CO$_2$ CAPTURE SOLVENT SELECTION BY COMBINED ABSORPTION-DESORPTION ANALYSIS

Ugochukwu E. Aronu[1], Hallvard F. Svendsen[1], Karl Anders Hoff[2]
[1] Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway; Email: ugochukwu.aronu@chemeng.ntnu.no, hallvard.svendsen@chemeng.ntnu.no
[2] SINTEF Materials and Chemistry, N-7465 Trondheim, Norway; Email: Karl.A.Hoff@sintef.no

Abstract
A method was developed for selection of promising solvents based on CO$_2$ absorption experiments at 40°C and 9.5 kPa CO$_2$ partial pressure followed by desorption of same solvents at 80°C down to 1.0 kPa CO$_2$ partial pressure. The experiments conducted under atmospheric conditions revealed the solvents absorption and desorption characteristics and were compared with 1.0M, 2.5M, 5.0M and 10.0M MEA. Results showed that only absorption or stripping data alone was not sufficient in making robust solvent selection decisions; combined data analysis was necessary. 1.0M tetraethylenepentamine (TEPA) and 5.0M MEA showed the best performance in terms of absorption rate. 1.5M Bis-(3-dimethylaminopropyl) amine (TMBPA) was easy to desorb, has high absorption capacity; and when promoted it has the best performance in terms of CO$_2$ carrying capacity. At the test conditions, 1.5M TMBPA promoted with 1.0M PZ showed the most outstanding potential for efficient CO$_2$ removal at reduced cost of all systems tested. Its cyclic capacity in molCO$_2$/mol amine was found to be 70% higher than 5M MEA.

Keywords: CO$_2$ absorption, desorption, screening, TEPA, TMBPA

1. Introduction

Climate change has been associated with increased emissions of carbon dioxide from anthropogenic sources and is identified as the most important contributing green house gas[1]. It is thus pertinent that carbon dioxide emissions from combustion exhaust gases must be reduced. Many technologies exist today for separation and capture of CO$_2$ from gas streams[2] with absorption by amine based solvents being the most common for CO$_2$ removal from combustion exhaust gases. Commonly used amine absorbents include monoethanolamine (MEA) and Mitsubishi Heavy Industries, KS1. Efficient absorption has its challenges mainly from high energy demand of the process which is linked to the characteristics of the solvent used in the process. Development of more efficient solvents is thus crucial in reducing the cost of CO$_2$ capture.

This work aims at finding new solvents with high potential for low energy demand in CO$_2$ absorption by analysis of the absorption-desorption properties of pre-selected solvents including comparison with MEA. Solvent pre-selection focused mostly on solvents with potential for high absorption capacity and fast reaction kinetics. These features were accessed using structure and pKa considerations of solvents. Overall, an increase in absorption capacity with increase in chain length between different functional groups in alkanolamines[3] is found, while increase in alkyl groups and also increased chain length between amine functional groups increases pKa[4]. Bis-(3-dimethylaminopropyl) amine TMBPA has 3 amine sites (one secondary and two tertiary) indicating a potential for high absorption capacity of 3molCO$_2$/mol and a loading of 2.9molCO$_2$/mol has been achieved[5]. Two tertiary amine sites could result in probably lower reaction rate[6] but presence of one secondary amine site and longer chains (3 carbon atoms) between the secondary and tertiary sites, shows better possibilities for improved kinetics[4] than would be expected for a tertiary amine. Because TMBPA has two tertiary amine sites it was suspected that the reaction rate could be low to some extent and it was decided to activate it with promoters which will act as a shuttle, as they react rapidly with CO$_2$ to reduce mass-transfer resistance and facilitate fast transport of CO$_2$ into the liquid phase[6,7]. Mixing a primary or secondary amine with a tertiary amine, could improve the CO$_2$ selectivity in the presence of H$_2$S as well as reduce regeneration cost[8]. Promoters selected were 2,2-dimethyl-1,3-propanediamine (DMPDA), 3-methylaminopropylamine (MAPA), monoethanolamine(MEA) and piperazine (PZ). Structure and pKa considerations for other systems tested in this work have been described in earlier work[9].

