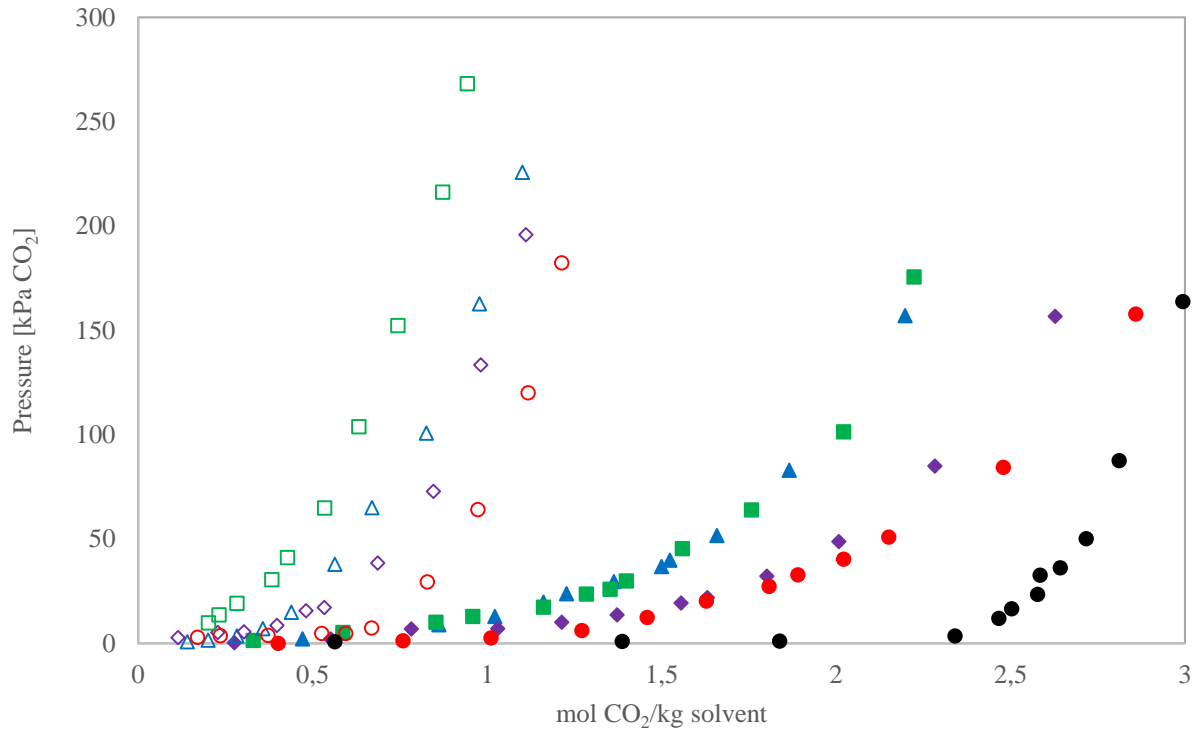


Figure 7: CO₂ loading vs CO₂ pressure for 3 M 2-Et-4-MeIm with 1 M MEA (▲), PZ (◆), MAPA (●) and DEA (■) at 40 °C (filled markers) and 80 °C (hollow markers). MEA 30 wt% (●) at 40 °C used for comparison.

