PIPERAZINE *(PZ)* AND METHYLDIETHANOLAMINE *(MDEA)* INTERRELATIONSHIPS IN CO_2 ABSORPTION BY AQUEOUS AMINE MIXTURES

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Summary

- The use of ***a-MDEA (MDEA + PZ)*** as industrial solvent in CO_2 capture process is highlighted
- Very little however is known on the actual behaviour of the absorbent mixture
- Experiments were carried out to throw some light on the problem
- Main results show that interaction between PZ and MDEA is quite limited (e.g. no shuttle effect)

a-MDEA as absorbent medium

BASF
We create chemistry

22/5/2019 Amines washing machine - BASF Intermediates

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Amines washing machine

BASF's process makes gas treatment history

From the pilot plant to leading supplier status for natural gas treatment: success stories like BASF's aMDEA® technology are few and far between.

It all started with ammonia. BASF wanted to reduce the cost of producing ammonia. In the early 1970s, BASF was therefore exploring methods for separating carbon dioxide (CO_2) more efficiently from the synthetic gas used in the production process.

News

BASF to increase capacity for Alkylethanolamines in Ludwigshafen
April 10, 2019
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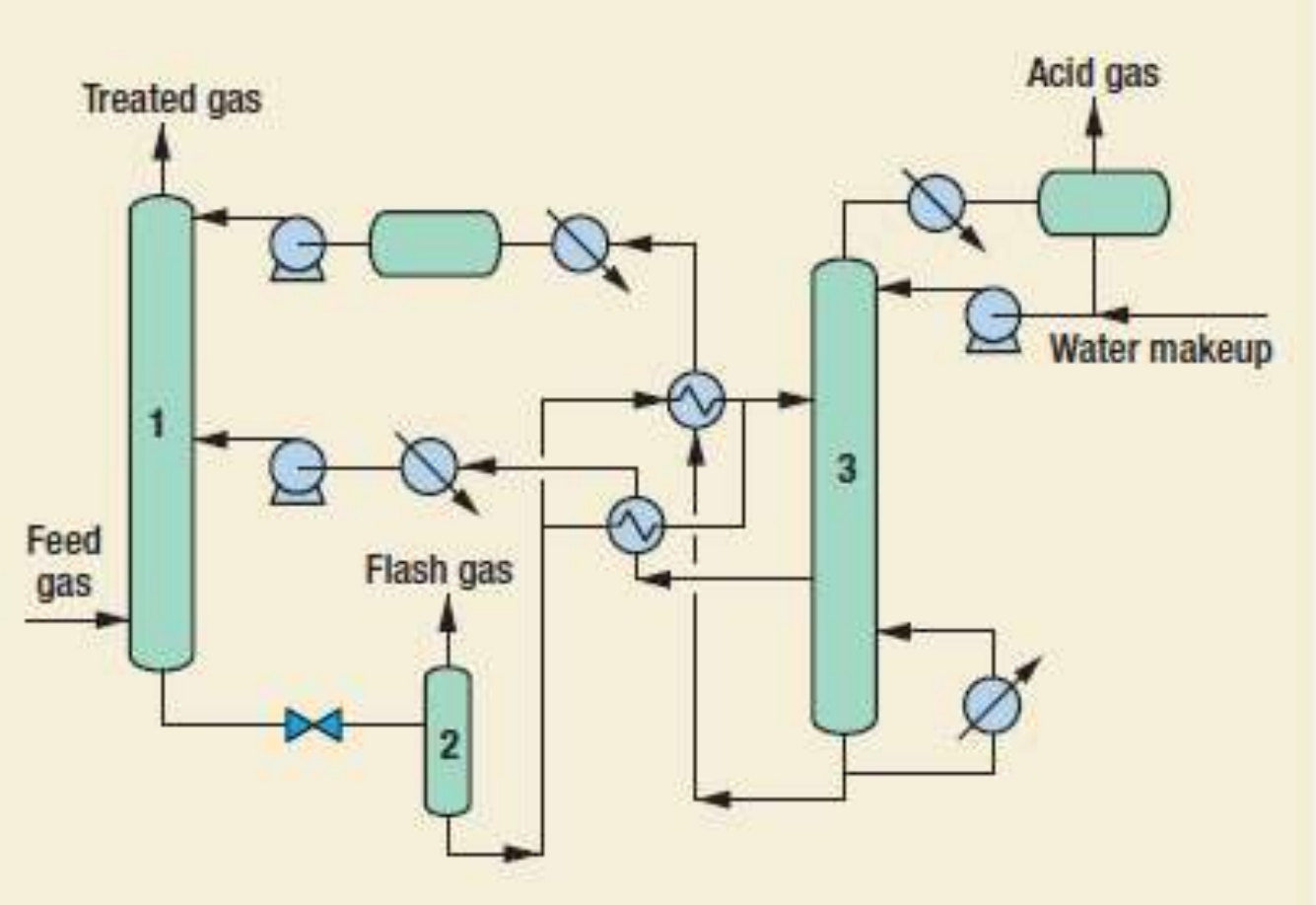
This is one of the places where aMDEA is used: production of natural gas on Melkoya island off the coast of Norway.