2. Screening Experiments

2.1 Materials

Amine absorbents used with their purity were obtained as follows; monoethanolamine, MEA (Sigma-Aldrich, purity≥ 99.9 mass %); TMBPA (Aldrich, purity > 97 mass %); TEPA (Fluka, purity ~ 85% mass %); DMPDA (BASF, purity > 97.5 mass %); while MAPA (purity > 99 mass %); PZ (anhydrous 99%); 2-amino-2-methyl-1-propanol, AMP (purity > 99 mass %); N, N'-di- (2 hydroxyethyl) piperazine, DIHEP (purity > 99 mass %) and N-2-hydroxyethylpiperzine, HEP (purity > 98.5 mass %) were obtained from Acros Organics. The solvents were used without further purification. All solution samples were prepared with deionized water. The CO_2 (purity > 99.99mol %) and N_2 (purity > 99.99 mol %) gases used were obtained from AGA Gas GmbH.

2.2 Methods

Absorption and desorption experiments were carried out using a screening apparatus designed to operate at atmospheric conditions and up to 80^oC. The method which involves absorption of CO_2 with solvent at 40^oC up to 9.5 kPa CO_2 partial pressure and stripping of the same solvent at 80^oC down to 1.0 kPa gas phase CO_2 concentration is used to acquire first hand knowledge on the behaviour of each solvent system in an absorption process. Experiments are as described in Ma'mun et al.[10]; however, the apparatus was modified to allow stripping operations, Aronu et al.[9,11]. It gives a fast relative comparison of absorption rate and absorption capacity as well as the stripping rate; thus enables estimation of the relative cyclic capacity of each solvent. Apart from these factors, other properties such as foaming, precipitation and possible discolouration upon CO_2 loading which may be indicative of solvent degradation could be observed. The base case solvent used is MEA; thus to provide a broad basis for comparison, different concentrations of MEA, 1.0M, 2.5M, 5.0M and 10.0M were tested. It is however not possible to have all solvent in same molar concentration due to molecular weight and/or viscosity issues as well as solvent cost. In general, a concentration of 2.5M of each solvent or solvent mixture were used and at same time using concentrations not too far from 30 wt% of amine solutions. Due to high molecular weight and viscosity of TMBPA and TEPA, concentrations of 1.5M and 1.0M respectively of each were used. For DIHEP and HEP a mixture with same mole fractions, 0.42M DIHEP and 0.58M HEP, as proposed by Hakka and Ouimet[12] was used. It should be noted that comparison of the experimental data here is semi-quantitative since there is no guarantee that the bubble structure, and thus the gas-liquid interfacial area were exactly the same in all experiments. However, the superficial gas velocities were the same, so the differencies would arise mainly due to interfacial tension, bubble coalescence properties and viscosity[10].

3. Results and Discussion

3.1 Absorption

The absorption rates versus loading (molCO2/mol amine) plots are presented in figure 1a. It shows that 1.0M TEPA has distinctively higher absorption rate and attained a highest loading of 1.916molCO2/mol while 1.5M TMBPA show high absorption capacity.TMBPA promoted with PZ and MAPA shows higher absorption rate and loading in practically all the loading range compared to all MEA concentrations. High cost of DIHEP and HEP do not allow tests to be carried out at high concentrations, however, its mixture of total concentration 1.0M tested shows that it has both lower rate and capacity than 1.0M MEA. 2.5M AMP has the lowest initial rate, and its rate was improved by activating with PZ. A look at absorption rate versus total amount of CO_2 absorbed in solution (molCO$_2$ per litre solution) in figure 1b gives a different perspective on the solvents performance. It shows that 10.0M MEA maintained the highest rate and absorbs the highest amount of CO_2 in solution over all concentration ranges for all solvents (except for 1.0M TEPA which has higher initial rate up to concentration point 0.708 molCO$_2$/Lamine). This is because solvent CO_2 absorption capacity in (molCO$_2$ per litre solution) is a function of its molar concentration. Increase in molar concentration results in increasing solvent absorption capacity. It is therefore expected that increased concentrations of TEPA and TMBPA will increase absorption capacity. However, this could be limited by associated viscosity and foaming problems. Initial screening experiments were conducted where half of the initial concentrations were used, and the results showed less foaming. Present results from figure 1a shows 1.0M TEPA as the best solvent while in figure 1b it is 10.0M MEA. This shows that assessment of only absorption plots is not sufficient to give complete information on absorption characteristics of solvents for quick decision on solvent performance; other factors are necessary.

