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DVS Application Note 114

Absorption of CO_2 in amine solutions in DVS and the influence of humidity

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A study on the sorption kinetics of CO_2 in low-volatility liquid amines using the DVS Carbon system was undertaken, with a focus on the influence of humidity on primary and tertiary amines, monoethanolamine (MEA) and methyldiethanolamine (MDEA) respectively. Under dry conditions, MEA exhibits significantly higher CO_2 uptake than MDEA, attributed to the faster reaction kinetics of MEA. The introduction of humidity has a modest positive effect on CO_2 uptake in MEA, but a more pronounced impact on mass transfer kinetics, particularly at lower CO_2 partial pressures. Conversely, for MDEA, whilst low humidity improves mass transfer due to increased reactivity, higher humidity levels introduce boundary layer effects that hinder the gas-liquid interface interactions. This leads to a shift toward diffusion-limited mass transfer and a lower dependence on CO_2 partial pressure. As expected, humidity enhances the overall CO_2 capacity of MDEA by promoting bicarbonate reaction pathways which allow for increased CO2 loading. These findings highlight the nuanced role of humidity in CO_2 capture processes and underscore the importance of optimizing water content for different amine systems to balance capacity and kinetics.

Introduction

Among the various carbon capture and storage (CCS) approaches used to mitigate anthropogenic carbon dioxide (CO_2) emissions, chemical absorption using aqueous amine solutions remains the most mature and widely implemented method due to its high selectivity, efficiency, and compatibility with existing infrastructure.

Amine based technology is predominantly based around the very strong interactions between amines and CO_2 and the large sorption capacity of the solvents. The amine used in these CCS process greatly affects the both the kinetics and capacity, with primary and tertiary amines having different reaction mechanisms.

In the CCS process, amines are typically diluted in water to about 30-40%wt to reduce the corrosiveness of the solutions used, reduce the loss of the amine solvent via evaporation, and in some cases increase the kinetics of the process. These water levels must be controlled to reduce amine emissions and maintain carbon capture efficiency[1]. The CCS process can introduce excess water to the solvent via humidity in the process stream or via the water wash used to capture evaporating amine solvent from the absorption tower.

Amine-based solvents, particularly monoethanolamine (MEA) and methyldiethanolamine (MDEA), have been extensively studied for their CO_2 absorption capabilities. MEA, a primary amine, reacts rapidly with CO_2 to form carbamate species, offering high absorption rates and capacities. However, MEA suffers from drawbacks such as a high regeneration temperature, corrosiveness, and high oxidative degradation.

MDEA, a tertiary amine, does not form carbamates but instead facilitates CO_2 absorption through base-catalysed hydration to produce a bicarbonate, meaning 2 mols of CO_2 can be absorbed for every 1 mol of amine resulting in lower reaction rates but improved uptake capacity under certain conditions. MDEA also has a higher thermal stability and reduced energy requirements for regeneration[2].

The contrasting properties of MEA and MDEA make these amines ideal candidates for a case study aimed at observing CO_2 capture performance under varying humidity, enabled by advanced SMS instrumentation.

Methods

The materials of study were the pure primary amine monoethanolamine (MEA) and the pure tertiary amine methyldiethanolamine (MDEA). HPLC grade water was used to generate humidity, along with 99.5% CO_2 used to measure uptake.

Absorption measurements at controlled humidity and temperature were monitored in-situ using a DVS Carbon instrument. During the experiments an average 70 ± 10 mg of sample material was pipetted into the sample pan, Figure 1.

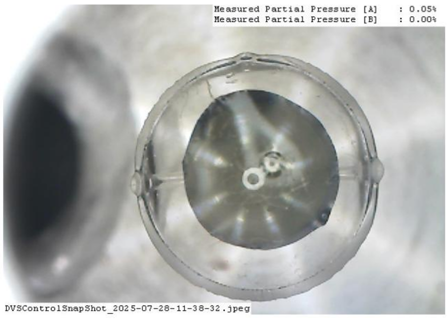

Figure 1. MEA amine on quartz sample pan in-situ image

The duration of the measurement was typically of the order of days due to the limited but very specific mass transfer area. Humidity or CO_2 was introduced to the sample until a complete weight equilibrium was achieved, depending on the applied humidity, which was changed between experiments between 0 – 40 %RH. The temperature was set to 20 °C and a total flow rate of 100 sccm to limit sample loss during the experiment via sample volatility. The data yielded weight-gain over time reported as a percentage of the initial sample mass.

