An Equilibrium Study of Carbamate Formation Relevant to Post Combustion Capture of CO₂

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy at the School of Environmental and Life Sciences, Chemistry University of Newcastle by

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Author’s Declaration

I hereby certify that the work embodied in this thesis is the result of original research and has not been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due references has been made in the text.

Signature & Date

Debra Fernandes
Thesis by publication

Acknowledgement of Authorship

I hereby certify that this thesis is in a form of series of published papers of which I am the lead/co-author. I have included as part of the thesis a written statement from each co-author, endorsed by the Faculty of Science and Information Technology, Assistant Dean (Research Training), attesting to my contribution to the publications/scholarly work.

Signature & Date

Debra Fernandes
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Dedication

This thesis is dedicated to my family
Publications and Conferences resulting from my project


**Papers in preparation**

8) **Fernandes, D.,** Conway, W., Wang, X., Burns, R., Lawrance, G., Puxty, G., Maeder, M., *The activity of the diamine “piperazine” and the formation of carbamate(s) from the reaction(s) with CO$_2$(aq) in aqueous solution at 25.0 °C for post combustion capture processes.* **2012, (Draft in preparation).**


**Conference Oral-Presentations**

1) **Debra Fernandes** – Interaction of piperazine with CO$_2$(aq) in post combustion capture, *International Conference on Carbon Reduction Technologies*, Poland, September **2011.**

2) **Debra Fernandes** – Amine Protonation and Implications for the Selection of Amines for PCC Applications, *9th Post Combustion Capture Day*, CSIRO-Melbourne, December **2011.**
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<th>Definition</th>
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<tr>
<td>AMP</td>
<td>2-amino-2methyl-1-propanol</td>
</tr>
<tr>
<td>AHPD</td>
<td>2-amino-2-hydroxymethyl-1-3-propandiol</td>
</tr>
<tr>
<td>BIS</td>
<td>2-amino-1,3-propandiol</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
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<tr>
<td>CCS</td>
<td>Carbon capture and sequestration</td>
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<tr>
<td>CFC’s</td>
<td>Chlorofluorocarbons</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>Carbonic acid</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>Carbonate</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>GHG’s</td>
<td>Greenhouse gases</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Hydrogen carbonate/Bicarbonate</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
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<tr>
<td>MORP</td>
<td>Morpholine</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methyldiethanolamine</td>
</tr>
<tr>
<td>¹H NMR</td>
<td>Proton Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>PIPZ</td>
<td>Piperazine</td>
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<tr>
<td>PCC</td>
<td>Post-combustion capture</td>
</tr>
<tr>
<td>PIPD</td>
<td>Piperidine</td>
</tr>
<tr>
<td>PYRR</td>
<td>Pyrrolidine</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>pKa</td>
<td>Protonation constant</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethanolamine</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
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<tr>
<td>VLE</td>
<td>Vapour-liquid equilibrium</td>
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Abstract

The global community is currently facing a significant challenge in the form of climate change. The increasing emissions of greenhouse gases, especially carbon dioxide $\text{CO}_2$ is threatening the constitution of the Earth’s climate. This fosters the need for the removal of $\text{CO}_2$ from coal-fired power plants as it is the largest contributor to global $\text{CO}_2$ emissions.

One possible option for mitigating climate change is by $\text{CO}_2$ capture and sequestration (CCS), employing post-combustion capture of $\text{CO}_2$ (PCC). PCC is a mature technology for the capture of $\text{CO}_2$, as it is currently used in industry for gas-sweetening processes. The typical flue gas in power plants consists of about 80% $\text{N}_2$ and about 15% $\text{CO}_2$, with the remainder mainly unused $\text{O}_2$. For PCC purposes, separation of the two gases $\text{N}_2$ and $\text{CO}_2$ is important for compression, transportation and storage of $\text{CO}_2$. This can be achieved by reversible chemical absorption using amine-based solvents. Application of chemical absorption technology to power plants is not straightforward and poses several new challenges for chemists and chemical engineers, especially with the high cost associated with the process.

