Speciation and Kinetics of CO₂ Uptake in Aqueous Amine Solutions

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An understanding of CO₂ uptake in aqueous amine systems has been essential to the maturity of post-combustion capture (PCC) as a technology ready for large-scale deployment. However, there remains a lack of a fundamental understanding of the reaction mechanism, rate expressions, and speciation during the reaction itself. This knowledge will not only inform but also improve the process operations designed to maximize efficiency and financial returns. To achieve this, a rigorous experimental approach with theoretical underpinnings must be used to achieve a complete understanding of the reaction kinetics and rate constants. This study is focused on doing this whilst addressing the impact of mass transfer and kinetic limitations on the CO₂-amine reaction.

Aqueous solutions (750 mL) of 30 mass% amine, (e.g. monoethanolamine (MEA) ≥99 wt% Sigma-Aldrich) were tested in a 1 L stirred and jacketed reactor, where a circulating bath provided temperature control. Pure CO₂ gas was bubbled at 1 bar through initially-degassed solutions at flow rates of 250 or 990 mL min⁻¹ (±10 mL min⁻¹), referred to as lower and higher respectively. The experiments were conducted across a relevant range of absorber temperatures: 25, 40, and 55 °C (±1 °C). Solutions were tested with and without stirring. During the CO₂ uptake process, the gas outlet flow rate, pH, and temperature of the solution were monitored; small (< 1 mL) samples were taken at regular intervals for ¹³C NMR analysis. Theoretical calculations [1] were used in analysis of the NMR data collected to distinguish between carbonate and bicarbonate species.

The impact of key variables, CO₂ gas flow rate and temperature, is demonstrated (Error! Reference source not found.a). All solutions reach equilibrium at approximately pH = 7.8. For MEA, the role of temperature has a limited impact on the pH change; in contrast, the CO₂ gas flow
rate is significant. At the higher flow rate, the MEA solution reaches saturation faster (and therefore has a higher rate of reaction) than at the lower flow rate investigated.

When the variable of time is non-dimensionalized (with the time $t_{sat}$ required to reach saturation), the influence of CO$_2$ gas flow rate is strongly evident (Figure 1b). For the higher flowrate tested, a sharp decrease in pH is observed and saturation is reached relatively quickly. By contrast, at a lower CO$_2$ flow rate there are three distinct regions apparent before reaching saturation. An initial, and brief, sharp decrease in pH, similar to that for the high flow rate, is observed. However, when a critical pH is reached, the rate of pH change slows demonstrably. This second region ends at a second critical pH (9.08 at 40 °C), after which the rate of pH change decreases more sharply again. Only the first two regions can be explained by the CO$_2$ capture reactions traditionally attributed to primary amines (i.e. zwitterion or termolecular) [2].

To understand the three pH regions, the solution composition was examined using aliquots taken for analysis with $^{13}$C NMR (an example is shown in Figure 3 for the case of 250 mL min$^{-1}$ and 40 °C). The concentration of MEA decreases non-linearly with time and the formation of carbamate results in an apparent non-linear increase in concentration. These behaviours are generally consistent with the theoretical predictions where the rate law is first order in amine concentration:

$$r = \frac{k_1[CO_2][RNH_2]}{1 + \frac{k_{-1}}{k_B}[B]}$$  \hspace{1cm} (1)

However, the formation of carbonate and bicarbonate products is not predicted by the mechanism, nor addressed by the rate expression in the first instance.

Figure 2: Speciation diagram for 30 mass% aqueous MEA solution loaded at 40 °C with a 250 mL min$^{-1}$ flow rate of CO$_2$.

Experimental measurements: (●) MEA, (●) MEAH$^+$, (■) carbamate, (▲) bicarbonate, (♦) carbonate; Theoretical predictions: (----) MEA, (-----) carbamate, (……) bicarbonate. pH (◊) is on the secondary axis.

The presence of carbonate and bicarbonate is only observed towards the completion of the experiment, when saturation of the solution has occurred. The formation of these species is hypothesized to occur from the hydrolysis of CO$_2$, where the formation of carbonic acid will, in turn, form bicarbonate in equilibrium (Equation 2). The rate of this reaction is far slower than that of the reaction between CO$_2$ and a primary amine. As such, this reaction only becomes favourable when a large proportion of the amine species are already reacted with CO$_2$ (i.e. high CO$_2$ loading in solution), which is indicated by reaching the second critical pH value. The theoretical predictions for this
mechanism match well to the experimental data collected (Figure 2). The subsequently sharp decrease in pH is due to the proton product forming from the same reaction.

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CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-
\] (2)

The critical pH at which the additional reaction is observed is suggested to be defined with respect to the pK\textsubscript{a} of MEA. This is predicated on the understanding that [MEAH\textsuperscript{+}] cannot react with CO\textsubscript{2}. As such, when the pH drops below the pK\textsubscript{a}, the greater concentration of [MEAH\textsuperscript{+}] than [MEA] results in increased favourability for the hydrolysis of CO\textsubscript{2}. The experimentally determined pH values of the critical point (for all the three temperatures tested) are closely aligned with the pK\textsubscript{a} values from a peer-reviewed publication [3]. This finding highlights that there is a continued need to address the variables which are influencing not only the mechanism of CO\textsubscript{2} uptake but also the reaction rate measured.