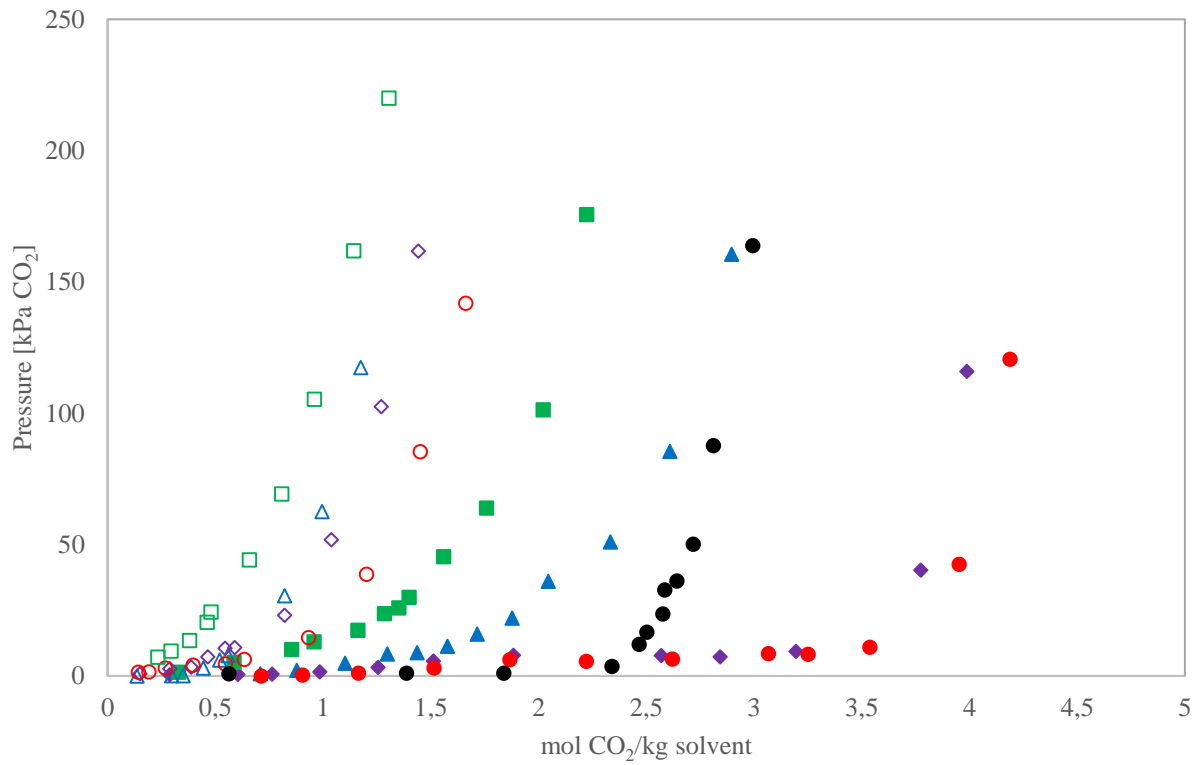


Figure 8: CO₂ loading vs CO₂ pressure for 3 M 2,4,5-MeIm with 1 M MEA (▲), PZ (◆), MAPA (●) and DEA (■) at 40 °C (filled markers) and 80 °C (hollow markers). MEA 30 wt% (●) at 40 °C used for comparison.