The two-film theory method was used for the calculation of mass transfer rates[3] following Equation 1:

$$\ln\left(1-\frac{m_{(t)}}{m_{(\infty)}}\right) = -K_G \cdot a \cdot t \qquad (1)$$

Where, $m_{(t)}$ is the mass measured at time = t
$m_{(\infty)}$ is the mass measured at equilibrium
a is the interfacial area of the amine per unit volume
K_G is the gas mass transfer coefficient

Results

Pure absorption equilibria

Measurements of water sorption in the amines were first undertaken to investigate the interactions between amine and humidity, and to observe the solubility of water achieved at certain humidity values. The change in mass was observed in MEA and MDEA over humidity between 0-90 %RH. The absorption isotherms are shown below in Figure 2.

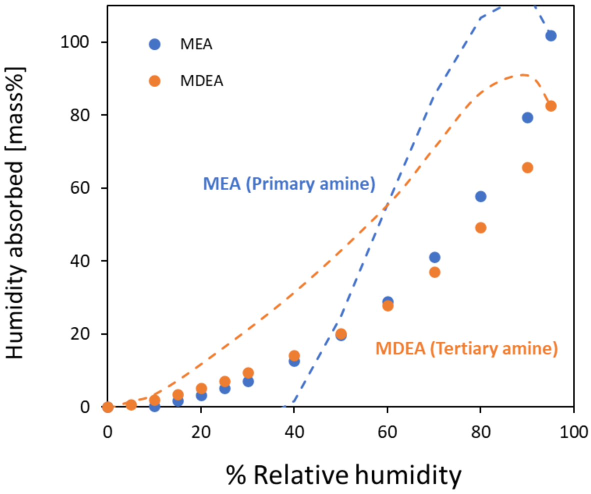

Figure 2. DVS plot of H_2O solubility in MEA and MDEA (25 °C)

As shown in Figure 2, the water uptake in the tertiary amine was higher than that of the primary amine at low %RH by small amounts, this is likely a result of the larger MDEA sample volume which facilitated water uptake at low concentrations. At higher %RH the uptake in MEA is higher than that of

MDEA due to the availability of the primary NH_2 group, compared to the tertiary NR_2H group. At higher relative humidity, especially seen in the desorption curve, the hysteresis is large with uptake observed when decreasing the exposed relative humidity. This increase in mass despite decreasing the %RH highlights the slow mass transfer kinetics of water uptake in the amines.

Before measuring the effects of humidity on CO_2 uptake, the uptake of dry CO_2 was also observed between 0-100 %CO_2. The results obtained are shown below in Figure 3.

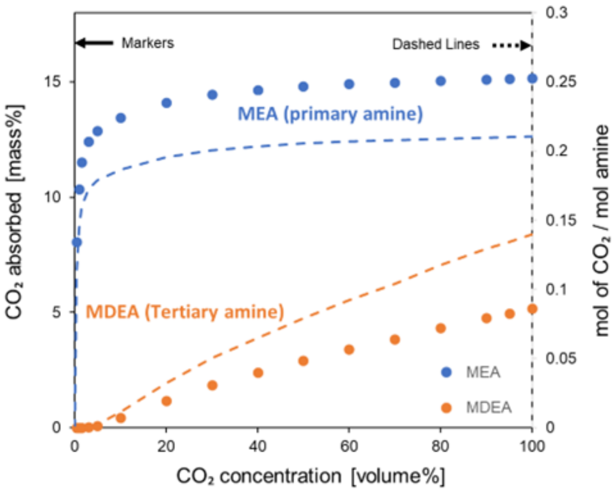

Figure 3. DVS measurements of CO_2 uptake isotherms in MEA and MDEA (25 °C)

As shown by the CO_2 uptake data, the uptake in MEA is much higher than that of MDEA both at low partial pressures and overall; this results in 0.21 mol of CO2/mol amine with MEA compared to 0.14 found for MDEA. This is primarily a result of the slow uptake kinetics of CO_2 in the tertiary amine, and the time limit of 300 mins that was applied to each sorption step in this experiment. If each experiment step was allowed to progress to equilibrium indefinitely then the tertiary amine would absorb the same quantity of CO_2.

