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## Activity-based Kinetics of the Reaction of Carbon Dioxide with Aqueous Amine Systems. Case studies: MAPA and MEA

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### Abstract

The kinetics of CO<sub>2</sub> reacting monoethanolamine (MEA) and 3-(methylamino)propylamine (MAPA) solutions are studied by conducting absorption rate experiments in two different apparatuses: a wetted wall column and a string of discs column. It is shown that the apparatuses give comparable results.

The results are modeled using the direct kinetic mechanism with activity-based rate expressions, and good representation is obtained.

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### 1. Introduction

The kinetics of CO<sub>2</sub> reacting in amine and caustic solutions have been widely studied by conducting absorption rate experiments. Versteeg *et al.* [1] and Aboudheir *et al.* [2] present comprehensive literature reviews concerning alkanolamines as solvents.

Two reaction mechanism models are normally used to describe CO<sub>2</sub> reactions with amines: the zwitterion formation and the direct (or termolecular) mechanism [3, 4]. Depending on the assumptions made, both mechanisms will lead to the same rate expression for CO<sub>2</sub> absorption, and can be used

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indistinguishably. However, the results obtained by applying these models in their original concentration-based form do not seem to be able to catch the variations of the kinetic constants with the concentration of the solution.

Haubrock *et al.* [5] and Knuutila *et al.* [6] show that modifying the rate models so that activities of the species are taken into consideration (and not their concentrations) can lead to better representations respectively on caustic and carbonate solutions. This modification is made to take into account the strong non-ideality of the reaction mixtures. Also, Dugas and Rochelle [7] apply direct kinetics with activity-based rate expressions to model mass transfer experiments of CO<sub>2</sub> into monoethanolamine (MEA) and piperazine (PZ).

In this work, CO<sub>2</sub> reaction rates in monoethanolamine (MEA) and 3-(methylamino)propylamine (MAPA) are represented using the direct mechanism kinetics with activity-based rate expressions. Experimental data are generated using both a wetted wall column and a string of discs contactor.

It is interesting to notice that activity-based rate models are being successfully applied for modeling reactions other than CO<sub>2</sub> absorption, such as the esterification of 1-butanol with acetic acid [8] and the enzymatic production of decyl acetate [9].

## 2. Experimental Apparatus and Procedure

The reactive absorption studies were conducted in two different apparatuses. MEA absorption experiments were conducted both in a wetted wall column (WWC) and in a string of discs contactor (SDC), while MAPA experiments were done only in the SDC. The WWC was described by Luo *et al.* [10] while the SDC was described by Ma'mun *et al.* [11] and Knuutila *et al.* [12] among others.

In both apparatuses, a gas stream (mixture of N<sub>2</sub> and CO<sub>2</sub>) and an aqueous amine solution flow in countercurrent mode. The apparatuses are instrumented so that it is possible to calculate a mass balance for CO<sub>2</sub> over the apparatus and thereby determine the rate of absorption. The main difference between the apparatuses is the mass transfer area, which is 2.19\*10<sup>-2</sup> m<sup>2</sup> in the SDC and 1.69\*10<sup>-3</sup> m<sup>2</sup> in the WWC. The smaller contact area makes the WWC column unfeasible for studying the kinetics of slow systems. As both amines considered in this study are relatively fast (MEA is a primary amine, MAPA has one primary and one secondary group), it is possible to use both apparatuses to evaluate all solutions.

MAPA unloaded solutions with concentrations of 1M, 2M, 3M, 4M and 5M were tested. MEA experiments were conducted with 5M solutions, with loading varying from 0 to 0.5. The reactions were performed within the temperature range of 25°C to 60°C.