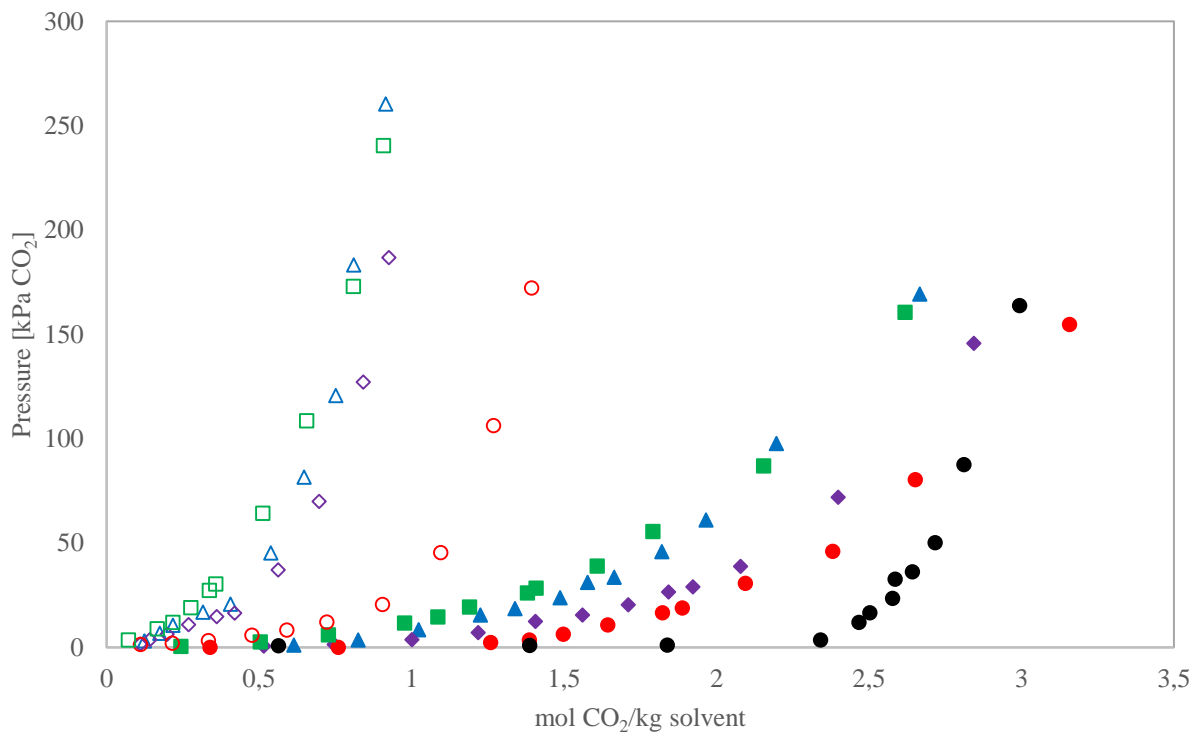
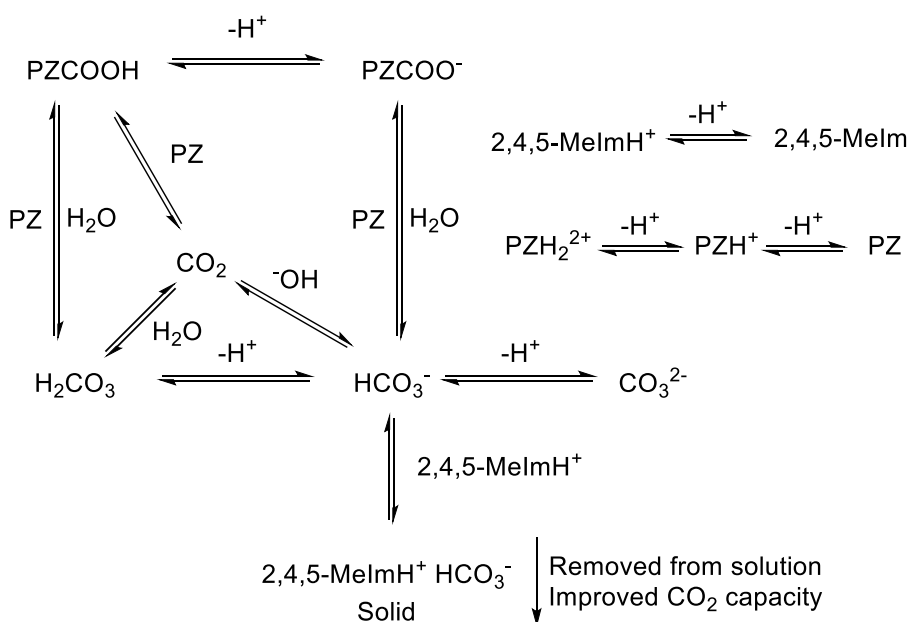


Figure 9: CO₂ loading vs CO₂ pressure 3 M 1,2,4,5-MeIm with 1 M MEA (▲), PZ (◆), MAPA (●) and DEA (■) at 40 °C (filled markers) and 80 °C (hollow markers). MEA 30 wt% (●) at 40 °C used for comparison.



Scheme 1: Proposed reaction pathways towards 2,4,5-MeImH⁺ bicarbonate formation in solution with PZ. PZ dicarbamate formation reactions²¹ are omitted for clarity.

To evaluate the cyclic capacity of the blends, experiments were conducted at 80 °C for the imidazole-promoter systems, shown in Figures 6-9. A similar approach has been previously used in several studies.²² Cyclic capacities were calculated by subtracting CO₂ loadings at 80 °C and 10 kPa from loadings at 40 °C and 10 kPa. Another option would have been to estimate the lean loading at 80 °C and 1 kPa.²³⁻²⁵ However, this would be inappropriate in this case, due to the uncertainty in the pressure measurements. 2,4,5-MeIm showed the highest capacity followed by 1,2,4,5-MeIm. 2-MeIm and 2-Et-4-MeIm had the lowest cyclic capacities. PZ solutions typically gave the best performance. Apart from 2,4,5-MeIm, the imidazoles show low cyclic capacities with promoters because of low absorption capacity at 40 °C. However, 2,4,5-MeIm showed excellent cyclic capacity with PZ and MAPA. Unlike at 40 °C, no precipitation was observed for 2,4,5-MeIm/PZ or 2,4,5-MeIm/MAPA solutions at 80 °C. As a result, the solubility of CO₂ into the 2,4,5-MeIm/promoter blends is radically reduced with increasing temperatures, and almost all the CO₂ can be removed by heating the solution to 80 °C. The cyclic capacity from 40-80 °C was 2.86 mol CO₂/kg solvent (12.5 wt%) for 2,4,5-MeIm/PZ and 2.75 mol CO₂/kg solvent (12.1 wt%) for 2,4,5-MeIm/MAPA. In comparison, Bernhardsen et al. obtained 2.1 mol CO₂/kg solvent for 10 kPa at 40 °C and 1 kPa at 80 °C.¹⁸ The improvement is due to the greater absorption capacity of the 2,4,5-imidazole blends. Despite the pK_a of 2,4,5-MeIm being lower than the ideal pK_a for alkanolamine/MAPA solutions, higher cyclic capacity was obtained.