BASF's researchers succeeded: they invented a process relying on methyldiethanolamine (MDEA) as a "gas scrubbing agent" to which a special activator lends exceptional reactivity. This "activated methyldiethanolamine" - aMDEA, for short - combines more easily with CO_2, separating it more efficiently from the syngas than the traditional monoethanolamine or potassium carbonate. The process requires clearly less energy input and achieves much higher plant capacity.

BASF originally used the process in its own ammonia and syngas plants only but then started licensing it to other ammonia manufacturers. The idea of selling the aMDEA technology to oil and gas companies occurred to some clever BASF employees in the early 1990s. After all, gases like liquefied natural gas (LNG) also need to be scrubbed, i.e., freed of any impurities like CO_2 or hydrogen sulfide. Potential customers were reluctant, however. Never before had the aMDEA process been used in an LNG facility. There was simply no plant that could serve as a reference.

Breakthrough was achieved in 1997 on the Indonesian island of Borneo, two hours by car north of the equator. Here, right in the jungle of Kalimantan, was the location of what was then the world's largest LNG facility. And national operator Pertamina had been convinced to try out aMDEA in one of its seven production lines. The trial was an overwhelming success, the new process proved to be highly efficient.

a-MDEA PROCESS



advantages lauded…

Table 2
ECONOMIC COMPARISON OF RYAN HOLMES AND BASF aMDEA PROCESSES

	RYAN-HOLMES	BASF aMDEA
CAPITAL COST		
Acid Gas Removal	233% Base	Base
CO_2 LP Compression	60% Base	Base
CO_2 Dehydration	Not Required	Base
Feed Gas Dehydration	78% Base	Base
Total	**154% Base**	**Base**
OPERATING COST		
Power	87% Base	Base
Fuel Gas	117% Base	Base
Total	**106% Base**	**Base**