3.2 Desorption
The solvents attained different loadings and absorbed different amounts of CO_2 in solution. Desorption tests at 80°C give indication of the relative CO_2 carrying capacity for these solvent systems under these experimental conditions. Figure 1c shows stripping rate versus loading (molCO_2/ mol amine). 2.5M AMP and 0.42M DIHEP + 0.58M HEP attained lowest lean loads, thus showing high desorption ability.The figure also shows that TMBPA attains both low lean loading (0.31) and high rich loading (1.62) while TEPA has high rich loadings (1.92) but much higher lean loading (0.81) under the same conditions when compared to MEA. This gives an indication of good desorption characteristics of TMBPA and its potential for lower regeneration energy demand than TEPA. In figure 1d the stripping rates are plotted for the amines showing the amount of CO_2 removed in mol/L solution. The curves show that 10.0M MEA absorbed the highest amount of CO_2 (4.74 molCO_2/L), however, only small amount of this could be desorbed at the conditions used, resulting in 2.73 molCO_2/L solution at the lean end. 2.5M AMP and 1.5M TMBPA clearly shows that low lean CO_2 concentrations are obtainable even though they achieved high rich loadings. Blends of 2.5M AMP with 0.5M PZ and all activated 1.5M TMBPA show low concentrations of CO_2 at the lean end but not in activation with 1.0M MAPA and 1.0M DMPDA . The plots also show that the lowest lean end concentration of CO_2 is achieved in 0.42M DIHEP + 0.58M HEP. This gives an indication of high desorption ability of this mixture when compared to 1.0M MEA and 1.0M TEPA. It is necessary however to observe that this solvent has the lowest rich concentration of CO_2 in solution.
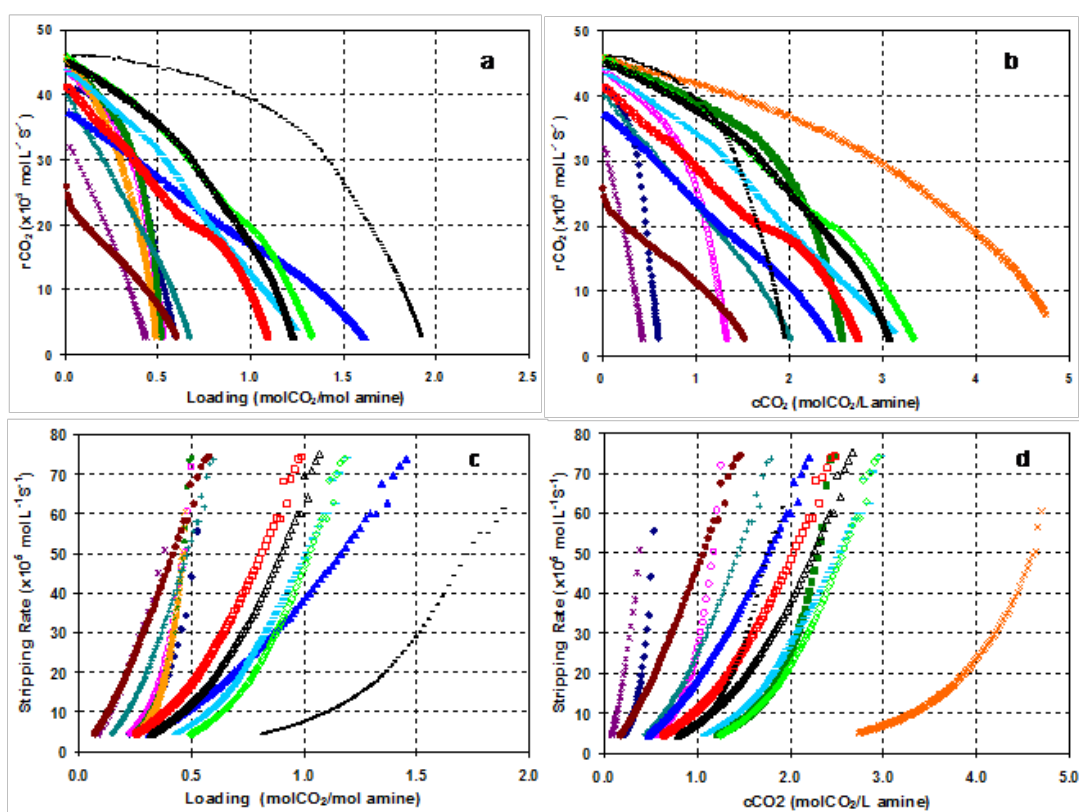

