

PROMOTED AMINES FOR CO₂ REMOVAL

Ralph Weiland, Optimized Gas Treating, Inc., USA, discusses the use of piperazine as a reaction promoter in combination with N-methyldiethanolamine for enhancing carbon dioxide removal rates.

This article reviews the application of piperazine as a reaction promoter for enhancing carbon dioxide (CO₂) removal rates from syngas preparatory to its conversion to ammonia and from natural gas prior to liquefaction. Apart from a few tangential references, the focus is on piperazine-promoted N-methyldiethanolamine (MDEA), this being the most increasingly used solvent today in most CO₂-removal applications. After addressing CO₂-piperazine chemistry and piperazine degradation products, consideration is given to CO₂ vapour-liquid equilibria in aqueous piperazine and MDEA-piperazine composite solvents. Reaction kinetics between CO₂ and piperazine are critical to its successful application, both in amine systems and in hybrids such as Shell's Sulfinol-M® process.

CO₂ reactions with piperazine-MDEA solvents

CO₂ absorption by tertiary amines is fundamentally different from absorption by primary and secondary amines in that the latter react rapidly and exothermically

with CO₂ to form carbamates, whereas the former do not. Thus, regeneration of primary and secondary amines is comparatively more energy intensive, making a tertiary amine like MDEA preferable from an energy standpoint. Its disadvantage is that it does not react directly with CO₂, so absorption rates are not enhanced by reaction with the amine. However, reactivity can be gained in a tertiary amine system if the solvent is spiked with a relatively small amount of a very fast-reacting amine. This produces a blended solvent just as alkaline as before (and therefore with the same high CO₂ capacity), but now with high reactivity and therefore able to absorb CO₂ much more rapidly.

Deep CO₂ removal is achieved by using a relatively small concentration of a highly reactive amine such as piperazine. Piperazine reacts very quickly with CO₂ which greatly enhances absorption rates, and then the piperazine carbamate gradually decomposes and releases the CO₂ back into solution as bicarbonate. The hydrogen ion (acid) produced in the original piperazine reaction is mopped up by MDEA (base) which, therefore, really acts just as a sink for hydrogen ions:



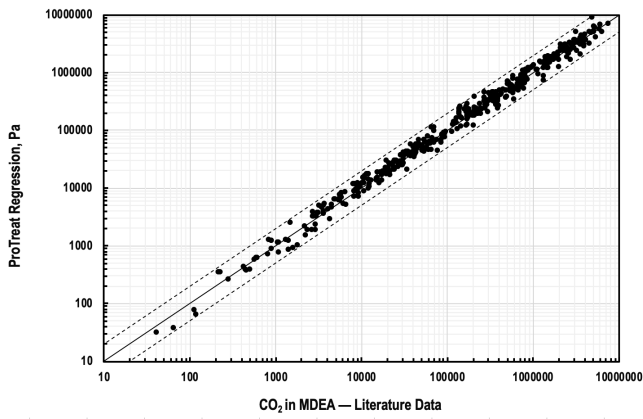


Figure 1. Parity plot of CO₂ partial pressure over MDEA solutions (435 measurements) dashed lines indicate ± factor of two deviation from mean.

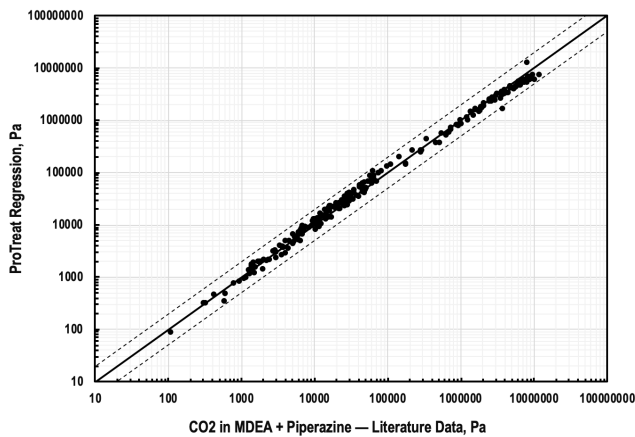


Figure 2. Parity plot of CO₂ partial pressure over MDEA + piperazine solutions (238 measurements). Dashed lines indicate ± factor of two deviation from mean.

