Speciation modelling of the CO₂-H₂O-alkanolamine system for single amines and their blends

Klaus-J. Jens¹,*, John A. Svendsen¹, Ida M. Bernhardsen³, Zulkifli Idris², M.H.W.N. Jinadasa¹, C. Perinu¹

¹Department of Process, Energy and Environmental Technology, University College of Southeast Norway, Postbox 235, NO-3603 Kongsberg, Norway

²SINTEF Tel-Tek, SINTEF Industri, Kjølnes Ring 30, 3918 Porsgrunn, Norway

³Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

*Corresponding author: Klaus.J.Jens@usn.no

Abstract

The gas-liquid absorption process for post combustion capture (PCC) and industrial point source CO₂ capture is one of the technologies closest to implementation¹, ², but it still shows a large improvement potential. The main challenges for PCC are energy requirement and possible process emissions. Hence, the search for optimal technology is still ongoing. Modelling and optimization of process flowsheets and solvent performance is central in this respect; solvent speciation in particular, is an important input to these activities.

Although solvent speciation is important, such data are tedious and difficult to obtain. Typically it requires access to specialized and expensive, e.g. NMR equipment.

A typical CO₂ gas-liquid absorption solvent consists of aqueous alkanol amine or other Brønsted base containing solution. CO₂ solvent loading can be monitored by pH measurement³, ⁴, since this is an acid-base neutralization reaction. Hence, pH value input has been used to model gas-liquid equilibrium of CO₂ absorption into AMP solution⁵ as well as modelling of equilibrium speciation profiles for the CO₂- DEA (or AMP)-water systems⁶.

In this contribution we provide a facile method for speciation of the CO₂-H₂O-alkanolamine system applicable to primary or secondary mono amines as well as primary or secondary, tertiary amine blends. The method requires determination of the pH vs CO₂ loading values of the amine system of interest. This information, together with respective pKa and equilibrium constant values are input data into a speciation model containing the CO₂-H₂O-alkanolamine mass balance described by the respective equilibrium reactions.

Speciation model
The mass balance equilibrium equations are a mixture of linear and nonlinear algebraic equations with respective unknown concentrations. The system of equations is solved numerically with an initial guess for each concentration and a specified accuracy for the numeric solution. The final solution represents the equilibrium speciation of the chemical system.
The determined pH value at equilibrium may be expressed as, for example, by equation (1), where 
PpK<sub>a</sub>' is the apparent acidity constant for reaction (1). The apparent acidity constant includes the activity coefficients of the respective species (reaction 2). The relation of equation (1) and (2) is also valid for equation (3) to (6). Thus, the activity coefficients of these reactions are taken into account in the model<sup>6</sup>.

Formation of carbonate: 

\[ \text{HCO}_3^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \]  

(3)

Dissociation of protonated amine: 

\[ \text{R}_1\text{R}_2\text{NH}_2^+ + \text{H}_2\text{O} = \text{R}_1\text{R}_2\text{NH} + \text{H}_3\text{O}^+ \]  

(4)

Formation of carbamate: 

\[ 2 \text{R}_1\text{R}_2\text{NH} + \text{CO}_2 = \text{R}_1\text{R}_2\text{NH}_2^+ + \text{R}_1\text{R}_2\text{NCO}^- \]  

(5)

Carbamate hydrolysis: 

\[ \text{R}_1\text{R}_2\text{NH}_2^+ + \text{R}_1\text{R}_2\text{NCO}^- + \text{H}_2\text{O} = \text{R}_1\text{R}_2\text{NH} + \text{R}_1\text{R}_2\text{NH}_2^+ + \text{HCO}_3^- \]  

(6)

For reactions (3) – (6): R<sub>2</sub>=H, R

**Experimental**

The changes in pH of the amine solution during CO<sub>2</sub> absorption was monitored using an automated Metrohm 905 Titrando apparatus. Solution CO<sub>2</sub> loading was monitored online through the changes in Raman spectral intensity using a Raman RXN2 Kaizer Optical Systems Inc. spectrometer<sup>7</sup>.

**Speciation model results**

Figure 1 demonstrates the method for 30 wt% MEA solvent. The model is validated by comparison with published<sup>8</sup> quantitative <sup>13</sup>C NMR speciation data. The contribution will include amine blend speciation modelling validated by respective <sup>13</sup>C NMR measurements. The results will be discussed.

**Figure 1:** MEA-CO<sub>2</sub>-H<sub>2</sub>O speciation model (lines) vs. in-situ <sup>13</sup>C NMR analysis (open symbols)<sup>8</sup>.