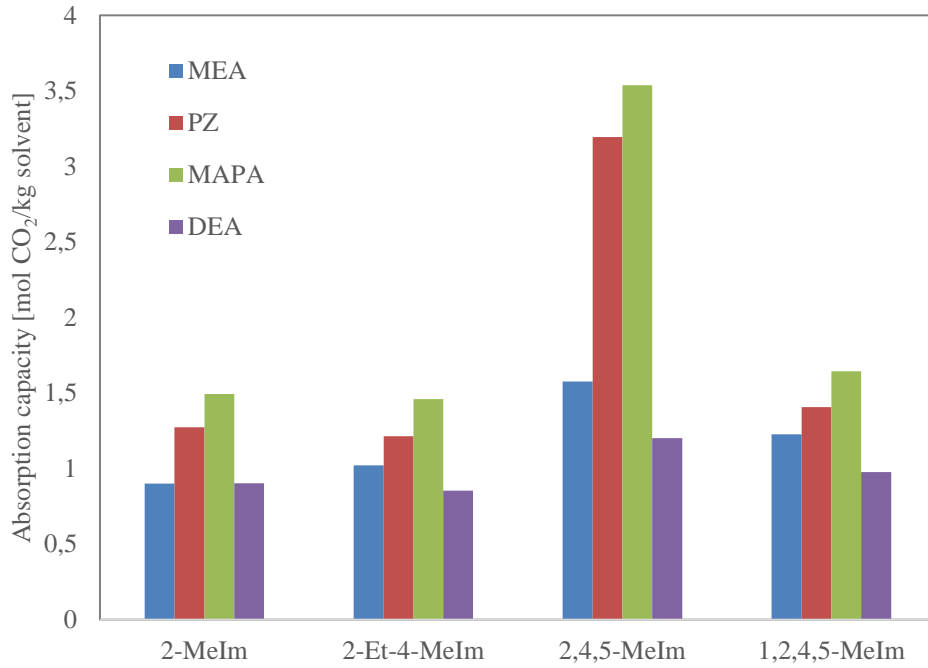


Figure 10: Absorption capacity [mol CO₂/kg solvent] at 10 kPa, 40 °C for 3 M imidazole/1 M promoter blends.