## 3. Mass transfer modeling

The CO<sub>2</sub> absorption flux ( $N_{CO_2}$ ) is determined experimentally. Using a mass transfer model, as the two-film theory or the penetration theory, the CO<sub>2</sub> absorption flux can be correlated with the mass transfer parameters. The correlation obtained by using the two film theory is shown in equation 1. The

experiments are carried out in the pseudo-first order regime so that the enhancement factor is equal to the Hatta number.

$$N_{CO_2} a = \frac{P_{CO_2}}{\frac{1}{ak_G} + \frac{H_{CO_2}}{Eak_L^0}} = \frac{P_{CO_2}}{ak_G + a\sqrt{k_{obs}D_{CO_2}}} \tag{1}$$

Here  $k_{obs}$  is the observed pseudo-first order kinetic constant. Since all other quantities on the right-hand side of equation 1 can be assessed experimentally, this equation can be solved for  $k_{obs}$ . Under the reaction conditions prevailing in our experiments the concentration of OH<sup>-</sup> is very small, so the effect of hydroxyl ions within the observed pseudo-first order kinetic constant is negligible. The reaction rate of CO<sub>2</sub> is commonly described by the simple expression in equation 2. This is called the concentration based model. If the concentrations are replaced by the activities of the components, then we have the activity based model. In equation 3, the activities are represented as the product of the concentration by the activity coefficients. In this equation,  $k_{obs}$  and  $k_2$  are represented with a superscript  $\gamma$ , to indicate that they were obtained by using the activity based model.

$$-r_{CO_2} = k_{obs} [CO_2] = k_2 [Am][CO_2] \tag{2}$$

$$-r_{CO_2} = k_{obs}^\gamma [CO_2]\gamma_{CO_2} = k_2^\gamma [Am]\gamma_{Am} [CO_2]\gamma_{CO_2} \tag{3}$$

A direct mechanism scheme for carbamate formation is shown in Figure 1. According to this mechanism the forward reaction rate model in its activity form can be described by equation 4.

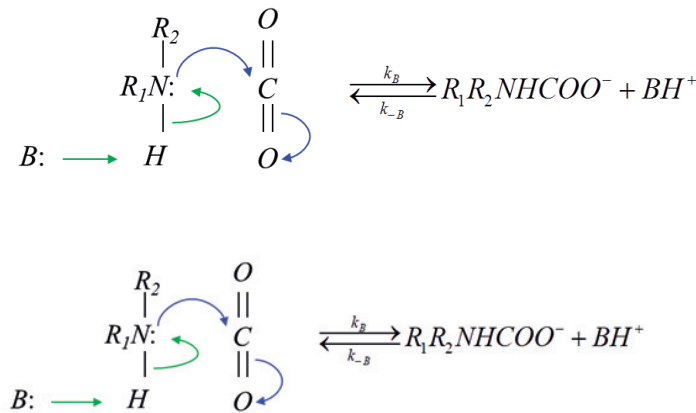


Figure 1 – Direct mechanism scheme

$$-r_{CO_2} = \left( \sum_{bases} k_B [B] \gamma_B \right) [Am] \gamma_{Am} [CO_2] \gamma_{CO_2} \quad (4)$$

For all the experiments addressed in this work, it is reasonable to consider that water and the amine itself are the only bases present in significant concentrations in the systems. Hence, the rate expression simplifies to the one presented in equation 5.

$$-r_{CO_2} = ([Am] \gamma_{Am} + [H_2O] \gamma_{H_2O}) [Am] \gamma_{Am} [CO_2] \gamma_{CO_2} \quad (5)$$

Comparing equation 5 to equation 3, the expressions for the observed pseudo-first order and the second order kinetic constants are obtained as:

$$k_{obs}^\gamma = ([Am] \gamma_{Am} + [H_2O] \gamma_{H_2O}) [Am] \gamma_{Am} \gamma_{CO_2} \quad (5a)$$

$$k_2^\gamma = ([Am] \gamma_{Am} + [H_2O] \gamma_{H_2O}) \gamma_{Am} \gamma_{CO_2} \quad (5b)$$

When the reaction rate and the system physical properties are known, and a thermodynamic model (extended UNIQUAC or electrolyte NRTL) is available to evaluate the concentrations and activity coefficients, the kinetic and mass transfer coefficients can be determined.

#### 4. Results and discussion

The modeled second order kinetic constant for the MAPA system is in good agreement with the values experimentally determined, as can be seen in Figure 2. Data for 1M, 2M, 3M and 4M MAPA solutions are well represented by the proposed correlations. However, for 5M MAPA, either the representation is not very good or there are two outliers.

When using a concentration based model, the obtained average absolute relative deviation (AARD) was 23%. However, by introducing the activity-based model, the AARD was reduced to 10%, which is within the experimental uncertainty. This gives an indication that treating the non-idealities of the system leads to improved results.

