Simulated concentration profiling of liquid-phase products in the quaternary solvent system of (carbon dioxide + monoeth-anolamine / diethanolamine + triethanolamine + water)

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Abstract. An understanding of the potential environmental impacts of amine solvents used in Carbon Capture and Storage (CCS) is important as more of these technologies are moving to the pilot stage of development and will be more regularly operated. It is clear that solvents with otherwise promising performance may have challenges and considerable inherent problem due to by-product formation, of which often neglected. In this regard, it is also necessary to study the concentration profiles of the by-products formed in aid of treating liquid waste streams. The study also includes the chemistry and reaction mechanisms of amine transformation products. The studied quaternary systems in varying blends were generally written as CO_2-amine-TEA-H_2O, where amine could be MEA or DEA. TEA corresponds to triethanolamine, MEA to monoethanolamine, and DEA to diethanolamine. The simulation was done using Aspen Plus® v8.6 at different mass flow rates (kg/h): 500, 750, and 1,000; temperatures (^oC): 25, 30, 35, 40, 45, and 50; and pressures (atm): 1, 2, and 3. The results shows direct proportionality between the efficiency and solvent's flow rate, pressure, higher secondary amines ratio along with temperature in majority. At constant temperature, pressure, and mass flow rate, the highest removal efficiency was that of MEA-TEA (10-20 %wt) and the lowest was DEA-TEA (10-20 %wt). In addition, the results yield reasonable predictions on liquid-phase product concentration profiles. The components behave according to their expected trends and the results are very promising.

1. Introduction

An understanding of the potential environmental impacts of amine solvents used in Carbon Capture and Storage (CCS) has received a lot of attention and become increasingly more important in recent years as more of these technologies are moving to the pilot stage of development and will be more regularly operated in the light of climate change fears. The utilization of alkanolamines for carbon dioxide (CO_2) capture has been commercially used in two processes namely absorption and desorption. In these processes, significant problems arise such as the degradation of solvents and corrosion in the equipment. In general, alkanolamines have high water solubility and low to moderate vapor pressures. It is known that alkanolamines is unlikely to partition in the atmosphere, but they would partition primarily into the aqueous compartment at equilibrium. There are several reactions involved during the contact between the solvents and the gas. The environmental impacts of the solvent have been studied by Eide-Haugmo *et al* [1] where it provides the information on environmental impacts such as aquatic toxicological information, bioconcentration potential, and degradation potential. There is a

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possibility that the reaction products might generate more impacts in the liquid wastewater streams instead. Therefore, it is necessary to investigate more about the concentration of products generated during the process, especially in the water stream.

This paper profiled the concentrations of liquid-phase products of varying blended alkanolamines during CO_2 absorption process via Aspen Plus® v8.6 simulation. Here, the effects of varying solvent composition, temperature, pressure, and solvent flow rate were discussed based on percent CO_2 removal, on top of the assessment of the products concentration.

2. Materials and methods

2.1. Electrolyte NRTL activity coefficient model and rate-based modeling

The Electrolyte Non-Random Two Liquid (NRTL) model is the most versatile electrolyte property method that is used to represent the CO_2 capture system in Aspen Plus®. The Electrolyte NRTL model in Aspen Plus® can handle a wide range of concentrations from very low to very high concentrations as well as aqueous and mixed solvents. It is a model for the excess Gibbs free energy of an electrolytic solution. The Electrolyte NRTL model assumes that the excess Gibbs free energy in the electrolyte system is the sum of two contributions [2-4]: (*i*) short-range forces between all the species that includes the local ion-molecule, ion-ion, and molecule-molecule interactions; and (*ii*) long-range electrostatic ion-ion interactions. Thus, the expression for the excess Gibbs free energy as calculated by the Electrolyte NRTL model can be expressed as shown in equation (1).

$$g^{ex*} = g^{ex*,\,LR} + g^{ex*,\,local} \tag{1}$$

The long range contributions are represented as a combination of the Pitzer-Debye-Hückel contribution [5] and the Born expression [6]. The local interaction contribution is derived as per the NRTL model.

Aspen RateSep, the rate-based mode of RadFrac allows for the rate-based modeling of absorption and desorption columns [7]. It is a stage based model, shown in figure 1, which allows the modeling of mass and heat transfer phenomena as well as the kinetics of chemical reactions. Aspen RateSep uses the solution proposed by Alopaeus [8] to solve the Maxwell-Stefan multicomponent mass transfer equation [9]. It uses the two-film theory and allows for film discretization which is useful to get an accurate concentration profile in the film for fast reactions. It also combines the film equations with separate balance equations for the liquid and vapor phase, diffusion and reaction kinetics, electrolyte solution chemistry, and thermodynamics [9].