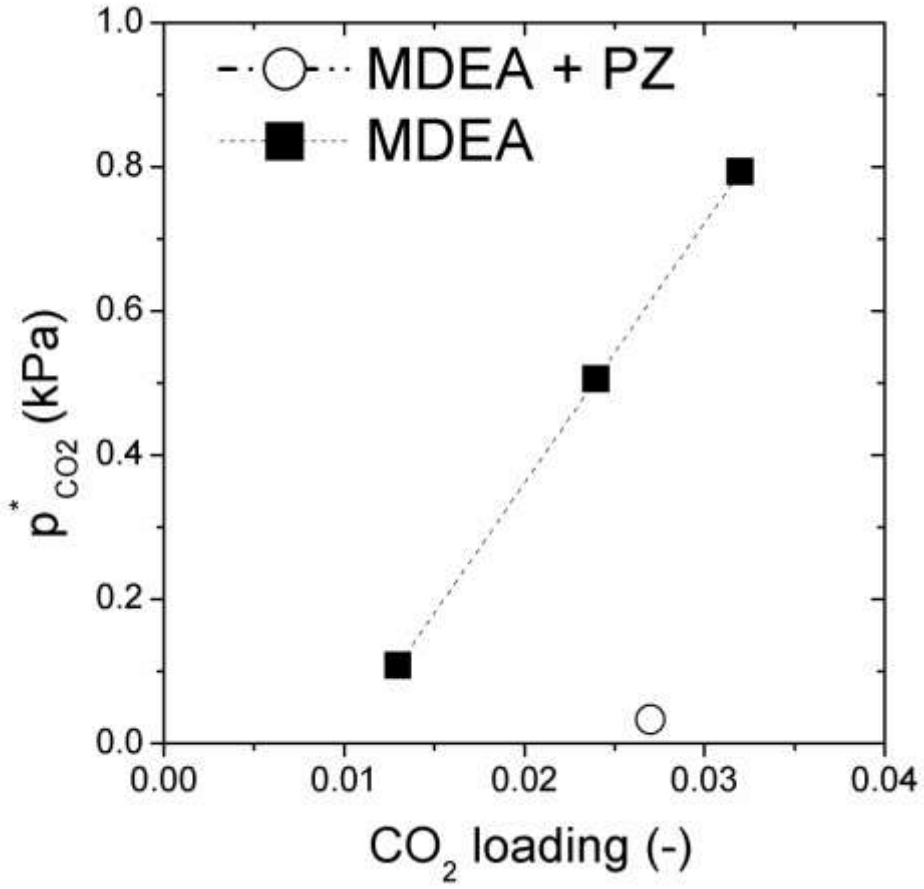
more advantages lauded…

Table 2 Effect of Piperazine on Treating

Wt% Piperazine	Treat (ppm CO_2)	Lean Load (mol/mol)	% Rich Equilib'm	Reflux Ratio
0 (22 trays)	85,300	0.0015	70	2.2
0 (50 trays)	48,300	0.0015	83	2.0
0 (100 trays)	48,000	0.0015	83	2.0
5 (22 trays)	51	0.016	91	1.2
7 (22 trays)	39	0.021	89	1.1
9 (22 trays)	10	0.026	87	1.0