It is important to stress that the activity coefficients were fitted using the e-NRTL model against available vapor-liquid equilibrium (VLE) and CO<sub>2</sub> solubility data. While the VLE data are completely independent from the kinetic results, the CO<sub>2</sub> solubility data are used (in the form of Henry's law coefficient) when applying equation 1. As long as the modeling assumptions are correct and data used consistent, improved representation is expected because the modified model takes into account the non-idealities of the systems.

All the MAPA systems tested within this work were thermodynamically modeled as unloaded systems (regarding the systems properties models). It should be noted that while running the experiments, CO<sub>2</sub> reacts with the amine and thus some loading occurs. The effect of the loading on the system properties

was neglected, since the maximum loading achieved during the experiments was of the order 0.01 mol CO<sub>2</sub>/mol MAPA for the experiment with 5M MAPA solution at 60°C.

Since MAPA is a diamine with one primary and one secondary group, it actually forms two distinct carbamates when reacting with CO<sub>2</sub>. Hence, the carbamate formation reaction measured in the experiments is actually the lumped sum of the two carbamate reactions taking place in the system. With the current set-up, it is not possible to distinguish between them. However, since there is one primary and one secondary amine group in MAPA, and as the final loadings achieved during the experiments always

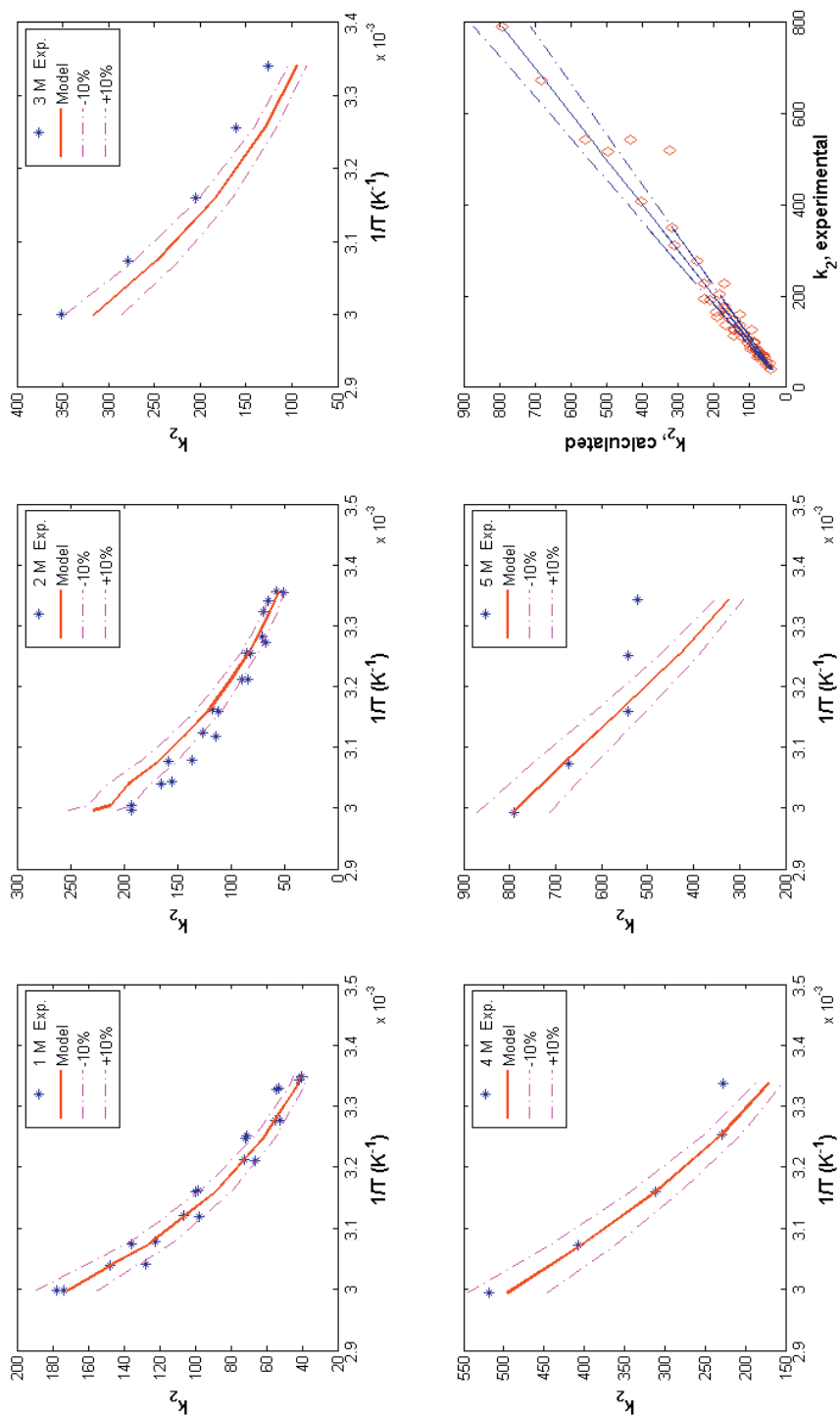


Figure 2 – Model and experimental values for the second order kinetic constant of formation of MAPA carbamate, in  $\text{m}^3\text{mol}^{-1}\text{s}^{-1}$

were lower than 0.01 mol CO<sub>2</sub>/mol MAPA, it is believed that the kinetic results are more representative of the primary amine group reaction.