Figure 1. Screened amines absorption curves at 40°C; (a) absorption rate as function of loading in molCO_2/mol amine; (b) absorption rate versus amount of CO_2 in mol/L solution: Screened amines desorption curves at 80°C; (c) stripping rate as function of loading in molCO_2/mol amine; (d) stripping rate versus amount of CO_2 in mol/L solution ♦,1.0M MEA; ○,2.5M MEA; ■,5.0M MEA; ×,10.0M MEA; ж,0.42M DIHEP + 0.58M HEP; ●,2.5M AMP; +,2.5M AMP + 0.5M PZ; ▲ 1.5M TMBPA; ─,1.5M TMBPA + 1.0M DMPDA; ◊,1.5M TMBPA + 1.0M MAPA; □, 1.5M TMBPA + 1.0M MEA; Δ,1.5M TMBPA + 1.0M PZ; −,1.0M TEPA.

3.3 Observed solvent characteristics
During desorption tests some of the solvents flashed or foamed up to the condenser as soon as N_2 was introduced to start the stripping process. Flashing was observed in AMP and TMBPA and in all the mixtures as well as in TEPA. Strongest flashing was observed in 2.5M AMP + 0.5M PZ, 1.5M TMBPA + 1.0M PZ, 1.5M TMBPA + 1.0M MAPA and 1.0M TEPA. Four factors are believed to be likely contributors to this phenomenon; high CO_2 desorption potential, foaming ability, solvent vapour

pressure and viscosity. Flashing of AMP and TMBPA is believed to be due to their high desorption potentials which allows high amounts of CO_2 in gas phase during the heating up process already at $80^{\circ}C$, thus it flashes off immediately when stripping starts with the introduction of N_2. High vapour pressures of PZ and MAPA contributes to flashing of their solvent mixtures. Foaming could also contribute to boiling up of TMBPA and TEPA as well as viscosity. It was generally believed that foaming is a contributor to flashing problems, thus to be able to strip the solvents under these conditions, flashing was suppressed using foam inhibitor. 1.0M TEPA changed from colourless to yellow solution during stripping while 1.5M TMBPA was found to changed from light yellow to light brown after stripping. 1.5M TMBPA + 1.0M MEA changed from light yellow to brownish orange and 10.0M MEA changed to yellow after absorption and stripping.

3.4 Absorption-desorption cycle analysis

Performance of each solvent system was also assessed by the consideration of their cyclic capacity ($molCO_2$/mol amine). Percent CO_2 removed during desorption as well as ΔCO_2 removed per litre solution allows for a true comparative analysis of the actual CO_2 carrying capacity (difference in CO_2 concentration in $molCO_2$/L solution between the rich and lean ends). Absorption rates at lean loading and 90% equilibrium loading were also determined. These give indications of how fast the lean solution reacts when pumped back to the absorber and the absorption rate towards equilibrium respectively. The absorption-desorption cycle calculation procedure is presented by Aronu et al.[11]. Table 1 shows summary of absorption-desorption experiments results. It shows that the highest rich loading in $molCO_2$/mol amine was attained by 1.0M TEPA and lowest lean loading was achieved in 0.42M DIHEP + 0.58M HEP while 1.5M TMBPA has the highest cyclic capacity. Highest percent CO_2 removal per cycle was found in 2.5M AMP while all promoted 1.5M TMBPA show high carry capacity with highest value found in 1.5M TMBPA + 1.0M PZ. 1.0M TEPA has the highest absorption rate at lean loading while 5.0M MEA showed the highest absorption rate at 90% equilibrium approach.