MEA has a higher second order CO_2 uptake rate constant than MDEA[4], typically 1000x higher (between 4000-6000 and 2-6[5] m^3/kmol.s respectively) This reduced rate of uptake of CO_2 by MDEA arises from the lack of availability of the nitrogen electron pair.

As shown in Figure 3, the ratio of CO_2/amine is lower for the tertiary amine than the primary amine at 14% and 21% respectively. This low ratio highlights the mass transfer limitations of the amine systems (a low surface area and absent of any mixing), the sample pan does however allow for a uniquely defined surface which may be used to determine mass transfer coefficient, as performed in a later section.

Humidity impacts on MEA equilibrium

To observe the impact of humidity on sorption capacity of the MEA primary amine, DVS measurements were made between 0-50% CO_2, at different humidity values (0, 10, 20, 40 %RH). From previous water sorption experiments, Figure 2, at humidity levels between 0-50 %RH water loading in the MEA should be somewhat equal to that of MDEA. Figure 5, below, shows the sorption isotherms.

As shown in Figure 5a, the introduction of humidity does not appear to significantly impact the uptake capacity of CO_2 in MEA. This uptake behaviour is expected as the primary reaction mechanism, shown in Figure 4, between CO_2 and primary amines does not involve any water interactions, instead reacting with CO_2 directly and 2 mol of amine being responsible for the uptake of 1 mol CO_2 as a carbamate, leading to a 0.5 mol CO_2/amine maximum stoichiometric limit.

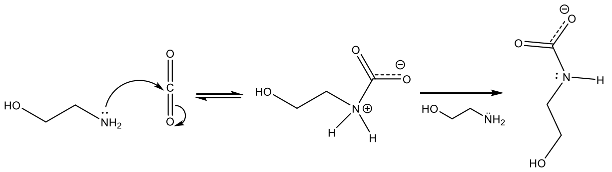

Figure 4. The primary reaction pathway for CO_2 and MEA

Interestingly, when zooming into the low partial pressure region of the isotherms, Figure 5b, the majority of the uptake occurs between 0-1 %CO_2 indicating very strong interactions between amine and CO_2, with humidity responsible for a small but distinguishable increase in capacity at these low concentrations.