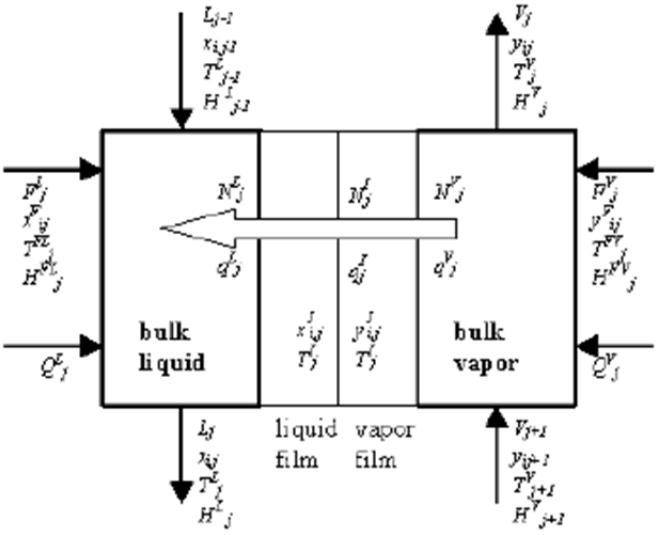


Figure 1. Aspen representation of a stage (adapted from AspenTech, 2008 [7]).

2.2. Aspen plus® simulation

Typical amine based CO_2 capture system includes two main elements: the absorption column (absorber) and the desorption column (stripper) however, only absorption was considered in this study. Figure 2 shows the 20-stage rigorous vapor-liquid fractionation model RadFrac (absorption column) for amine based CO_2 capture system, in which aqueous solutions with 10/20%wt. TEA and 20/10%wt. amine were selected as solvent. Moreover, the blended aqueous solutions were simulated with varying (*i*) mass flow rates (kg/h): 500, 750, and 1,000 kg/h; (*ii*) temperatures (°C): 25, 30, 35, 40, 45, and 50; and (*iii*) absorber pressures (atm): 1, 2, and 3.

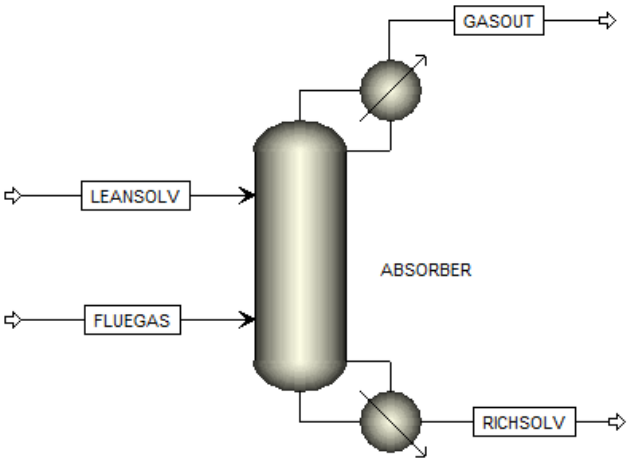


Figure 2. Absorption column with material streams.

The composition of the flue gas, given in table 1, is assumed to have no pollutants in such as NO_x and SO_x. The flue gas after desulfurization and denitrification is cooled down to about 40°C before it enters absorption column at 100 kg/h, in which the lean amine solution initially at 25°C is contacted with flue gas and absorbs CO_2 from it. Then, the CO_2-rich amine solution leaves from absorber bottom.

Table 1. Composition of the flue gas.

T/°C	Component	Chemical Formula	Volume Fraction (%)
40	Carbon Dioxide	CO_2	8.40
	Nitrogen	N_2	74.13
	Oxygen	O_2	12.05
	Water	H_2O	4.52

2.3. Chemistry and reactions of the TEA-MEA/DEA-H_2O solvent system

There are two categories of reactions for CO_2 - aqueous blended alkanolamine system; those that are rate controlling and those that are rapid to reach equilibrium. The equilibrium equations and rate controlling reactions are shown in Reactions (1) to (5) and (6) to (7), respectively.

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad \text{(R.1)}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \text{(R.2)}$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \quad \text{(R.3)}$$

$$R_1R_2NH^+COO^- + H_2O \leftrightarrow R_1R_2NCOO^- + H_3O^+ \quad \text{(R.4)}$$

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \quad (R.5)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (R.6)$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (R.7)$$

For the considered equilibrium reaction, the thermodynamic equilibrium formula that is temperature dependent, pressure independent, and are based on the mole fraction scale was used. In contrast, the Power Law Kinetic Expression was used for the rate controlled reactions where the rate is the product of kinetic factor and driving force.

3. Results and discussion

3.1. Liquid-phase product concentration profiles

In CO_2 absorption using aqueous alkanolamines, it has been known that chemical reactions play important roles. Those reactions usually lead to the production of carbamates, bicarbonates, and carbonates depending of amine used, whether it is primary, secondary or tertiary. Naturally, the reactions include protonation of amine and ionization of different species for all type of amine. Carbamate formation is an additional step in both primary and secondary amines [10].