Table 1. Absorption-desorption summary

Solvent	α_{abs}	α_{strp}	Cyclic Capacity	% CO2 Removed Per Cycle	Absorption Rate at Lean Loading	Absorption rate at 90% Equilibrium Loading	cCO2 Rich end	cCO2 Lean end	ΔcCO2 Per Cycle
							$molCO_2$/L	$molCO_2$/L	$molCO_2$/L
1.0M MEA	0.593	0.224	0.368	62.15	37.724	6.171	0.598	0.226	0.371
2.5M MEA	0.529	0.224	0.303	57.29	37.371	8.624	1.332	0.569	0.763
5.0M MEA	0.518	0.247	0.271	52.39	37.544	11.683	2.568	1.223	1.345
10.0M MEA	0.475	0.273	0.201	42.40	31.996	9.226	4.743	2.732	2.011
0.42M DIHEP + 0.58M HEP	0.430	0.080	0.350	81.43	28.847	4.791	0.430	0.080	0.350
2.5M AMP	0.600	0.078	0.523	87.02	20.907	4.459	1.527	0.198	1.329
2.5 AMP + 0.5M PZ	0.671	0.147	0.524	78.09	32.869	5.551	2.013	0.441	1.572
1.5M TMBPA	1.615	0.311	1.304	80.76	31.713	5.349	2.451	0.472	1.980
1.5M TMBPA + 1.0M DMPDA	1.245	0.431	0.815	65.42	33.386	6.048	3.113	1.077	2.037
1.5M TMBPA + 1.0M MAPA	1.332	0.499	0.833	62.53	35.560	7.089	3.329	1.247	2.082
1.5M TMBPA + 1.0M MEA	1.096	0.257	0.838	76.53	33.611	6.891	2.740	0.643	2.097
1.5M TMBPA + 1.0M PZ	1.231	0.320	0.911	74.02	39.756	8.130	3.076	0.799	2.277
1.0M TEPA	1.916	0.810	1.106	57.73	41.770	9.517	1.935	0.818	1.117

Units: α_{abs}, α_{strp} and cyclic capacity ($molCO_2$/mol amine); Absorption Rate ($\times 10^5$ $molL^{-1}S^{-1}$)

4. Solvent Performance Analysis

Cycle analysis results show that it is difficult to make any selection decision on the most promising solvent by consideration of single characteristics of the solvents.More concise solvent selection decision requires combined analyses of these properties. Combined absorption-desorption characteristics analysis was made possible using dot plots. In the plots solvents with best characteristics should appear at the top right hand corner. Figure 2a shows plots for amine absorption rates at lean loading as function of percent CO_2 removed. It shows that 1.0M TEPA followed by 1.5M TMBPA +1.0M PZ has the highest absorption rate for the lean solution, but 1.0M TEPA has lower desorption potential. 1.5M TMBPA +1.0M PZ shows both high absorption rates at lean loading and high desorption ability. Amine absorption rate at lean loading is plotted against the ΔCO_2 removed per cycle for each solvent system in figure 2b. This plot clearly shows that 1.5M TMBPA with all its mixtures as well as 10.0M MEA has particularly high carrying capacity compared to other amines. TMBPA and its family are of particular interest in this case considering their lower molar concentrations when compared to 5.0M and 10.0M MEA. They show high CO_2 carrying capacity with high desorption ability. The figure further shows that 1.5M TMBPA + 1.0M PZ has the best performance when absorption rate at lean loading is combined with solvent carrying capacity.