From a chemist’s point of view for PCC to be efficient the three main requirements are: 1) a fast reaction rate - this is the rate at which $\text{CO}_2$ interacts with the amine in aqueous solutions. For an ideal process the absorption of $\text{CO}_2$ has to be fast in order to minimise the size of the absorber column, 2) the stoichiometry of the amine-$\text{CO}_2$ interaction has to be 1:1 leading to a high loading capacity, and 3) the regeneration of the amine in the stripper column, the energy requirement of which is related to the protonation/deprotonation of the amine should be as low as possible, leading to a low cost and more efficient capture process.

A substantial number of studies on the interactions of amines and $\text{CO}_2$ have been published in the literature. However, most of the studies focus on the empirical functions but lack a mechanistic approach. As a consequence, the mechanism of the amine-$\text{CO}_2$ interaction is not clear. This thesis focuses on the molecular kinetics, the equilibria of carbamate formation in the reaction between amine and $\text{CO}_2$ in aqueous
solution, and the protonation constant of the amine. The amines investigated can be classified as primary, sterically-hindered primary, secondary, substituted-cyclic secondary and tertiary amines, with the aim of elucidating the possible effects of their chemical structures, electronic and steric effects, hydrogen bonding and substitution on the reaction rate of CO₂ absorption, carbamate stability and protonation/deprotonation of the amine.

As a result of this thesis we developed a complete reaction scheme in homogenous solution for the absorption of CO₂(aq) with H₂O/OH and amine. The reaction scheme is complicated and involves a number of kinetically observable reactions, defined by rate and equilibrium constants and protonation equilibria that are all coupled together. A detailed explanation of the scheme is given in all of the papers and also in the Introduction to this thesis.

The rate and equilibrium constants for a number of amines was investigated using stopped-flow spectrophotometry as this technique is capable of monitoring fast reactions occurring at the milliseconds time scale, while ¹H NMR spectroscopy was used to monitor slower reactions. Monoethanolamine (MEA) and ammonia (NH₃) were investigated from 15 °C to 45 °C, analysis of the rate and equilibrium constants in terms of the Arrhenius, Eyring, and van’t Hoff relationships gave the relevant thermodynamic parameters. For sterically-hindered amines, substituted cyclic amines and piperazine a Brønsted correlation relating the protonation constant of the amines to the carbamic acid formation rate and equilibrium constants at 25 °C were established. The resulting values are reported in this thesis (Papers 3, 4, 5, 7, 8 and 9).

A separate temperature dependence study of the equilibrium constant for the formation of carbamate and the protonation/deprotonation of the carbamate was undertaken using ¹H NMR spectroscopy. The outcome of the study was the determination of the equilibrium constants and thermodynamic parameters such as enthalpy, entropy and Gibbs free energy of reaction. A ΔHₘ°-ΔSₘ° plot generates a linear correlation for carbamate formation and this relationship helps provide a guide to the selection of an amine(s) solvent for CO₂ capture, in terms of enthalpy
considerations. A linear $\Delta H_m^\circ - \Delta S_m^\circ$ plot also occurs for carbamate protonation. All the relevant values are detailed in Papers 1 and 6.

The basicity of the amine is a very important characteristic in the absorption/desorption process; hence potentiometric titrations were used in the determination of the protonation constants of amines from 15 °C to 45 °C. The resulting protonation constants, enthalpies, entropies and Gibbs free energies are given in Paper 2. Also trends in $\Delta H_m^\circ$ are correlated with systematic changes in composition and structure of the selected series of amines/alkanolamines, while $\Delta H_m^\circ - \Delta S_m^\circ$ plots generated linear correlations for the mono-, di-, and trialkanolamines, the –CH$_2$OH and –CH$_2$CH$_2$OH substituted piperidines, and the alkylamines. These relationships provide a guide to the selection of an amine(s) solvent for CO$_2$ capture. Wherever possible, a comparison with the literature values for the kinetic, carbamate stability and the amine protonation are given in the papers.