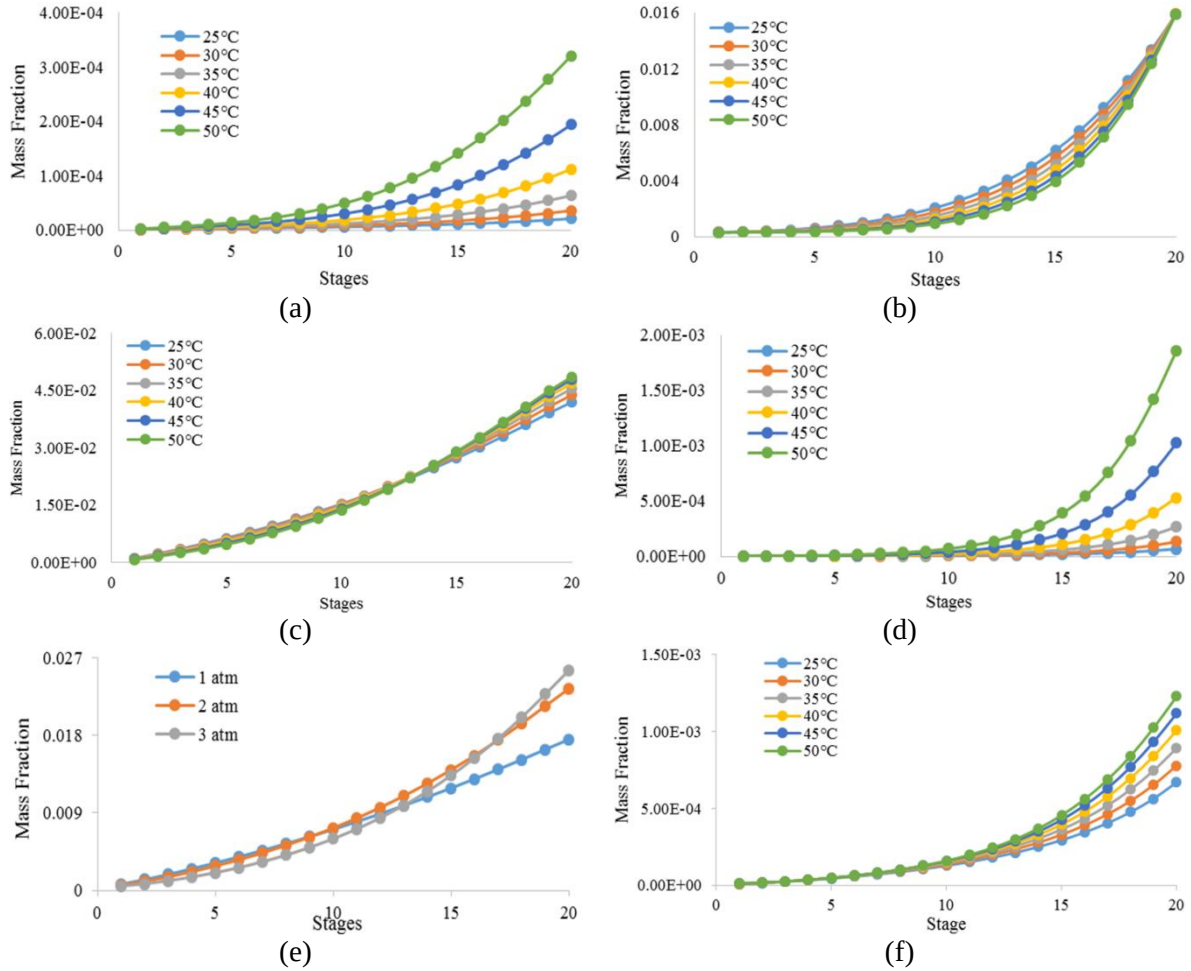


Figure 3. Plot of the liquid-phase product concentration profiles: (a) $MEACOO^-$ concentration profile for MEA-TEA (20-10 %wt.) at 500 kg/h and 1 atm; (b) HCO_3^- concentration profile for

DEA-TEA (20-10 %wt.) at 1,000 kg/h and 3 atm; (c) CO_3^{2-} concentration profile for DEA-TEA (20-10 %wt.) at 1000 kg/h and 1 atm; (d) $MEAH^+$ concentration profile for MEA-TEA (20-10 %wt.) at 1,000 kg/h and 3 atm; (e) $DEAH^+$ concentration profile for DEA-TEA (20-10 %wt.) at 1,000 kg/h and 30^{o}C; (f) $TEAH^+$ concentration profile for MEA-TEA (20-10 %wt.) at 1,000 kg/h and 1 atm.

