

FINDING GREEN SOLVENTS FOR IMPROVED CO₂ CAPTURE

VIC VAN DIJK

1. PREFACE

The warming effects of the anthropogenic greenhouse effect urges society to decrease carbon dioxide (CO₂) levels in the atmosphere. This can partially be done by capturing carbon dioxide from flue gas streams, for example from a coal fired power plant. Research done by Van Dijk (2009) investigates an amino acid salt as new CO₂ absorbent. This bachelor research was carried out under enthusiastic guidance of Magdalena Majchrowicz, Wim Brilman and Michiel Groeneveld from research group “Thermo-Chemical Conversion of Biomass” (tccb.tnw.utwente.nl) of University of Twente (Enschede, The Netherlands).

2. INTRODUCTION

Typically, coal fired power plants exhaust flue gas which contains up to 15 kPa of carbon dioxide. Carbon dioxide can be absorbed by the chemical liquid inside contained by an absorption column, thus cleaning the flue gas before being released into the environment. The CO₂ loaded absorbent is regenerated in a stripping column, see Figure 2.1.

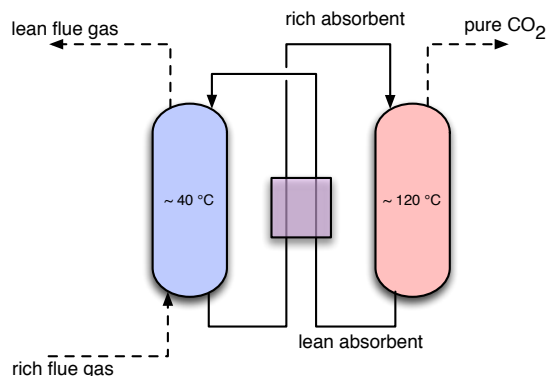


FIGURE 2.1. Carbon dioxide absorption/regeneration setup

Conventional carbon dioxide absorbents like for example monoethanolamine (MEA, see Figure 2.2) exhibit some major drawbacks. They are volatile (leading to solvent losses and emissions to the environment), tend to be corrosive, and susceptible to degradation by heat and oxygen.

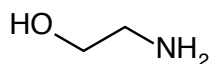


FIGURE 2.2. Monoethanolamine (MEA)

Research (e.g. Van Holst et al., 2009) shows that amino acid ions could be good alternatives for conventional CO₂ absorbents. Around twenty amino acids exist in nature; proteins are made of amino acids. Since every human, animal, plant etc. consists of amino acids these compounds are considered environmentally acceptable and are shown to be biodegradable. When an amino acid

is mixed with water and an equimolar amount of potassium hydroxide (KOH), an aqueous amino acid salt (AAS) is formed.

The amino acid ion of this salt solution can bind carbon dioxide through the amine functional group. Due to the ionic nature of the salt, the vapour pressure of the solvent is very low, and hence the evaporative losses are minimal. The oxidative and thermal stability of these compounds are also considerably better. A further interesting aspect is that these solvents can form precipitates (at higher loadings) which opens up new CO₂ capture and storage opportunities. However, the carbon dioxide absorption behaviour of this new class of solvents is not yet known. This research aims at the determination of the vapour-liquid equilibrium (VLE) of CO₂ in an aqueous amino acid salt solution. The development of a VLE-model is crucial for the evaluation of the solvent in a process applications and e.g. for predictions of the enthalpy effects involved.

3. THEORY

CO₂ loading α of a solution is defined by:

$$(3.1) \quad \alpha \equiv \frac{n_{\text{absorbed CO}_2}}{n_{\text{absorbent}}} = \frac{[\text{absorbed CO}_2]}{[\text{absorbent}]} \quad (-)$$

Aboudheir et al. (2003) have developed a concentration-based model which describes the vapour-liquid equilibrium of carbon dioxide in MEA quite well. The model consists of nine nonlinear equations comprising nine unknowns. An easier solving method than described by Aboudheir et al. (2003) was developed in this work, using a program written in Java. The physical solubility of carbon dioxide in the absorbent is one of the required input parameters to solve the model. That is, the solubility in the purely hypothetical situation the absorbent would not chemically react with any carbon dioxide. This cannot be determined directly, but a well-established estimation method (S. Weisenberger (1996)) was used. Basically, this method relates the solubility of CO₂ in plain water to the solubility in a solution of known (ionic) composition. Some ion-specific parameters (which require further evaluation) were assumed zero due to lack of experimental data.

4. EXPERIMENTAL SETUP

A stirred cell setup is used to determine VLE, see Figure 4.1. The setup is mainly operated in open, continuous mode; a N₂/CO₂ gas flow of known composition flows into the reactor and comes into contact with the absorbent solution. At the reactor outlet the carbon dioxide content of the gas flow is measured. When equilibrium has been reached (inflow matches outflow composition) liquid samples can be taken for further analysis.

Preloading of the absorbent in closed batch mode with carbon dioxide was used to shorten equilibration times in open continuous mode. The final concentration of absorbent and CO₂ are each determined by a titration method. Both titration methods were calibrated using samples of known concentrations.

