Interactions of Sulfur(IV) Species with Aqueous Amine Solutions and their Impact on CO₂ Capture in the Post Combustion Capture Process

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M.Sc. (Chem.)

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

School of Environmental and Life Sciences
Discipline of Chemistry
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Dedication

To my family and my wife, Azadeh

For their endless love, support and encouragements
Acknowledgments

I would like to thank all people who have helped me throughout the years I spent at the University of Newcastle. My sincere gratitude goes to my supervisors Prof. Marcel Maeder, Dr. Robert Burns and Dr. Graeme Puxty for their continuous encouragement, invaluable assistance and guidance. I am grateful to them in believing in me and giving me the opportunity to pursue and develop my ideas. This study would not have been successful without their knowledge, advice and expertise.

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I wish to convey my sincere thanks to my family and my wife’s family for their faith, continuous support and motivation to succeed. However, the person who joined me somewhere in this journey and agreed to accompany me through all the ups and downs of my life, my soul mate Azadeh, is the person to whom I should say a very special “thank you”. I could not have done this without your continued love, support and patience!
**Declaration**

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

This thesis contains no material which has 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 reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968.

Yaser Beyad
Statement of Contribution

The work in this thesis is presented in the form of four original research publications. As a corresponding author in publications (1) and (3), and main author in publications (2) and (4), I, Yaser Beyad, was involved in the planning and conducting of all spectrophotometric titrations and $^1$H-NMR spectroscopic measurements, data analysis, and in the preparation of all manuscripts. The contribution made by the co-authors is attributed to the planning of and assistance in experiments, assistance in data interpretation, manuscript revision, and general support and guidance.

I, as a co-author, attest that Research Higher Degree candidate Yaser Beyad contributed to the publications as stated above.

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*Assistant Dean Research Training
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Notes on the structure and format of this thesis

This thesis is submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in the form of a series of publications. Chapter 1 provides an introduction to the subject of this thesis. Chapter 2 contains a summary of relevant results that have been reported in the literature. Chapters 3 to 6 consist of published or submitted for publication journal articles where the author of this thesis is the main and/or corresponding author. Additional publications where the author is a co-author are presented in Chapter 7. The experimental work and writing of all of the publications have been completed during the period of candidature. References for Chapters 1 and 2 are given at the end of this thesis.
List of publications included as part of this thesis


List of additional publications


Abstract

Carbon dioxide (CO₂) capture from flue gas using aqueous amine solutions is considered as one of the mature and most effective techniques among other carbon capture technologies. In addition to CO₂ and depending on the sulfur content of the fossil fuels, different amounts of SO₂ are present in flue gas resulting from the combustion of fuels in thermal power plants. Sulfur dioxide is known to interfere in CO₂ capture in the amine-based post combustion capture (PCC) process from flue gas. The focus of this project is to investigate the interactions of S(IV) species with aqueous amine solutions. The results of this study have been applied to the development of an amine-based PCC technique that is capable of capturing SO₂ in a single stream normally used to capture CO₂.

After a brief introduction (Chapter 1), a broad literature review is presented, which covers all of the reactions of S(IV) species in aqueous amine solution (Chapter 2). A comprehensive investigation of S(IV) speciation in aqueous solution over a wide range of pH was conducted by employing ultraviolet spectrophotometric titrations. As a result, the equilibrium constants of the reactions of S(IV) species in aqueous solutions were accurately determined. Further, an additional equilibrium in the solution, the protonation of disulfite, was identified and quantified for the first time. The molar absorption of S(IV) species have also been reported over the studied wavelength range (Chapter 3).

A problem was encountered in the data analysis step of the spectrophotometric titration study of S(IV) speciation in aqueous solution. Since high concentrations of sulfite were required to achieve a measurable amount of disulfite formation, the recorded absorbances at some wavelengths exceeded the linear absorption range of the instrument. All such data points were excluded from the analysis. Therefore, an innovative adaptation of the traditional linear regression method was developed in order to use all available information in the analysis while ignoring the missing values. The algorithm is based on the insight that multivariate linear regression can be formulated as a set of individual univariate linear regressions. All available information is used and the calculations are explicit (Chapter 4).
In another study the possible interaction of S(IV) species with monoethanolamine (MEA) in aqueous solutions at high temperature was investigated by following the $^1$H-NMR spectrum of the solution. The $^1$H-NMR spectra did not show any interaction between S(IV) species and the amine. As there is no direct interaction between SO$_2$ and MEA, the impact of increasing amounts of accumulated SO$_2$ on the cyclic capacity of the MEA solution in CO$_2$ capture was modelled. Moreover, the impact of similar conditions on the reaction rate of CO$_2$ absorption in the solution was simulated (Chapter 5).