3.1.1. Carbamate (COO^-). Only primary and secondary amines form carbamate species while tertiary amines cannot form carbamates and do not react directly with CO_2. For MEA-TEA system, the effect of temperature and pressure are almost negligible as the solvent approaches the bottom stages. Based on the figure 3(a), it is evident that low amount of carbamate is formed at a high temperature in the middle stages, but as it proceeds to a higher stage this trend changes. This trend is observable for solvent flow rates of 500 and 750 kg/h while the temperature and pressure effect becomes negligible for a flow rate of 1,000 kg/h. The difference between these systems is because primary amines produce stable carbamates than secondary amines. Also, the rate of reaction of MEA forming carbamate ions is higher compared to DEA.

3.1.2. Bicarbonate (HCO_3^-). Bicarbonate formation appears only in tertiary or sterically-hindered amines. Due to this, higher bicarbonate ions are present in alkanolamine systems with more tertiary amines present. The amount of bicarbonate in the liquid stream increases with temperature and pressure (see figure 3(b)). This is the result of increasing rate of reaction as we increase the temperature, based on the Arrhenius Equation or Power Law Expression in Aspen Plus® simulation.

3.1.3. Carbonate (CO_3^{2-}): At a higher temperature and pressure, more carbonate ions are formed in the case of DEA-TEA and MEA-TEA mixtures. By increasing the temperature and pressure, carbonate ion concentration increases for DEA-TEA mixtures (see figure 3(c)). Though, it should be noted that at some conditions for MEA-TEA systems, the effect of the absorber pressure varies; and that the carbonate formation is related to the amount of bicarbonate.

3.1.4. $MEAH^+$: Lower temperature would lead to higher $MEAH^+$ considering only the first 15 stages. As the number of stages increases, the effect becomes negligible as shown in figure 3(d). Same trend can be observed to the pressure effect wherein more $MEAH^+$ ions would be formed at a higher pressure as we reaches stages 18-20.

3.1.5. $DEAH^+$: The temperature effect for the formation of this ion is negligible for all systems containing DEA as it proceeds to bottom of the absorber. In figure 3(e), for DEA-TEA mixtures, the $DEAH^+$ ions formed is inversely proportional to pressure at stages 1-10 but becomes proportional to pressure as it reaches the bottom part of the absorber.

3.1.6. $TEAH^+$: At a constant pressure, increasing the temperature resulted to a higher $TEAH^+$ for both MEA-TEA and DEA-TEA systems (see figure 3(f)). Varying the absorber pressure, resulted to the same trend with the formation of $DEAH^+$ in DEA-TEA mixtures, wherein the ion formation is inversely proportional to pressure at stages 1-10 but becomes proportional to pressure as it reaches the bottom part of the absorber. While for MEA-TEA systems, same profiles can be observed for the effect of pressure in both $MEAH^+$ and $TEAH^+$.

3.2. Potential Risk of the Amine Products

It is important to choose solvent that has low environmental effect when large amount of solvents is needed in the absorption. During the process, solvent used may be released through accidental spills or during maintenance. In marine environment, MEA and DEA are more degradable than TEA; therefore, they have longer persistence. TEA is also reported to be out of eco-toxicity limit [1]. Aside from solvent itself, when the solvent or liquid products react with certain compound, it may also react to

generate undesirable compound. Some problems that may be encountered are solvent loses, foaming, corrosion, fouling and high viscosity. At absorber, solvents are degraded through oxidative degradation from the presence of oxygen in the flue gas and carbamate polymerization which occurs in the presence of CO_2. Although the reactions of carbamates and protonated amine formation are reversible, it is important to have an eye on these concentrations since the irreversible degradation reaction may take place.

4. Conclusion

Overall, the percent CO_2 removal will increase when the temperature is increase. Similar behavior is applied; by increasing the pressure and mass flow rate at all systems will also increase CO_2 removal efficiency. The mixture of MEA-TEA (10-20 %wt.) is the most promising blended alkanolamine for CO_2 absorption among the chosen solvents as the mixture yielded the highest removal efficiency.

The product concentration of the alkanolamine system is mainly dependent on their respective reaction. The reaction of primary and secondary is different with tertiary amines, wherein bicarbonate is only formed with tertiary amine as it lacks free proton. Compared with primary and secondary amine which directly reacts with CO_2 to form carbamate ions.

The formation of following ions is directly proportional with temperature: carbamate, bicarbonate, hydronium, and $TEAH^+$. Meanwhile the profiles of $MEAH^+$ and $DEAH^+$ are different as it proceeds to the bottom stages. The pressure effect varies at the stage location for the profiles of $MEAH^+$, $DEAH^+$, and $TEAH^+$. While carbamate, bicarbonate, and carbonate have a higher concentration as the pressure increases throughout the absorber.

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