5. EXPERIMENTAL RESULTS AND DISCUSSION

In order to validate the measurement technique and applicability of the VLE-model, the vapour-liquid equilibrium of MEA was measured at 25 °C and compared to literature data and model calculation results, see Figure 5.1.

For the aqueous amino acid salt, vapour-liquid equilibrium was determined at 25 °C, see Figure 5.2. The VLE-model developed for MEA was adapted for the case of the amino-acid salt solution. Only a few solubility coefficients and one reaction equilibrium constant (K_8) were unknown parameters in the new model. Therefore, model lines were plotted using the unaltered K_8 parameter (taken from MEA) and using a value fitted from shown experimental VLE data. For comparison, model lines of MEA are also included in the plot. It can clearly be noticed that the new solvent (data-points) shows improved absorption capacity (higher α value) when compared with the MEA reference solvent (thick lines).

Deviations of the experimental results from the vapour-liquid equilibrium model are thought to originate mainly from non-ideality and lack of some solubility parameters (which need further identification) and the equilibrium parameter K_8 . A quick regeneration experiment using CO₂



FIGURE 4.1. Photograph of the core of the stirred cell setup in continuous mode

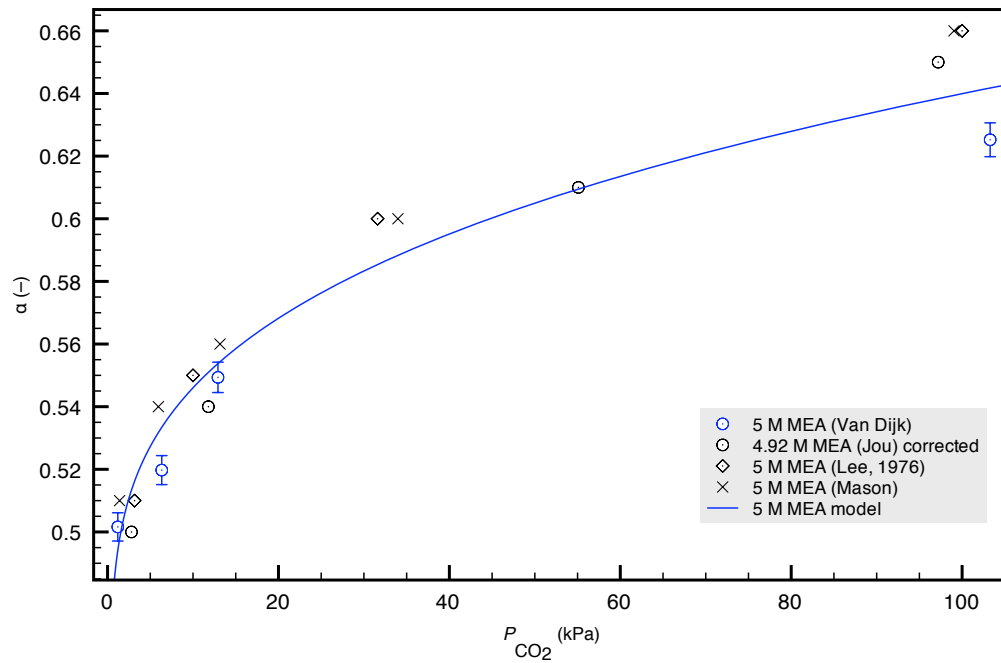


FIGURE 5.1. Results equilibrium loading experiments 30 wt% MEA, 298 K compared to literature and model data

loaded aqueous amino acid salt solution at elevated temperature was performed to make sure it is possible to reverse the absorption reaction.