The effect of piperazine on CO_2 treat is nothing short of stupendous—it allows promoted MDEA to reach a few tens of ppmv while MDEA alone cannot do better than 8.5% in the same equipment, and it cannot reach below 4.8 mol% CO_2 even with 100 trays in the column under otherwise identical conditions.

gas-liquid CO_2 equilibrium



data taken from Bishnoi (2000)

not quite clear how it works!

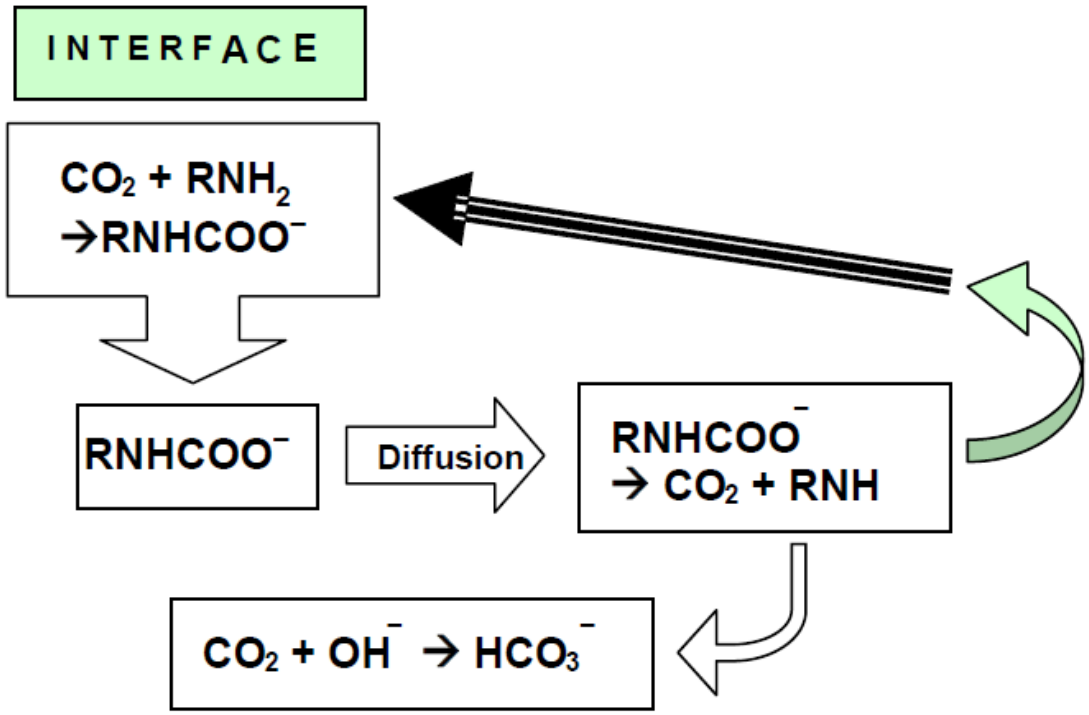
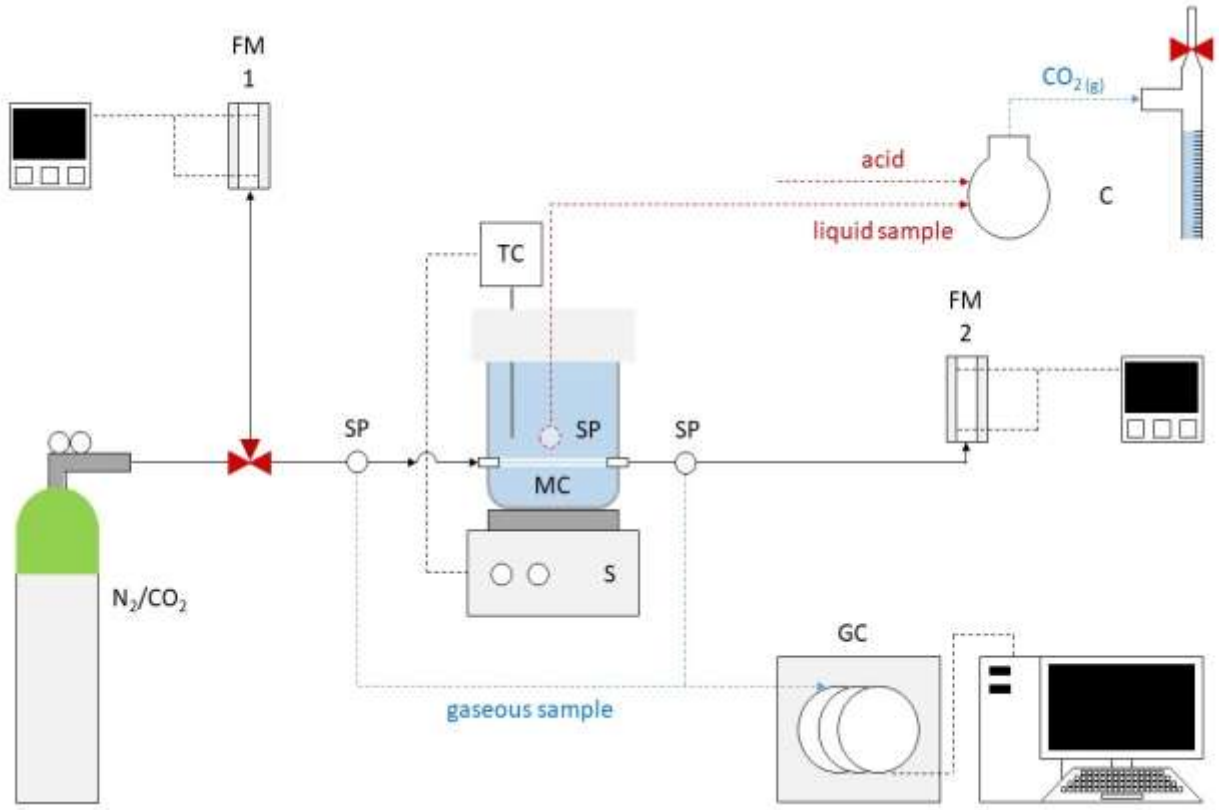