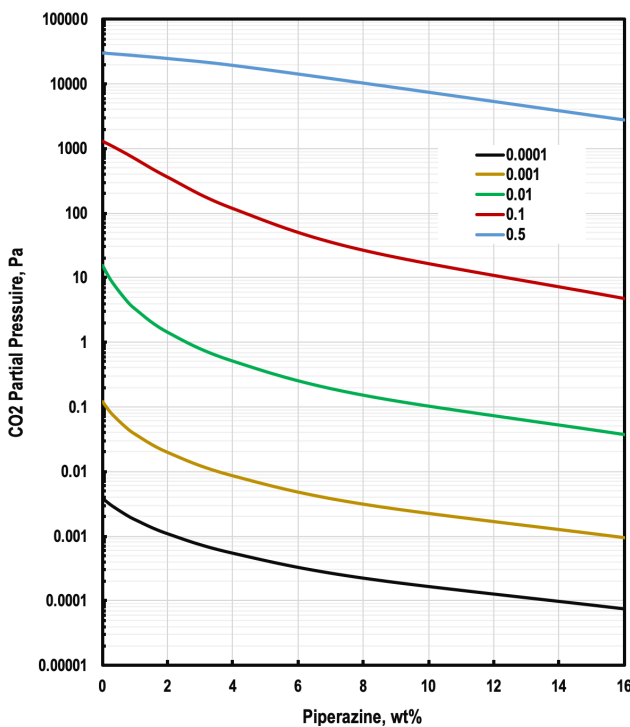
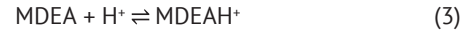


Figure 3. Simulated effect of piperazine concentration on CO₂ partial pressure with CO₂ loading as parameter. Temperature = 35 °C, 40 wt% total amine strength, ProTreat® simulation.



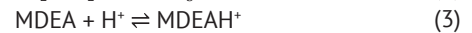
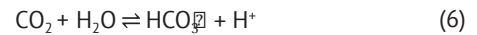
There is a little more to the chemistry than this, however, because piperazine is a diamine. Thus, piperazine monocarbamate can react with another CO₂ molecule to form the dicarbamate, and the dicarbamate can hydrolyse to reform the monocarbamate and release a bicarbonate ion:



Piperazine is a very effective activator, although it is not the only one used commercially. Regardless of which promoter is employed, when using an activated MDEA solvent, one is dealing with a highly reactive system in which a substantial amount of heat is released by:

- The physical dissolution of CO₂ into the liquid solvent.
- Its subsequent reaction with a low concentration of the reactive amine (small heat effect).
- The titration reaction of tertiary amine with released hydrogen ions (substantial heat generated).

When the solvent contains only MDEA, CO₂ absorption generates bicarbonate and hydrogen ions, MDEA does not react with CO₂, but each hydrogen ion neutralises an MDEA molecule:



One of the more interesting technical aspects of the CO₂-piperazine-MDEA system is that the role of MDEA is not to react with CO₂ but to remove hydrogen ions from the solution. Keeping the hydrogen ion concentration low virtually eliminates one of the chemical components (H⁺) that would push back against CO₂ dissolution into water via Equation 6 and hamper bicarbonate formation. The high capacity of MDEA for CO₂ comes from its ability to act as a sponge for hydrogen ions – low absorption rates result from its nonreactivity, a deficiency overcome by piperazine.

Figures 1 and 2 indicate the variability in the literature data on the solubility of CO₂ in MDEA and in MDEA + piperazine, respectively, and they also show the goodness of fit of ProTreat's® thermodynamic model to the data. An interesting question is what effect piperazine has on the equilibrium CO₂ partial pressure. There are several ways to pose this question.

Commercially, practitioners think of amine concentration in terms of the units of weight (or mass) percent, probably because solvents are bought and sold by weight. However, when the solvent contains two (or more) amines, a rational study of blend formulation is not so straightforward. Should a comparison between 2 wt% and 8 wt% piperazine be based on a fixed MDEA concentration, or a fixed total amine concentration? Or should the basis be wt% at all? On balance, this is a thermodynamic question, and the language of solution thermodynamics is molality, not mass fraction, or mass percent. Which units to use depends on whether the results are to be applied commercially (mass basis) or to achieve deeper scientific understanding (molal basis).