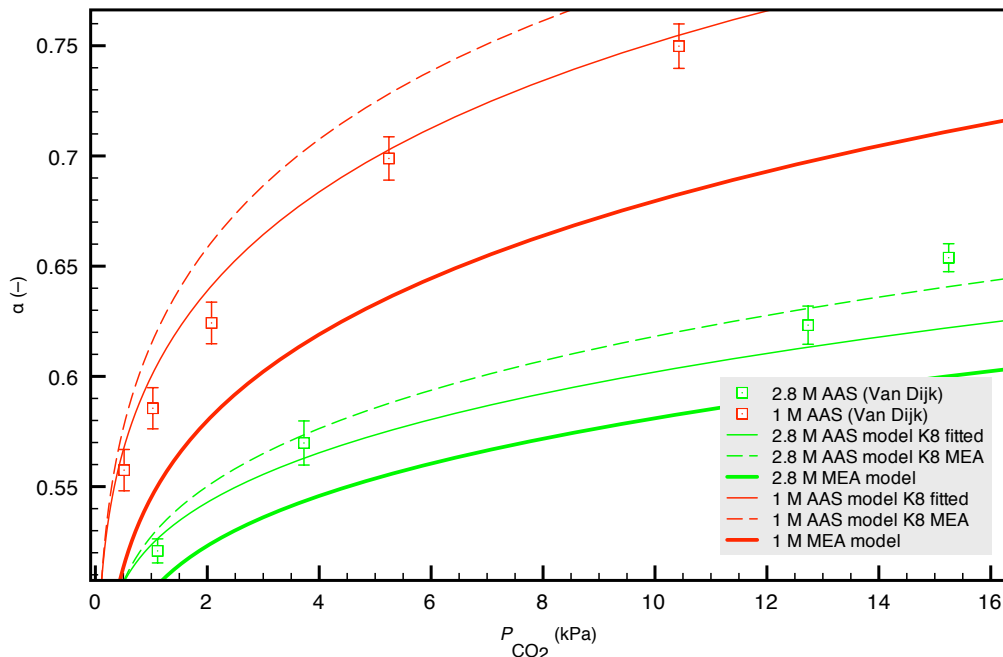


FIGURE 5.2. Plot of results for amino acid salt (AAS) at 298 K, 1 and 2.8 M and corresponding model lines for MEA at flue gas conditions

Using the Van 't Hoff relation

$$(5.1) \quad \ln K = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

the absorption enthalpies of CO_2 in aqueous MEA and amino acid salt were estimated for calculated data using the VLE model. The calculated enthalpies using the VLE-model for MEA are in good agreement with experimental data for MEA from Kim and Svendsen (2007) and McCann et al. (2008). Since the AAS experiments were performed at one temperature, the correctness of the VLE-model for the temperature effect must first be validated. Only after that reliable enthalpy predictions for AAS can be made.

6. CONCLUSIONS AND RECOMMENDATIONS

Developed VLE model represents experimentally determined VLE data for aqueous monoethanolamine, amino acid salt and CO_2 at 25 °C quite well. Model improvement comprises experimental determination of the currently missing equilibrium constant (K_8) and solubility parameters for AAS (e.g. using N_2O physical solubility experiments). Calculation of the heat of absorption using the VLE model and Van 't Hoff's relation is in good agreement with experimental enthalpy data for MEA, but for AAS more VLE-experiments at different temperatures are required.

The aqueous amino acid salt solution used in this work absorbs more carbon dioxide than aqueous monoethanolamine at flue gas conditions and 25 °C. The regeneration speed seems acceptable but again, more experimental work is needed. Used amino acid was selected from natural amino acids only. Thus, it would be interesting to estimate carbon dioxide absorption properties for other, synthetic amino acids and measure the VLE (as well as the reaction kinetics) for the most promising ones.

When the VLE model for AAS is completely verified (including absorption enthalpies) and kinetic data is available, a model for industrial application of AAS can be made. This could lead to less energy consuming applications of carbon dioxide capture from flue gases using absorption. Captured CO_2 could be used to feed algae or as growth enhancer in greenhouses, and thus re-enter the carbon cycle without contributing to the anthropogenic greenhouse effect.

7. LIST OF SYMBOLS

Symbol	Unit	Description
H	J mol ⁻¹	Enthalpy
K	<i>depends on reaction</i>	Reaction equilibrium constant
n	mol	Amount of substance
P	Pa	Pressure or partial pressure
R	J mol ⁻¹ K ⁻¹	Gas constant
S	J mol ⁻¹ K ⁻¹	Entropy
T	K	Temperature
α	–	Loading (Equation 3.1)
$\ $	mol L ⁻¹	Concentration of a compound

Subscript	Description
CO ₂	Carbon dioxide

Superscript	Description
∅	Standard conditions (most stable form of compound at 1 bar and 25 °C)

REFERENCES

- Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R., 2003. Kinetics of the reactive absorption of carbon dioxide in high co₂-loaded, concentrated aqueous monoethanolamine solutions. *Chemical Engineering Science* 58 (23-24), 5195–5210.
URL <http://dx.doi.org/10.1016/j.ces.2003.08.014>
- Kim, I., Svendsen, H., 2007. Heat of absorption of carbon dioxide (co₂) in monoethanolamine (mea) and 2-(aminoethyl)ethanolamine (aeea) solutions. *Industrial & Engineering Chemistry Research* 46 (17), 5803–5809.
URL <http://dx.doi.org/10.1021/ie0616489>
- McCann, N., Maeder, M., Attalla, M., 03 2008. Simulation of enthalpy and capacity of co₂ absorption by aqueous amine systems. *Industrial & Engineering Chemistry Research* 47 (6), 2002–2009.
URL <http://dx.doi.org/10.1021/ie070619a>
- S. Weisenberger, A. S., 1996. Estimation of gas solubilities in salt solutions at temperatures from 273 k to 363 k. *AIChE Journal* 42 (1), 298–300.
URL <http://dx.doi.org/10.1002/aic.690420130>
- van Dijk, V., January 2009. Vapour-liquid equilibrium of co₂ in an aqueous amino acid salt solution: a simple model including experimental verification.
- van Holst, J., Versteeg, G., Brilman, D., Hogendoorn, J., 2009. Kinetic study of co₂ with various amino acid salts in aqueous solution. *Chemical Engineering Science* 64 (1), 59 – 68.
URL <http://dx.doi.org/10.1016/j.ces.2008.09.015>