Figure 1 Schematic of Shuttle Mechanism

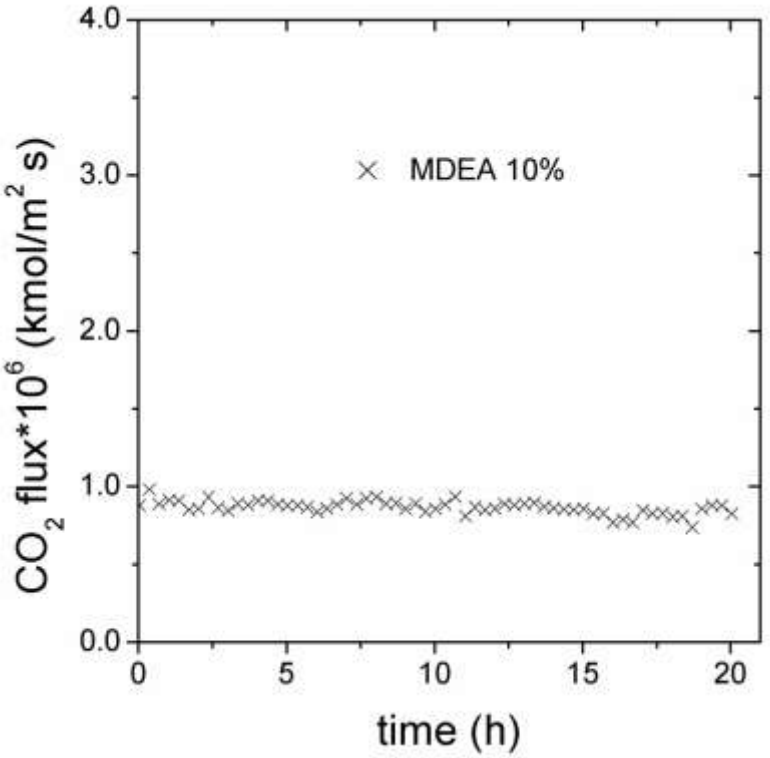
experimental investigation



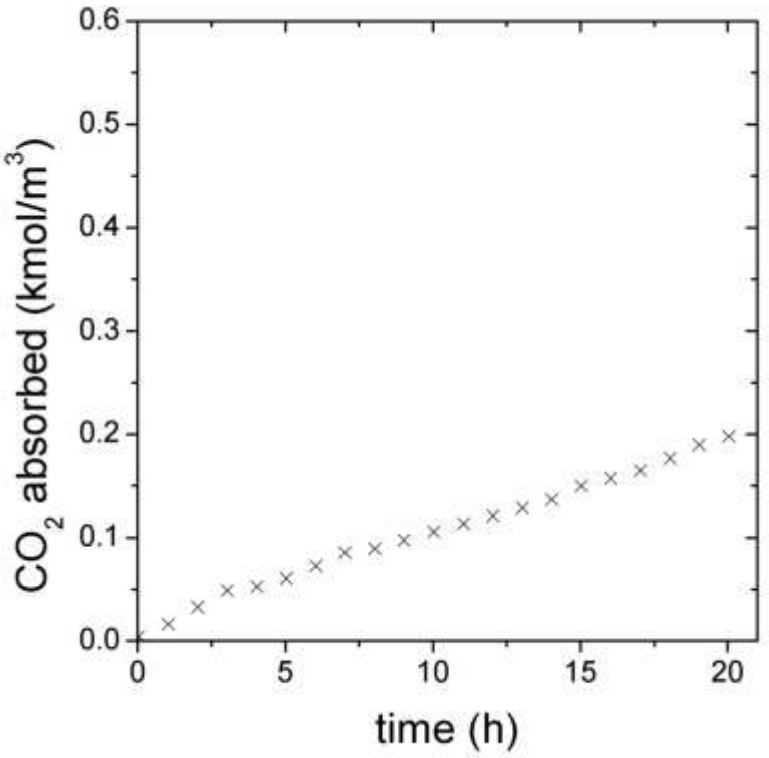
FM: flow meter; SP: sampling point; TC: temperature controller; MC: membrane contactor; S: magnetic stirrer; GC: gas chromatograph; C: calcimeter

MDEA 10% (0.84 M)

gas side



liquid side



(practically no enhancement on the process rate compared to pure water)

MDEA + CO_2 *(chemistry)*

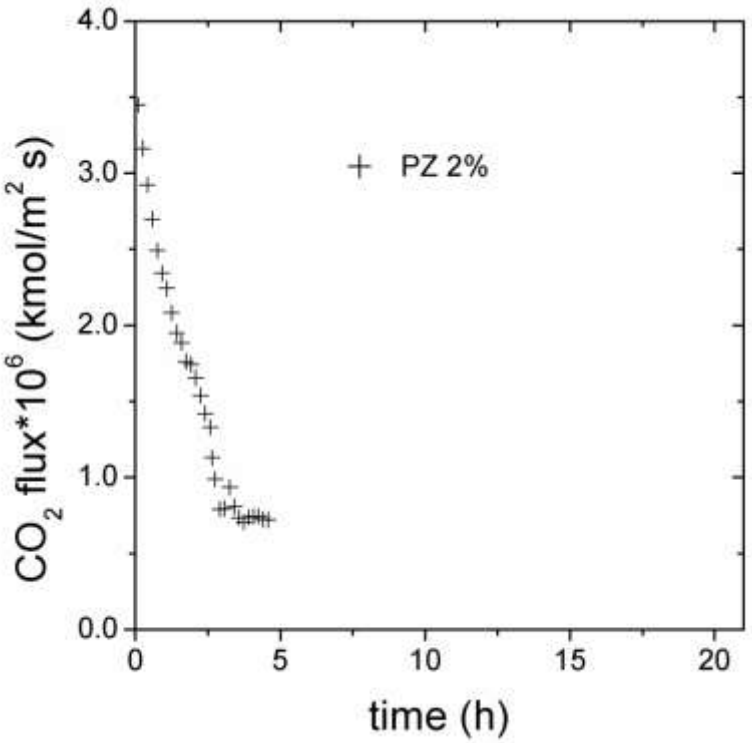
$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad \text{(R1)}$$
$$2H_2O \rightleftharpoons OH^- + H_3O^+ \quad \text{(R2)}$$
$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad \text{(R3)}$$

Protonation:

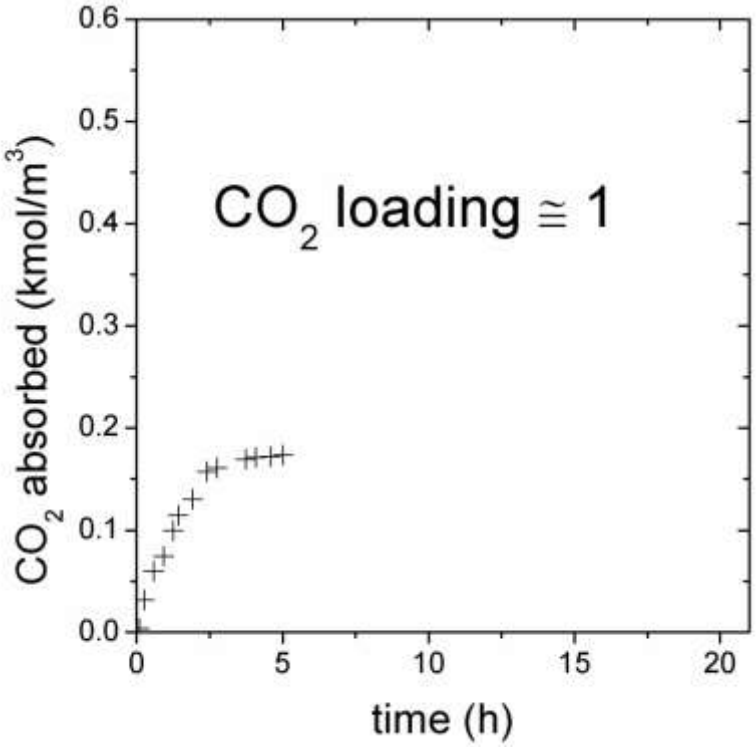
$$MDEA + H_3O^+ \rightleftharpoons MDEAH^+ + H_2O \quad \text{(R4)}$$

PZ 2% (0.23 M)

gas side



liquid side



(the enhancement on the process rate evident for about 3 h)

PZ + CO_2 *(Chemistry)*

$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad \text{(R1)}$$
$$2H_2O \rightleftharpoons OH^- + H_3O^+ \quad \text{(R2)}$$
$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad \text{(R3)}$$

Carbamate and dicarbamate formation:

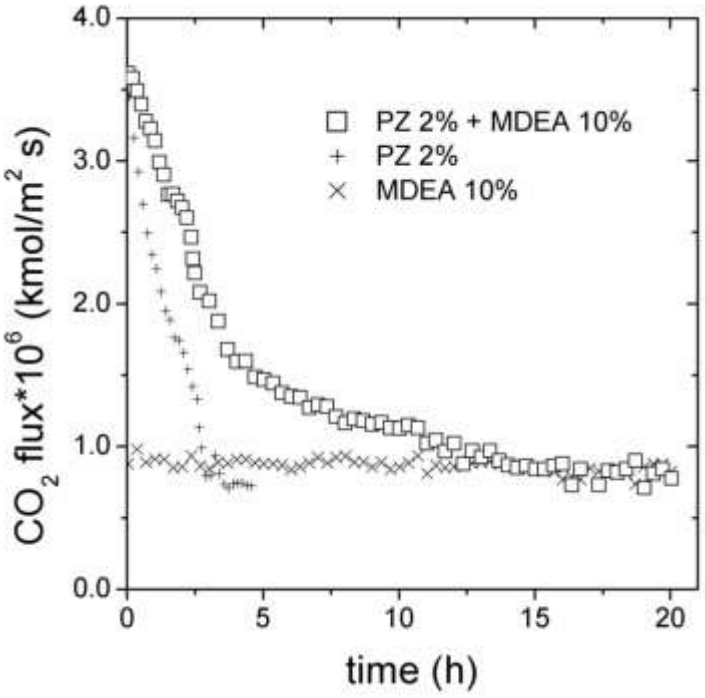
$$PZ + CO_2 + H_2O \rightleftharpoons PZCOO^- + H_3O^+ \quad \text{(R5)}$$
$$PZCOO^- + CO_2 + H_2O \rightleftharpoons PZ(COO^-)_2 + H_3O^+ \quad \text{(R6)}$$

Protonations:

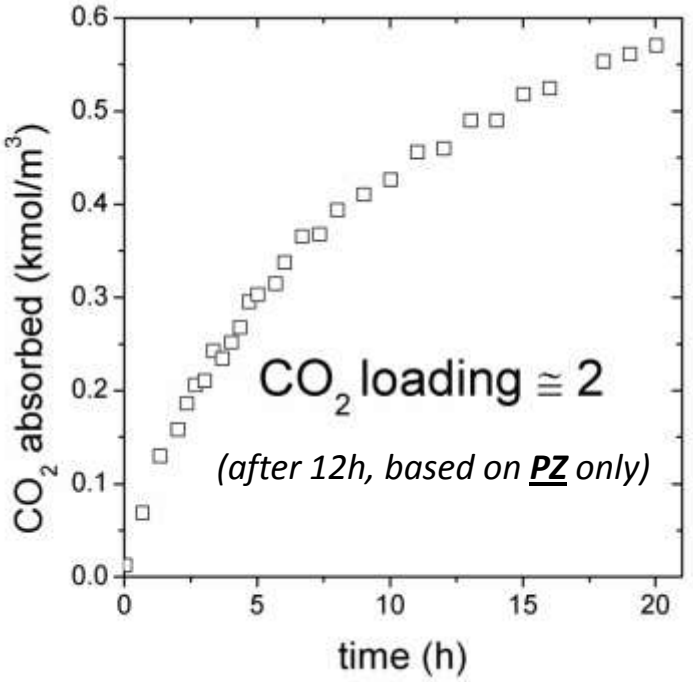
$$PZ + H_3O^+ \rightleftharpoons PZH^+ + H_2O \quad \text{(R7)}$$
$$PZCOO^- + H_3O^+ \rightleftharpoons H^+PZCOO^- + H_2O \quad \text{(R8)}$$

10% MDEA + 2% PZ

gas side



liquid side



(the enhancement on the process rate evident for about 12 h)

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MDEA + PZ + CO_2 CHEMISTRY

$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad \text{(R1)}$$
$$2H_2O \rightleftharpoons OH^- + H_3O^+ \quad \text{(R2)}$$
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Protonation:

$$MDEA + H_3O^+ \rightleftharpoons MDEAH^+ + H_2O \quad \text{(R4)}$$

Protonations:

$$PZ + H_3O^+ \rightleftharpoons PZH^+ + H_2O \quad \text{(R7)}$$
$$PZCOO^- + H_3O^+ \rightleftharpoons H^+PZCOO^- + H_2O \quad \text{(R8)}$$

which protonation will prevail?

protonation reactions are the only step where the two absorbents may interfere

$$f_{MDEA} = \frac{\frac{K_{eq,4}}{K_{eq,7}}\frac{C_{MDEA}}{C_{PZ}}}{1 + \frac{K_{eq,4}}{K_{eq,7}}\frac{C_{MDEA}}{C_{PZ}}}$$

R4 will prevail over R7 with the result of freeing PZ, which become available for more CO_2 absorption

SIMPLIFIED MDEA + PZ + CO_2 CHEMISTRY

$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad \text{(R1)}$$
$$2H_2O \rightleftharpoons OH^- + H_3O^+ \quad \text{(R2)}$$
$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad \text{(R3)}$$

Carbamate and dicarbamate formation:

$$PZ + CO_2 + H_2O \rightleftharpoons PZCOO^- + H_3O^+ \quad \text{(R5)}$$
$$PZCOO^- + CO_2 + H_2O \rightleftharpoons PZ(COO^-)_2 + H_3O^+ \quad \text{(R6)}$$

Protonation:

$$MDEA + H_3O^+ \rightleftharpoons MDEAH^+ + H_2O \quad \text{(R4)}$$

~~*Protonations:*~~

~~$$PZ + H_3O^+ \rightleftharpoons PZH^+ + H_2O \quad \text{(R7)}$$~~
~~$$PZCOO^- + H_3O^+ \rightleftharpoons H^+PZCOO^- + H_2O \quad \text{(R8)}$$~~

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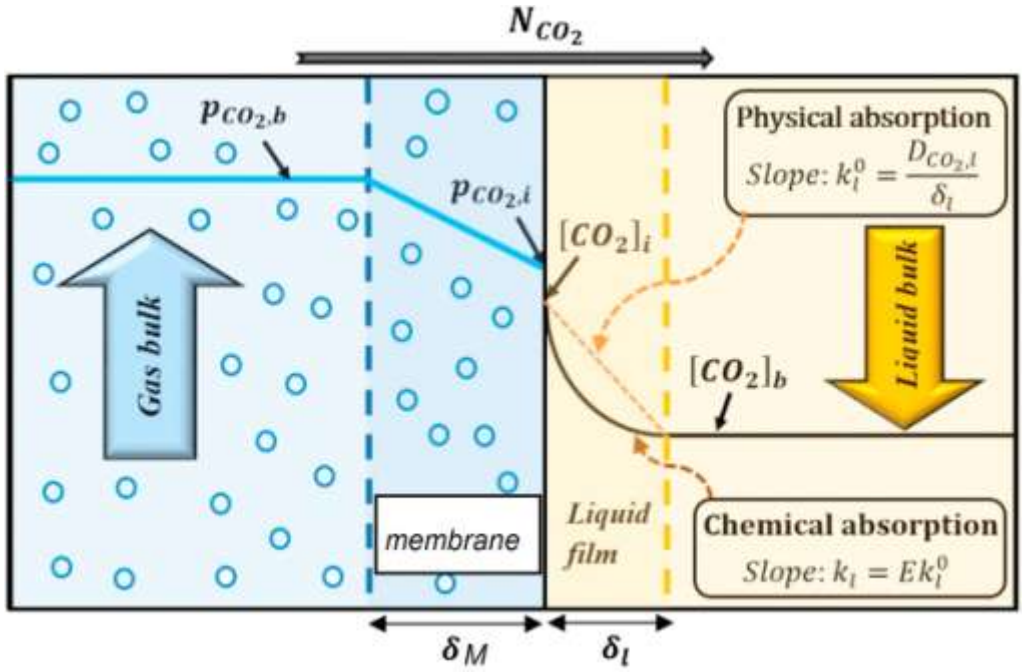
bit of modelling…