Finally, based on the understanding of the physical and chemical properties of SO$_2$ absorption into aqueous amine solutions, an improved CO$_2$ capture process has been designed that uses a single solvent and is SO$_2$ tolerant. SO$_2$ absorption is carried out in the bottom of the absorber column into a bleed stream from the bulk solvent in which a recycle flow allows the absorbent to be near saturation in SO$_2$. Principles underlying the concept, specifically kinetic selectivity of SO$_2$ absorption over CO$_2$ and reactivity with amines, have been studied in the laboratory. There are clear advantages to a CO$_2$ capture process that is able to restrict the effects of SO$_2$ to only a fraction of the solvent with minimum disruption to the carbon capture process. In addition, the new design will result in reduced complexity and cost compared to existing options for SO$_2$ treatment (Chapter 6).
Overview

Sulfur dioxide is an environmentally important gas and a common air pollutant. As SO₂ is an acid gas, the immediate impact of its increasing concentration would be the acidification of the environment upon dissolution in air moisture and thus the formation of acid rain. Sulfur dioxide production worldwide from burning fossil fuels for electricity generation makes a significant contribution to the sulfur content of the atmosphere. Flue gas desulfurization (FGD) technologies have been developed to remove SO₂ from the exhaust flue gas of power plants. Carbon dioxide is another acid gas which is also produced in much larger scale in thermal power plants from burning fossil fuels. Variety of techniques has been developed to reduce carbon foot print from its main anthropogenic source. Among these techniques using aqueous amine solutions such as monoethanolamine (MEA) in a process called amine-based post combustion capture technology (PCC) is the most promising technology to capture CO₂ from flue gas in a reversible approach. As sulfur dioxide coexists with carbon dioxide in the flue gas, there would be significant advantages in being able to capture the two acidic components of the flue gas using an alkaline amine solution. This is of special importance for countries like Australia where power plants are not equipped with any FGD technologies.

In order to investigate the possibility of capturing CO₂ and SO₂ using a single amine as a solvent, initially a comprehensive study of S(IV) species in aqueous solution was carried out by ultraviolet spectrophotometric titrations. As a result of this study the equilibrium constants of S(IV) species in aqueous solution were accurately determined. The problem faced during data analysis as a result of the missing data (i.e. absorbance values) was addressed by developing an efficient algorithm for multivariate linear regression.

Then, the possible interactions of S(IV) species with aqueous amine solutions were examined by following the ¹H-NMR spectra of the mixture of sulfite solutions with MEA at different pH values and at relatively low and high temperatures. Qualitative ¹H-NMR spectroscopic studies did not show any evidence of reaction between S(IV) species and amine. However, at high temperature thermal degradation of MEA occurs as three peaks are observed, which may be attributed to the ammonium ion, and which exhibits increasing intensity with time. In addition,
the sulfur dioxide accumulation effect on the cyclic capacity of an MEA solution for CO₂ capture and also on the rate of CO₂ absorption in solution was modelled. The results from simulations indicated that equilibrium and kinetic effects on CO₂ capture due to the accumulation of SO₂ is small at low concentrations of sulfur dioxide (up to an MEA:SO₂ ratio of 17:1), while the effects become noticeable at higher concentrations of SO₂.

Finally, it has been demonstrated that knowledge of the physical and chemical properties of SO₂ absorption into aqueous amine solutions allows for the design of an improved CO₂ capture process that uses a single solvent and is SO₂ tolerant. Experiments (including ¹H-NMR studies of the reaction between SO₂ and MEA as well as wetted-wall column experiments of mass transfer of CO₂ and SO₂ in aqueous amine solution) and modelling have been used to show the kinetic selectivity for SO₂ absorption over CO₂. This has led to the design of a new configuration that allows both CO₂ and SO₂ removal from a gas stream using a single absorber column and a single aqueous amine absorbent. The key is to concentrate the absorbed SO₂ in a small fraction of the total solvent inventory of a CO₂ capture plant. This allows solvent reclamation to be carried out using a small liquid volume that is concentrated in SO₂, rather than a large liquid volume dilute in SO₂. This will result in reduced complexity and cost compared to existing options for SO₂ treatment.