It is necessary to have an idea of the reaction rate of the solvents upon approach to equilibrium. In general the absorption rate is expected to decrease on equilibrium approach but a solvent with characteristics of fast reaction towards equilibrium is desired. Figure 2c, shows plots for absorption rate at 90% equilibrium loading against ΔCO_2 removed per cycle. It shows that 5.0M MEA has the highest absorption rate towards equilibrium followed by 1.0M TEPA and 10.0M MEA. 1.5M TMBPA + 1.0M PZ maintained a reasonable rate.
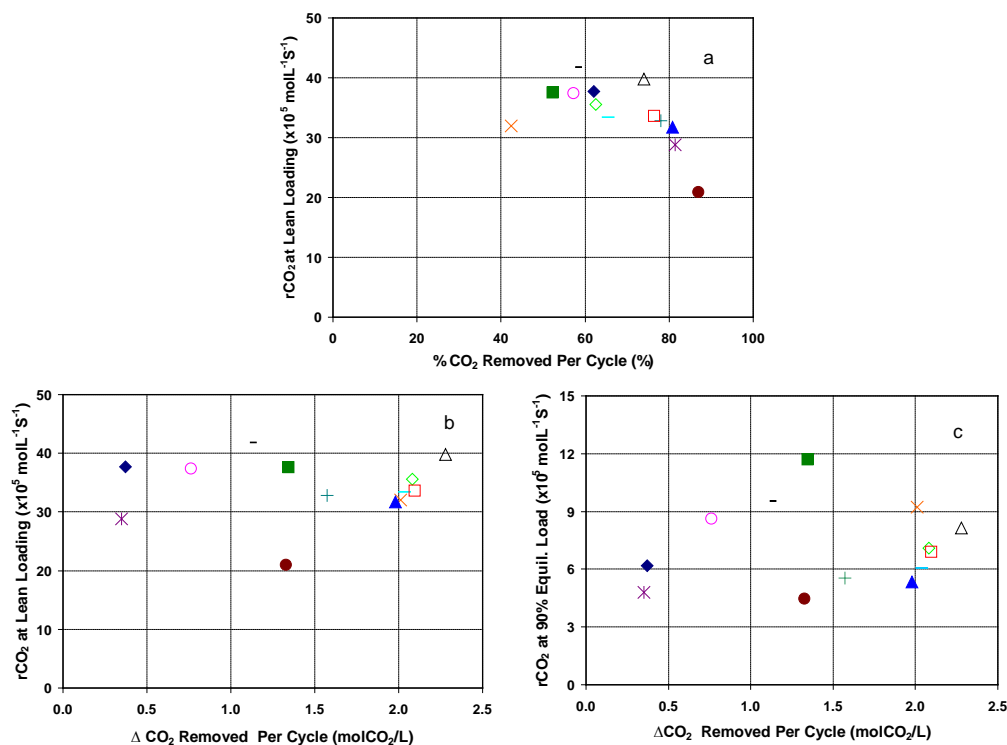

Figure 2. (a)Absorption rate at lean loading versus percentage of CO2 removed per cycle; (b) Absorption rate at lean loading versus ΔCO_2 removed per litre solution per cycle; (c) amines Absorption Rate at 90% Equilibrium Loading vs Amount of CO_2 Removed per litre solution.: ♦,1.0M MEA; ○,2.5M MEA; ■,5.0M MEA; ✗,10.0M MEA; ж,0.42M DIHEP + 0.58M HEP; ●,2.5M AMP; +,2.5M AMP + 0.5M PZ; ▲ 1.5M TMBPA; ─,1.5M TMBPA + 1.0M DMPDA; ◊,1.5M TMBPA + 1.0M MAPA; □, 1.5M TMBPA + 1.0M MEA; △,1.5M TMBPA + 1.0M PZ; ─,1.0M TEPA.

4.1 Overall performance in terms of CO2 absorption rate
Overall solvent performances in terms of rate were deduced using a plot of absorption rate at lean loading against absorption rate at 90% equilibrium loading, figure 3a. This shows how fast the lean solvent will react when returned to the absorber and how fast the rate will be maintained towards equilibrium. Solvents with best rate performance have potential of reducing absorber dimension; thus capital cost as well as operating cost. The figure shows that 1.0M TEPA and 5.0M MEA shows overall best performance in terms of rate while 2.5 AMP has poorest performance. 1.5M TMBPA + 1.0M PZ maintained a comparatively high rate performance.