For the MEA system, the representation is generally good, as can be seen in Figure 3. The results for experiments conducted in the string of discs and in the wetted wall column are in good agreement with each other. Unlike for the MAPA system, the activity-based rate model was found not to have any clear advantage over the concentration-based model. The deviations were an AARD = 27% for the concentration based model and an AARD = 23% for the activity based model. Unfortunately, when using loaded solutions in the experiments, the higher experimental uncertainties lead to scatter in the data that is so significant that the corrections for the non-idealities only gives a marginal improvement. It is still believed that using an activity based model is an advantage.

The concentrations and activity coefficients were obtained from the e-UNIQUAC model presented by [13].

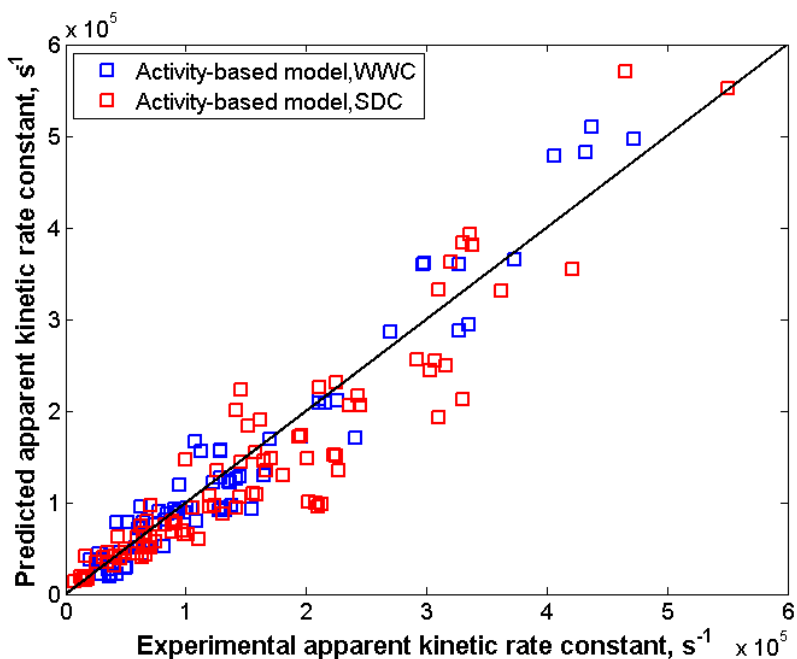


Figure 3 – Parity plot for the observed kinetic constant of formation of MEA carbamate

## 5. Conclusions

Kinetics of CO<sub>2</sub> reacting with monoethanolamine (MEA) and 3-(methylamino)propylamine (MAPA) solutions were studied by conducting absorption rate experiments in two different apparatuses: a wetted wall column and a string of discs column. It is shown that the apparatuses give comparable results.

The results were modeled using the direct kinetic mechanism with activity-based rate expressions, and good representation is obtained. For the reaction of CO<sub>2</sub> into unloaded MAPA a clear improvement was found when converting from concentration based to activity based kinetics. For the test with CO<sub>2</sub>-loaded MEA the data scatter hides any clear advantage of activity based kinetics.

## Acknowledgements

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