Mass Transfer Kinetics of CO\textsubscript{2} in Loaded Aqueous Monoethanolamine Solutions

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ABSTRACT
Carbon Capture and Storage (CCS) is identified as the most promising mitigation technology. Monoethanolamine (MEA) is the most studied absorbent with extensive data available, and it hence a convenient absorbent to use for various studies. Conclusions drawn are likely to be relevant also for other amine solutions. The kinetic mass transfer of CO\textsubscript{2} absorption in MEA solutions were investigated using a stirred cell as known from Danckwerts\textsuperscript{1} and Eimer,\textsuperscript{2} and details of this version have been previously published.\textsuperscript{3} Very few part data for reaction rates in partially loaded solutions has been found in the literature. Hence the present effort.
The kinetic mass transfer were collected on absorption experiments in the temperature range 303.15 – 313.15 K, MEA concentrations 3 M and 5 M, and a partial loading range 0.05-0.30 mol CO\textsubscript{2}/mol MEA (\(\alpha\)). To satisfy the criterion of pseudo first order reaction, low CO\textsubscript{2} partial pressure (3 - 5 kPa) was used, and a very low inert gas and solution vapor pressures (i.e. 3 kPa at 298 K) were kept to avoid significant gas phase resistance. The mass transfer flux (\(N_A\)) could be estimated by:
\[
N_A = \frac{dn_A}{dt} = \frac{1}{1/k_G + H_A/Ek_L} A(P_A - P_A^e) \tag{1}
\]
where \(P_A^e\) is the equilibrium pressure corresponding to the CO\textsubscript{2} absorbed in liquid bulk and this is not zero in the present case. However, due to the measurement being conducted over a very short time (30 s), the CO\textsubscript{2} concentration in liquid bulk can be assumed to be constant throughout any one experiment. \(E\) is the enhancement factor, \(k_G\) and \(k_L\) are the gas and liquid phase mass transfer constants, and \(1/k_G + H_A/Ek_L\) is the inverse of the overall mass transfer constant. According to the principle of conservation of mass it follows that
\[
-\frac{dP_A}{dt} = \left[\frac{RAT}{V_G(1/k_G + H_A/\sqrt{k_2C_{MEA}D_{CO2}})}\right] (P_A - P_A^e) \tag{2}
\]
By plotting (-\(dP_A/dt\)) vs. \((P_A-P_A^e)\) from equation (2) and neglecting the gas side mass transfer resistance, the slope, \(b\), becomes
\[
b = \frac{RAT \sqrt{k_2C_{MEA}D_{CO2}}}{V_GH_A} \tag{3}
\]
The pseudo first order reaction rate constant, \(k_{ps}\), is defined by equation (4), and shows its dependence on the concentration of free amine that will vary with the CO\textsubscript{2} loading.
\[
k_{ps} = k_2C_{MEA} = \left(\frac{bH_AV_G}{RAT}\right)^2 \left(D_{CO2}\right)^{-1} \tag{4}
\]
The derived $k_{ps}$ decreases with increased CO$_2$ loadings in the solvent and increases with increased temperature. Since the values of gas solubility, viscosity, diffusivity and density of the absorbent solution change when the loading changes, the calculation of the kinetic rate constant, $k_2$, should take this into account.

When pseudo first order reaction is a good approximation, $E = Ha$, and the rate of absorption is then proportional to $Ha$.

$$\frac{Ha^2}{k^2} = \frac{k_2C_{MEA}D_{CO_2}}{k_L^2} = \frac{(k_2C_{MEA}C_{CO_2}^0)\delta_j A}{k_L^2C_{CO_2}^0A} = \left(\frac{\text{max. chemical conversion rate}}{\text{max. diffusional mass transfer rate}}\right)_{\text{in liquid film}}$$

(5)

Then, $Ha/Ha^0$ ($Ha^0$ being the value at zero loading) can describe the trend of the CO$_2$ absorption with various loadings in the solution

$$\frac{Ha}{Ha^0} = \sqrt{\frac{C_{MEA}}{C_{MEA}^0}} = \sqrt{1 - 2\alpha}$$

(6)

Where $C_{MEA}^0$ is the amine concentration without CO$_2$ loading. It can be seen from figure 1 that the absorption rate goes down when the loading increases. Figure 2 shows that the 2nd order reaction rate constant for the reaction between CO$_2$ and MEA remains almost unaffected by the change in loading. This is as expected, but here confirmed by experiment.

![Fig. 1 Ha/Ha$^0$ vs. CO$_2$ loading](image1.png)

![Fig. 2 Reaction rate constant $k_2$ Vs. CO$_2$ loading for CO$_2$ + loaded 3M MEA.](image2.png)

**References**