we use the classical film theory

$$J_{CO2} = \frac{p_{CO2}}{\frac{1}{k_M} + \frac{H}{E k_L}}$$



bit of modelling…

in order to estimate E

$$D_j \frac{\partial^2 C_j}{\partial x^2} + \sum_i r_{ij} = 0$$

(with the pseudo-steady-state-hypothesis a reasonable assumption)

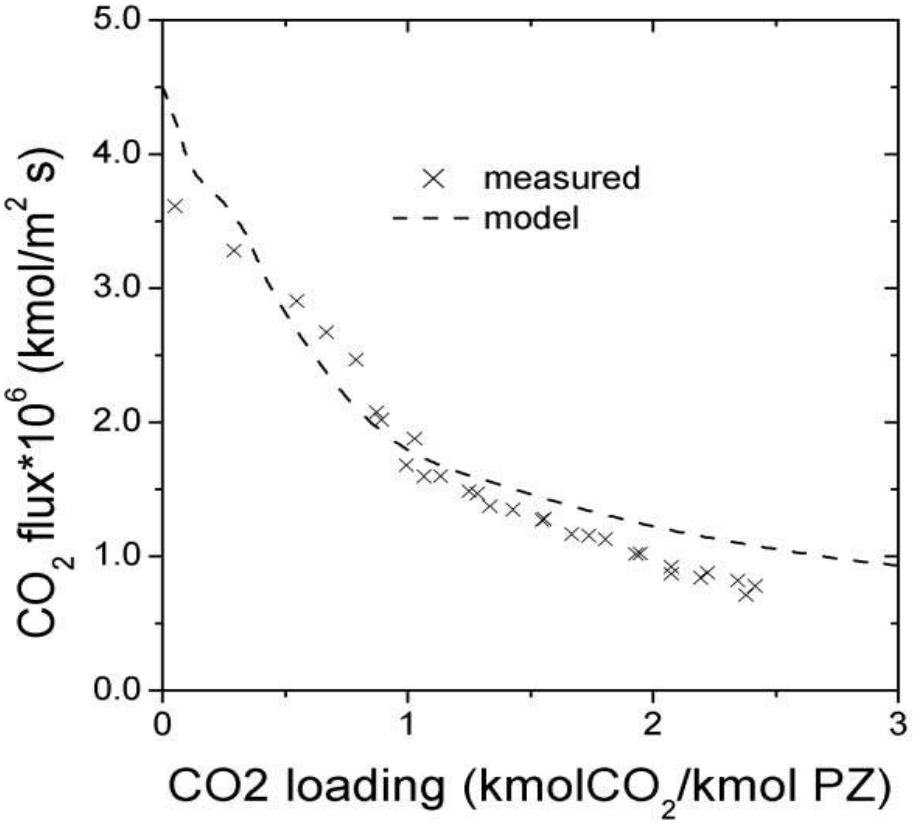
At *x*=0 (membrane-liquid interface)

$\frac{\partial C_j}{\partial x} = 0$ for every component *j* excluding CO_2 for which

$C_{CO2} = \frac{p_{CO2,M}}{H}$

At *x*=δ (liquid film-liquid bulk interface) $C_j = C_{j,b}$ valid for any components.

bit of modelling…



(*all necessary data from literature, no fitting parameters)*

CONCLUSIONS

- Observed behavior of the MDEA+PZ absorbing mixtures can be explained without the need to introduce «exotic» steps
- «Shuttle» mechanism can also be discarded
- Rather than *a*-MDEA, MDEA+PZ mixtures should be named *e*-PZ

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