In this case, the interest is commercial (vs theoretical) so Figure 3 shows an example of the effect of varying piperazine concentration (wt%) in a 40 wt% total amine solution as a function of CO₂ loading at 35°C with CO₂ loading as parameter. A typical CO₂ loading at the lean end of a CO₂ absorber in an LNG application is 0.01 mol/mol (green line in Figure 3). Here, 2 wt% piperazine lowers the CO₂ backpressure by a factor of 10 and 4 wt% piperazine lowers it by a factor of 25. These are substantial reductions, so it can be concluded that piperazine acts through both equilibrium and reaction kinetic effects. It is also worth noting that equilibrium CO₂ partial pressure is most responsive to piperazine addition at low concentration, although the response is also quite evident right across the whole range of piperazine concentrations. Reaction kinetics and equilibrium work together to determine the packing depth or tray count in an absorber, whereas equilibrium sets the maximum allowable loading to meet product specifications.

A new technology

In the area of CO₂ capture, a new technology called CESAR1 has emerged. This solvent consists of 40 wt% total amine with a piperazine-to-AMP (2-amino-2-methyl-1-propanol) molar ratio of 1:2.¹ Piperazine-to-AMP solvent blends are now being used commercially in post-combustion CO₂ capture applications. For example, several test campaigns are being conducted by RWE at their Niederaussem Innovation Centre, Bergheim, Germany, as part of the so-called Sustainable OPeration of post-combustion Capture plants (SCOPE) project. SCOPE is a follow-on from

the ALIGN project² and involves more than 20 partners from Germany, the Netherlands, the UK, Norway, India, and the US. This project seeks to overcome existing barriers to the accelerated implementation of carbon capture utilisation and storage (CCUS). This is to be achieved by making available recommendations on methods of reducing emissions based on representative pilot facility testing, simulations, cost-benefit analyses and case studies for the design and operation of amine scrubbers for carbon capture and the approval process. ProTreat is being used as SCOPE's simulation benchmark and is being updated as the project progresses.

AMP is a primary amine; however, it is sterically hindered so it does not react with CO₂. Because hindering blocks the access of CO₂ to the amino group, AMP exhibits the same chemistry as MDEA. Thus, most of the foregoing discussion concerning piperazine promoted MDEA also applies to CESAR1. CESAR1 solvent offers a 22% reduction in energy consumption for coal-fired and 15% for gas-fired power plants over 30 wt% MEA, heretofore the CO₂ capture standard.

Hazards

Except as a vapour, piperazine itself is not a particularly hazardous chemical, as witnessed by its safe and effective veterinary use as a livestock anthelmintic (dewormer) since 1953. Its use as a solvent component in gas treatment, however, has raised concerning issues. Piperazine, being a secondary amine, can form N-nitrosopiperazine and dinitrosopiperazine by reaction with nitrogen dioxide (NO₂) which absorbs into the solvent as nitrite. Nitrosopiperazine

is carcinogenic. This is concerning in general, but especially when piperazine is used as a component (or alone) in solvents for CO₂ capture. Combustion gases invariably contain substantial concentrations of nitrogen oxides (NO_x) of which NO₂ is a prominent species.

As discussed in an article by Fine et al. (2013),³ one approach to mitigating the generation of nitrosopiperazine is to pretreat the flue gas with a sulfite

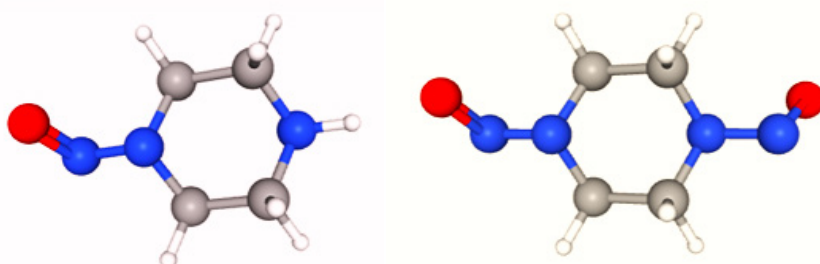


Figure 4. N-nitrosopiperazine (left) and dinitrosopiperazine (right).