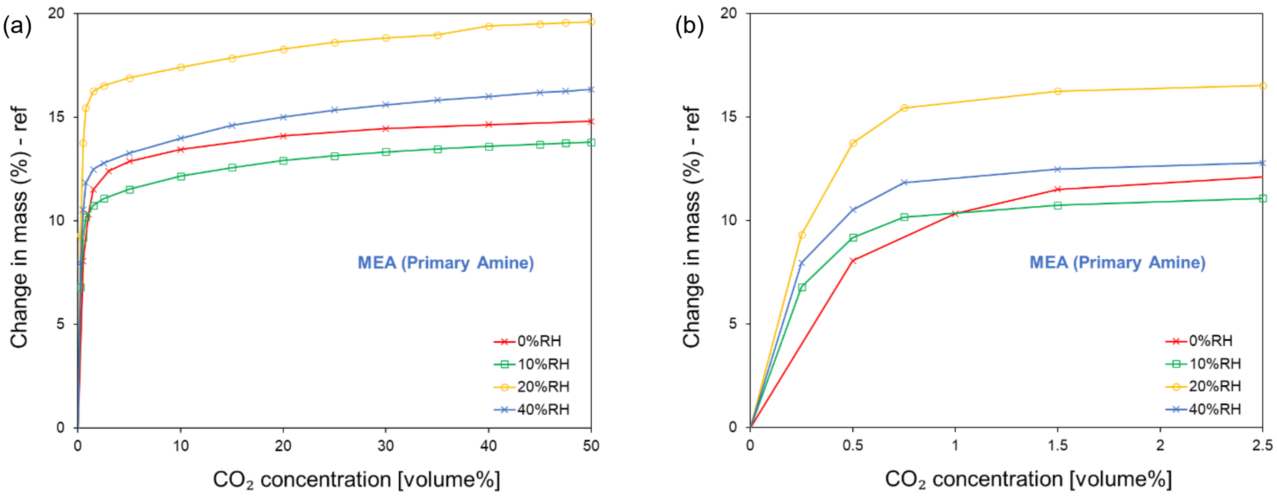

Figure 5. (a) DVS measurements of CO_2 uptake isotherms (25 °C) in MEA with increasing humidity (b) low partial pressures

Humidity impact on MDEA equilibrium

The same DVS experiments as those undertaken for MEA were carried on MDEA. It was expected that the effects of humidity would be significant for the tertiary amine, given that the primary reaction pathway for the sorption of CO_2 by MDEA is facilitated by the presence of water, shown below in Figure 6.

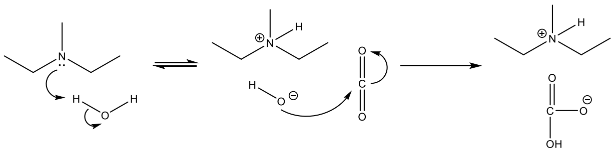

Figure 6. The primary reaction pathway for CO_2 and MDEA

As shown in Figure 7, the presence of increasing humidity does increase the CO_2 uptake capacity considerably, up to three times that of the dry capacity or up to a molar ratio of 0.5. This 3x increase can be explained as a contribution of two factors, the change in reaction pathway in the presence of humidity and the creation of a less viscous boundary which aids the penetration of CO2 into the bed.

Shown below in Table 1 is the water loading in MDEA at equilibrium under each relative humidity.

Table 1: Water loading in MDEA at equilibrium when exposed to % relative humidity

% Relative Humidity	Water loading in MDEA (%mass)
10	2
20	6
40	11

As shown in Table 1, the water loading in MDEA is linear with respect to the exposure %RH associated to a proportional increase of CO_2 uptake over the increasing exposure humidity.