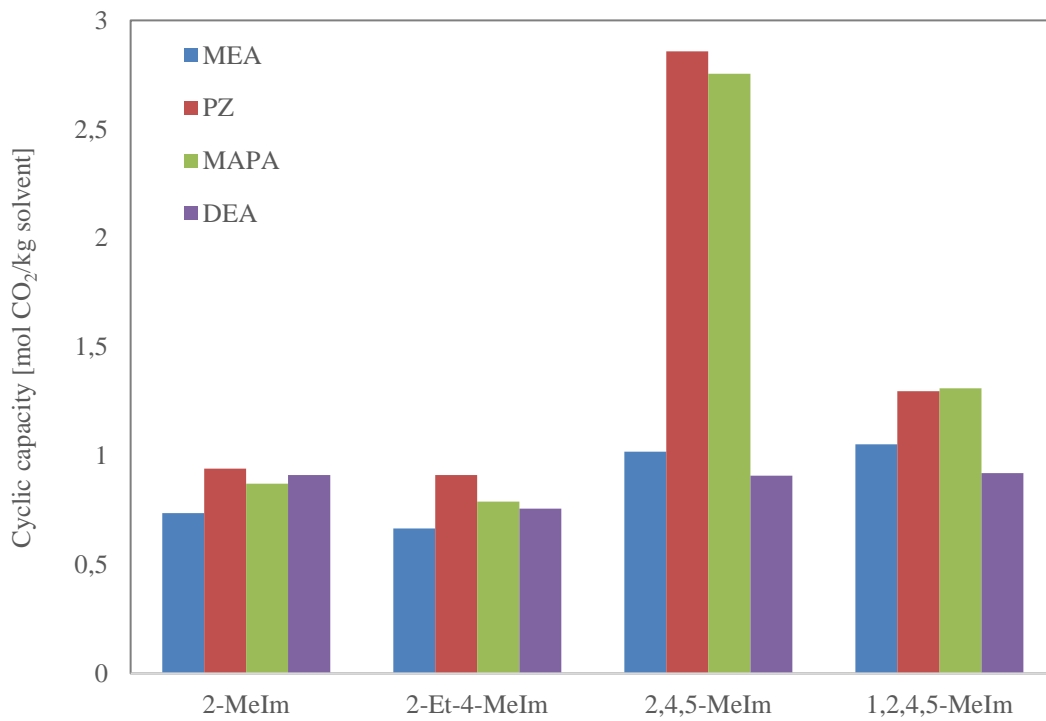


Figure 11: Cyclic capacity [mol CO₂/kg solvent] for 3 M imidazole/1 M promoter blends, from 10 kPa, 40 °C to 10 kPa, 80 °C.

3.4 CO₂ absorption performance of 2,4,5-MeIm/PZ

The highest absorption capacities and cyclic capacities were obtained for 2,4,5-MeIm/diamine blends. To understand the effect of component concentrations in 2,4,5-MeIm/diamine systems, solutions containing lower concentration of 2,4,5-MeIm and PZ were screened, Figure 12. MAPA was not selected for further studies, as it is more volatile and less stable than PZ.^{26, 27} Higher amine concentrations were not investigated. Significant precipitation was already observed for 3 M 2,4,5-MeIm/1 M PZ, and more precipitation was considered detrimental as an absorption capacity of 3.19 mol CO₂/kg solvent had already been achieved. Too high levels of precipitation may lead to a steep rise in viscosity and reduced mass transfer rates.²⁸ However, absorption capacities above 4-5 mol CO₂/kg solvent might be feasible with higher 2,4,5-MeIm concentrations.

By changing the 2,4,5-MeIm concentration from 3 M to 2 M, the absorption capacity decreased from 3.19 to 2.25 mol CO₂/kg solvent at 10 kPa. Reducing the 2,4,5-MeIm concentration to 1 M gave an absorption capacity of 1.10 mol CO₂/kg solvent. Lowering the promoter concentration to 0.5 M PZ, only gave a small reduction in absorption capacity from 3.19 to 2.80 mol CO₂/kg solvent at 10 kPa. These results clearly demonstrate that the 2,4,5-MeIm/diamine solution requires sufficient amounts of 2,4,5-MeIm to attain high absorption capacity. Based on the results, and previous amine kinetic studies,^{21, 29} the reaction mechanism, shown in Scheme 1, is proposed for the reaction pathway of CO₂ in 2,4,5-MeIm/PZ blends. When PZ and MAPA absorb CO₂, both carbamate and bicarbonate are formed. During absorption only 2,4,5-MeImH⁺ bicarbonate precipitates, due to poor solubility in water. However, enough 2,4,5-MeIm is required for precipitation to occur. Upon precipitation, the bicarbonate is removed from the carbamate-

bicarbonate equilibrium for the diamine, creating more bicarbonate, facilitating precipitation, Scheme 1. Furthermore, 2,4,5-MeIm is sufficiently alkaline ($pK_a = 8.95$)¹¹ to be protonated in solution with diamines, $pK_{a,2} = 5.27$ (PZ)³⁰ and $pK_{a,2} = 8.60$ (MAPA)¹⁸. MEA ($pK_a = 9.51$)¹⁸ is more alkaline than 2,4,5-MeIm and precipitation does not occur. Precipitation was observed for 2,4,5-MeIm/DEA, $pK_a = 8.83$ (DEA)³¹, suggesting the relative amine alkalinity is decisive for the behavior of the blends.