4.2 Overall performance in terms of CO2 carrying capacity
A plot of amount of ΔCO_2 removed per cycle against percent CO_2 removed in figure 3b gives an indication of the overall performance of each solvent system in terms of CO_2 carrying capacity; it gives a comparative indication of how much of the CO_2 absorbed by the solvent is finally removed. Solvents with best carrying capacity will reduce solvent circulation rate. Figure 3b shows that 1.5M TMBPA and its mixtures have the highest CO_2 carrying capacity with 1.5M TMBPA + 1.0M PZ, 1.5M TMBPA + 1.0M MEA and 1.5M TMBPA having the best performance. MEA at its various concentrations show generally lower carrying capacity with the best performance in 10.0M MEA. 1.5M TMBPA + 1.0M PZ appears to have the overall best performance of all the solvent systems tested and analysed. In terms of absorption rate, it shows high initial rate, high rate at 90% equilibrium approach and also high absorption rate at lean loading. In terms of absorption capacity, it attains a comparatively high loading of 1.231mol CO_2/mol amine, absorbs large amounts of CO_2 per litre
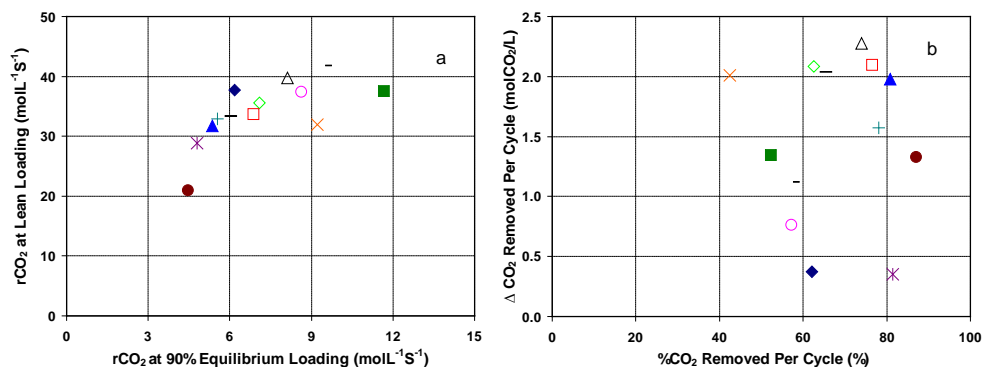
Figure 3. Solvents performance in terms CO_2 absorption of rate (a); Solvent performance in terms of CO_2 carrying capacity (b): ♦,1.0M MEA; ○,2.5M MEA; ■,5.0M MEA; ✗,10.0M MEA; ✹,0.42M DIHEP + 0.58M HEP; ●,2.5M AMP; +,2.5M AMP + 0.5M PZ; ▲ 1.5M TMBPA; —,1.5M TMBPA + 1.0M DMPDA; ◊,1.5M TMBPA + 1.0M MAPA; □, 1.5M TMBPA + 1.0M MEA; △,1.5M TMBPA + 1.0M PZ; −,1.0M TEPA.

solution (3.076mol CO_2/L) and desorbs about 74% of the CO_2 absorbed under the experimental conditions, making it the solvent with highest CO_2 carrying capacity (2.277mol CO_2/L). Its cyclic capacity in molCO_2/mol amine and ΔCO_2 per liter solution per cycle are respectivley 70% and 41% more than 5M MEA. It did not show a significant discolouration during the experiments indicating some degree of stability; flashing and foaming were however observed. Flashing could be result of high desorption ability of TMBPA, high vapour pressure of PZ, foaming of the solvent system or a combination of these factors. High desorption of 1.5M TMBPA + 1.0M PZ at 80°C shows potentials for lower regeneration energy; its high carrying capacity will result in lower solvent circulation rate. This solvent system thus appears to have a high potential for more efficient CO_2 removal at reduced cost.

5. Conclusions
Method of combined data analysis using absorption-desorption dot plots was very useful in solvent assessment from rapid screening experiments. Bis-(3-dimethylaminopropyl) amine (TMBPA) and tetraethylenepentamine (TEPA) showed good potential as solvents for CO_2 absorption. TEPA has both high absorption rate and capacity but lower desorption ability under the experimental conditions. TMBPA showed very high carrying capacity for CO_2 and relatively good kinetics. It requires a promoter for increased absorption rate, particularly on approach to equilibrium. Promoting 1.5M TMBPA with 1.0M MEA and 1.0M DMPDA showed higher foaming tendency while promoting with 1.0M MAPA showed lower desorption degree. Promoting 1.5M TMBPA with 1.0M PZ was found to have the best overall performance in terms of potential for efficient CO_2 removal at reduced cost for all the systems tested. Its cyclic capacity in molCO_2/mol amine was found 70% more than 5M MEA and it removes 41% more CO_2 per cycle per liter solution than 5M MEA at test conditions.

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