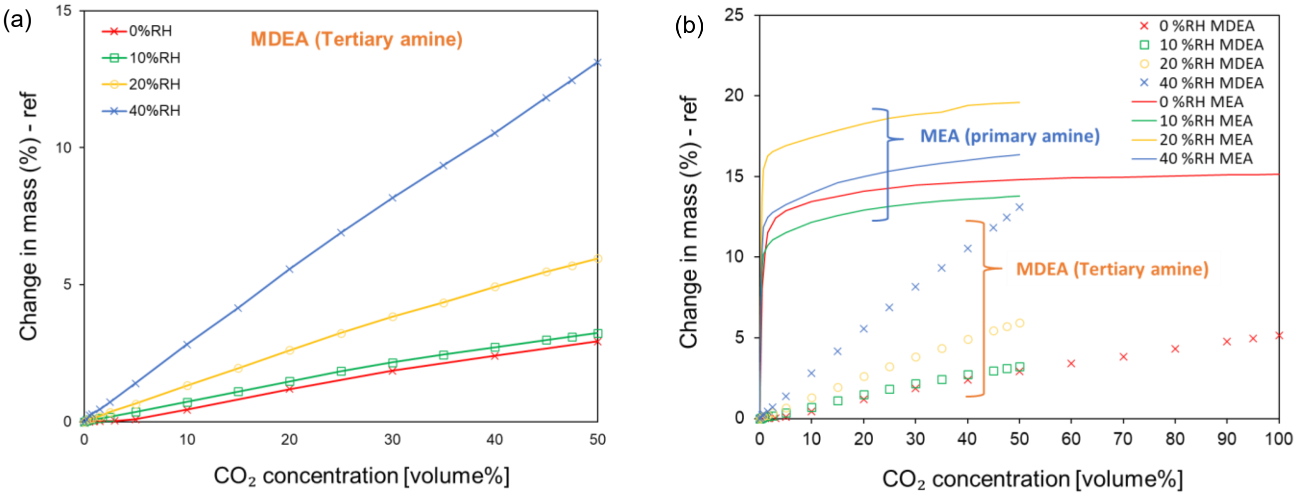

Figure 7. (a) DVS measurements of CO_2 uptake isotherms in MDEA with increasing humidity, 25 °C (b) comparison with MEA

Kinetic considerations

The time resolved data from the humidity and CO_2 uptake experiments on MEA and MDEA are highlighted below in Figure 8.

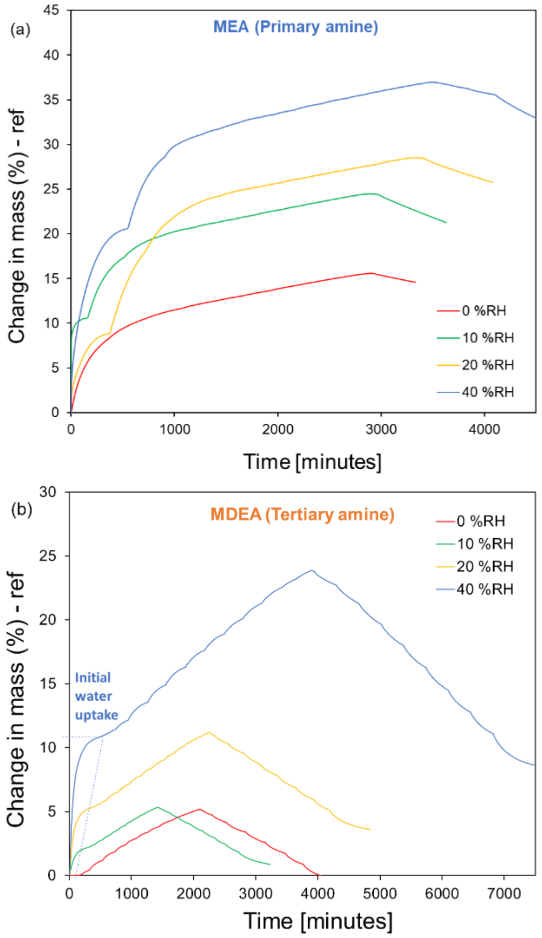

Figure 8. DVS measurements of CO_2 uptake isotherms (25 °C) in (a) MEA and (b) MDEA

Mass transfer coefficients, calculated from two-film theory, were determined from the humidity/CO_2 sorption experiments. The results are shown below in Figure 9 for (a) MEA and (b) MDEA, respectively.

For MEA, after the initial water uptake step, the overall uptake kinetics of CO_2 are not at first glance influenced by the presence of increasing humidity. However, after performing mass transfer calculations we can see that the presence of humidity does slightly increase the kinetics. This effect appears to be irrespective of the humidity level but clearly related to its presence.

From Figure 9, there is a clear positive relationship between CO_2 partial pressure and the mass transfer, both under humid and dry conditions. This is expected as a higher partial pressure increases the driving force. The effect of humidity is also positive, with humidity increasing the mass transfer coefficient regardless of the %RH. The rate of reaction in MEA is much higher than with MDEA, meaning the process remains concentration driven even at higher humidity.

For MDEA, it should be highlighted that the introduction of humidity does appear to have a significant effect on the kinetics, with the kinetics increasing from 0-10 %RH and then decreasing with %RH between 10-40%RH. This same trend is also observable by the mass transfer coefficients, displayed in Figure 9.

The mass transfer coefficient pattern is less clear. As discussed previously, the introduction of a small amount of humidity seems to have a beneficial effect on the mass transfer, whereas higher humidity seems to have a lowering effect.