For 3 M 2,4,5-MeIm/diamine solutions, the CO₂ partial pressure at which precipitation occurs, is below 10 kPa, ideal for post-combustion processes. The absorption capacity and cyclic capacity are superior to most other previously reported aqueous tertiary amine/promoter systems of comparable concentrations.^{16, 18} Apart from when a layer of precipitate was formed at the top of the liquid, 2,4,5-MeImH⁺ bicarbonate precipitation did not negatively affect the absorption performance of the solvent. The viscosity of the unloaded 3 M 2,4,5-MeIm/1 M PZ blend was comparable to aqueous single amine solutions (3-5 mPa·s at 40 °C), and similar mass transfer rates are expected.^{12, 32} Aqueous 30 wt% 2,4,5-MeIm solutions experience up to 40% increase in viscosity, from 2.08 to 2.97 mPa·s at 40 °C, when loaded with 0.4 mol CO₂/mol amine.¹² Hence, viscosities were significantly lower than amine-imidazolium IL-based systems, which typically possess viscosities >20 mPa·s.³³ Stirring in the precipitating solutions could be easily maintained with a small stirring rod as a very fine precipitate was obtained, removable with the liquid. These results suggest that a slurry was formed. Hence, utilization of 2,4,5-MeIm/diamines in conventional CO₂ capture plants could be feasible with little to no modification of current set-ups. A low temperature stripper would remove CO₂ captured as 2,4,5-MeImH⁺ bicarbonate at temperatures of 80 °C. Alternatively, a process where the formed particles are separated from the solvent is possible. In such a process, the concentrated slurry would be sent to the stripper, greatly

reducing the amount of absorbent needed to be treated in the stripper. Du et al. reported low degree over thermal degradation of imidazole/PZ mixtures, and improved stability with additional alkyl substituents on the imidazole, further emphasizing the potential of 2,4,5-MeIm systems.¹³ Overall, 2,4,5-MeIm/diamine blends represent a novel type of absorbent system with highly interesting and promising absorption properties. Investigations into potential 2,4,5-MeIm/diamine processes as well as the mechanism and conditions for 2,4,5-MeImH⁺ bicarbonate precipitation are currently underway.

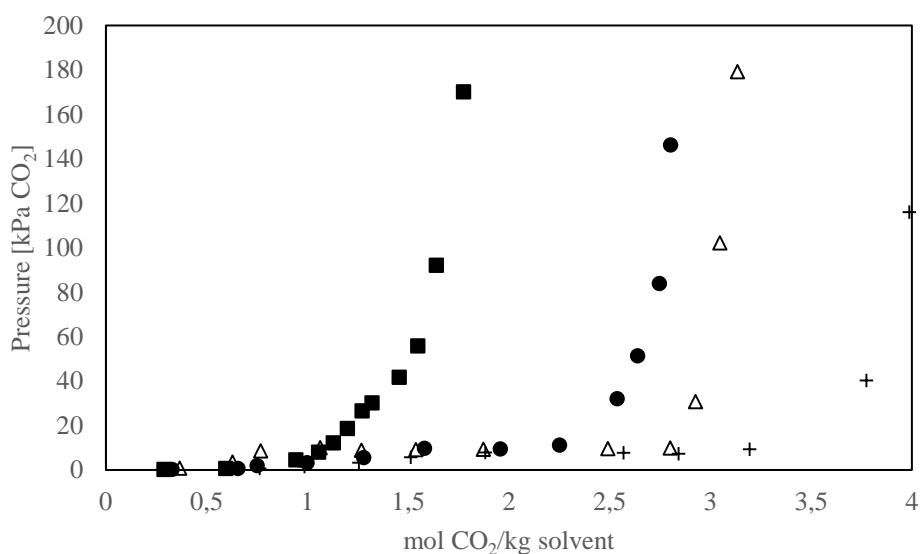


Figure 12: Comparison of CO₂ loading vs CO₂ pressure for different blends of 2,4,5-MeIm and PZ, 1 M + 1 M (■), 2 M + 1 M (●), 3 M + 0.5 M (△), 3 M + 1 M (+), at 40 °C.

4. Conclusion

In this study, CO₂ absorption performance experiments were performed on aqueous blends of four alkyimidazole (2-MeIm, 2-Et-4-MeIm, 2,4,5-MeIm and 1,2,4,5-MeIm) and four promoters (MEA, DEA, PZ and MAPA). The absorption capacity of imidazoles increases in the order of 2-MeIm < 2-Et-4-MeIm < 1,2,4,5-MeIm < 2,4,5-MeIm. 2,4,5-MeIm/PZ and 2,4,5-MeIm/MAPA blends

have exceptional CO₂ absorption capacities (14-16 wt%) and cyclic capacities (12 wt%). The high absorption capacity of 2,4,5-MeIm/diamine blends is result of selective 2,4,5-MeImH⁺ bicarbonate precipitation, forming a slurry. The results indicate that low temperature stripping is possible with high cyclic capacity. Novel 2,4,5-MeIm/diamine solutions are highly interesting and promising solvent blends for CO₂ capture.

AUTHOR INFORMATION

Corresponding author

*Email: hanna.knuutila@ntnu.no, telephone: +47 735 94 119

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Author Contributions

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

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