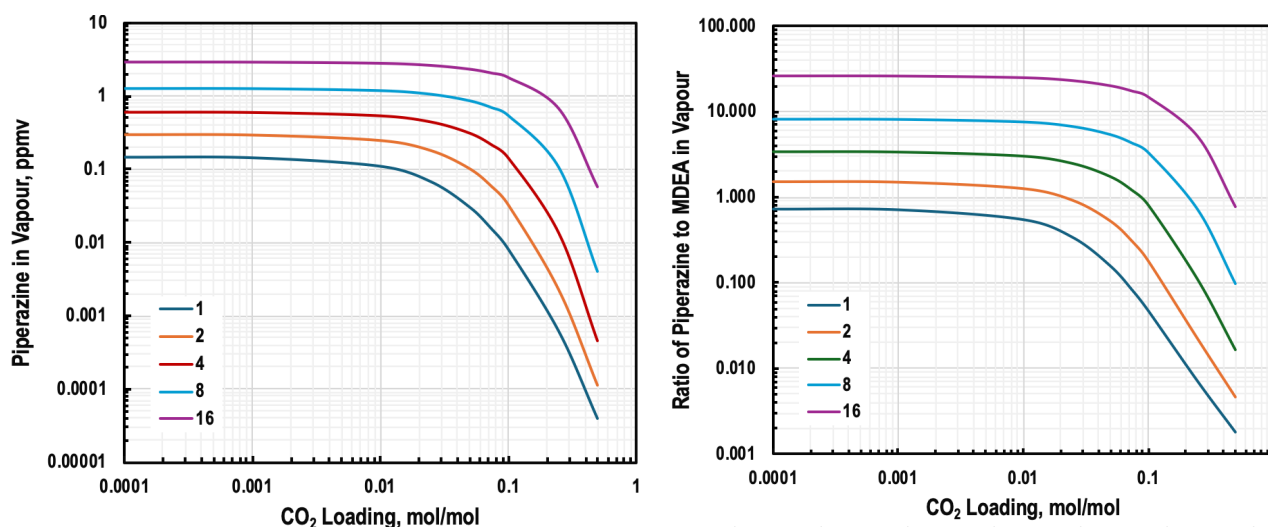


Figure 5. Piperazine in vapour (left) and molar ratio piperazine to MDEA in vapour (right). Effect of CO₂ loading (piperazine wt% as parameter) on equilibrium ppmv piperazine-to-MDEA ratio in the vapour. Temperature = 35 °C, 40 wt% total amine strength, ProTreat® Simulation.

solution in an absorber to remove NO_x . However, pretreatment via absorption could add substantially to the cost of CO_2 capture because of the large equipment needed to handle the enormous gas volumes and the energy required to overcome the additional pressure drop across the extra pretreating column. In a detailed article, Rochelle (2022) has discussed much about hazards that must be addressed in amine-based gas treatment.⁴

Amine volatility and recovery

All the alkanolamines used in gas treatment exhibit sufficient volatility to warrant the implementation of water washing of the treated gas to recover any small amine vapour content and to capture and retain solvent entrainment (second to leaks and spills, probably the principal way solvents are lost from the system). Spillage and entrainment are unique to each plant's operation; vaporisation losses are not. Piperazine has a relatively low molecular weight and a high enough vapour pressure for there to be comparable concentrations of piperazine and MDEA in the treated gas despite piperazine being only 2 – 3 wt% of the solvent while MDEA is at 10 – 20 times greater concentration.

Figure 5 shows how the equilibrium level of piperazine in the treated gas at 35°C varies with piperazine concentration and solvent CO_2 loading. Given that a typical absorber lean-end CO_2 loading is around 0.01 mol/mol in LNG applications, Figure 5 illustrates that piperazine could vaporise at nearly 30 times the rate of MDEA in a high-piperazine blend. In carbon capture applications, however, a CO_2 lean loading of 0.1 – 0.2 is more typical, and piperazine vaporisation is much lower.

Nevertheless, water washing the treated gas can greatly reduce amine losses, particularly piperazine. Entrainment capture is an added benefit, as is removal of nitrosamines.

Conclusion

Piperazine is an extremely fast reactor with CO_2 and is the most used reaction rate promoter in MDEA-based amine systems for gas treatment. There are enough high-quality literature data available to permit development of very accurate models for CO_2 absorption and solvent regeneration in both MDEA and piperazine-MDEA systems, and piperazine-AMP solvents are also being developed and tested. Simulation is the most obviously effective way fundamental data can be used in design and operations, and ProTreat is presently being used as the benchmark CO_2 -capture simulator in the multinational SCOPE project to commercialise the piperazine-AMP solvent process (called CESAR1). [LNG](#)

References

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