This is somewhat surprising, considering that water should aid the kinetics of the reaction pathways. However, in this experimental set-up, absent of any sample mixing it is likely that humidity absorbed by the solvent would be disproportionately held at the gas-liquid interface. This build-up of water will mean that although the reactivity may be increased, the MDEA is diluted lowering solubility and the driving force via a loss of partial pressure gradient (less CO_2 being removed from the interface via absorption). This is confirmed via the mass transfer plots, which shows the loss of CO_2 partial pressure dependence on mass transfer with increasing humidity.

The loss of the significant CO2 partial pressure relationship with the mass transfer coefficient is an interesting observation and suggests that under these conditions the system moves from a concentration driven process to one limited by diffusion through the boundary layer, due to a build-up of water or a switching of reaction mechanism.

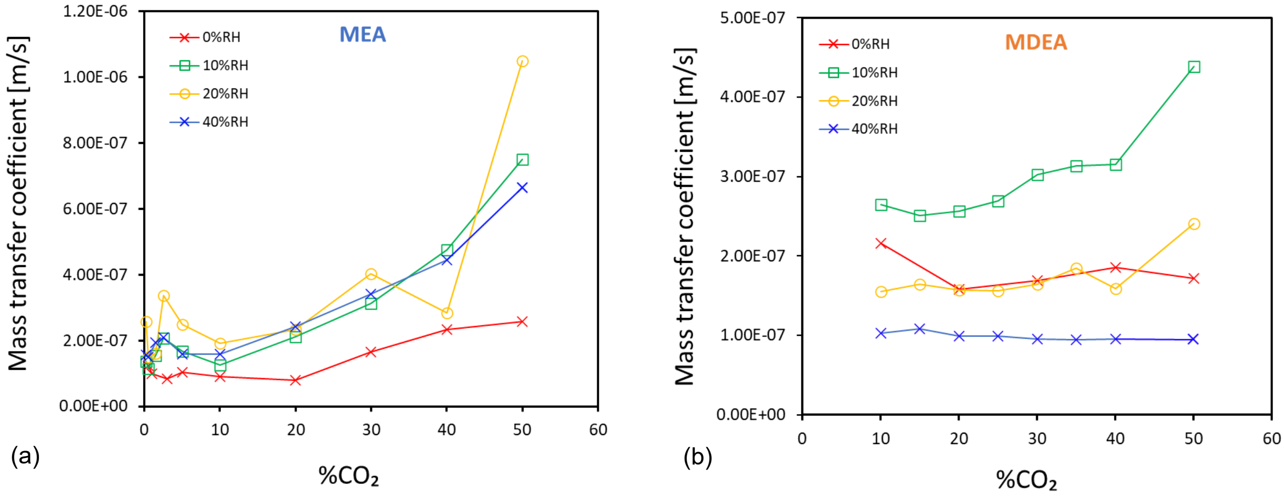

Figure 9. Two-film theory measurements of CO_2 mass transfer coefficients in (a) MEA and (b) MDEA

Conclusion

The DVS Carbon has been demonstrated to be a useful tool in probing the sorption kinetics of CO_2 in liquid amines of lower volatility. Investigations were made into the effects of humidity on primary and tertiary amines, MEA and MDEA. Under dry conditions MEA displays much larger CO_2 uptake than MDEA, three times higher, likely due to the equilibrium-based DVS measurements and the low reaction rate between MDEA and CO_2.

Humidity appears to have a small positive effect of the sorption of CO_2 in MEA, but a more noticeable effect on the mass transfer kinetics, with water loading aiding CO_2 uptake at lower partial pressures.

Conversely, humidity appears to have a limiting effect on the mass transfer between CO_2 and MDEA. At low humidity the mass transfer increases due to an increase in reactivity, however increasing the humidity contributes to increased boundary layer effects. These boundary layer effects appear to result in a shift to a diffusion limited mass transfer, with a loss of CO_2 partial pressure dependency on the mass transfer.

Humidity does increase the CO_2 capacity of MDEA by enabling more bicarbonate reaction pathways, with a 3x increase in the uptake and possible conversion when compared to the 10% conversion under dry conditions.

References

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