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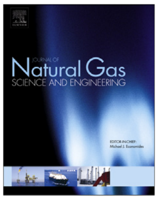

Reaction kinetics of carbon dioxide in aqueous blends of N-methyldiethanolamine and glycine using the stopped flow technique

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ABSTRACT

Carbon dioxide managements and its association with global worming remains a major concern among governments and the scientific community, with novel, energy efficient and more affordable technologies topping the research agendas. Despite the importance of amino acids, their use as reaction promoters in combination with alkanolamines has been overlooked by researchers. Here, stopped-flow technique was used for the first time to measure the pseudo-first-order reaction kinetics of CO_2 with various aqueous mixtures of N-methyldiethanolamine (MDEA) and glycine (Gly). The experiments were performed at a temperature range from 293 to 313 K and a total amine concentration up to 2 mol/l. The activation energy for CO_2-MDEA reaction obtained from this work was found to be 49.24 kJ/mol, and the overall rate constants (k_{ov}) increased with increasing temperature and with increasing proportion of Glycine in the solution mixture. Using the zwitterion mechanism to interpret the CO_2-MDEA-Gly reaction, we found that the glycine reacts with CO_2 (aq) with $k_2\ (M^{-1}\ s^{-1}) = 2.40 \times 107 \exp(-3887.5/T(K))$ with an activation energy of 22.95 kJ/mol.

1. Introduction

The increased greenhouse gas concentrations in the atmosphere continue to hold the attention of governments and the scientific community worldwide. Carbon dioxide, which is considered the most important contributor to these greenhouse gases and the resulting global warming, mainly originates from the combustion of fossil fuels for power generation. The reduction of carbon dioxide emissions is mandatory to keep earth a livable environment for mankind. This must be accomplished through the development of new and innovative solutions to efficiently improve carbon dioxide removal methods and/or improve existing ones to cope with surging challenges. Remarkable progress in CO_2 capture processes using reactive chemical solvents has been observed in the last few decades. Alkanolamines, are well known for their ability to selectively absorb CO_2 from natural and flue gases. Although, various solvents have been used to capture CO_2 (such as hot potassium carbonate, chilled ammonia and ionic liquids), the amine-based processes are still the most developed, durable and industrially applicable process in gas treatment. Solvents such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) are still the preferred choice in the industry for CO_2 removal owing to their established absorption regeneration process. Monoethanolamine (MEA), one of the first-generation solvents, is definitely the mostly studied absorbent (Rochelle et al., 2001a, 2001b) and is associated with low production cost and high selectivity towards CO_2. The high reaction rate of MEA with CO_2 can reduce the absorber height and ensure a stable operation of the process. However, several drawbacks are linked to MEA (Rochelle et al., 2001b) such as the high energy requirements (high enthalpy) needed to break the chemical bonding between CO_2 and MEA during the solvent regeneration step. In addition, MEA has a lower absorption capacity compared to tertiary amines such as MDEA, which must be compensated by increased circulation rate, causing an additional cost for the solvent pumping system (Rochelle et al., 2001b). It has also been reported that MEA is vulnerable to thermal and oxidative degradation, which forces compulsory periodic solvent make up in the absorber to maintain stable absorption performance (Rochelle et al., 2001a). Finally, the corrosion tendency of MEA results in considerable equipment

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maintenance costs (Rochelle et al., 2001a, 2001b). Accordingly, there is still a strong drive to develop novel absorbents to achieve high absorption/desorption performance, energy efficiency and thermal stability.

In literature, it was reported that liquid tertiary amines and amidines have shown a higher theoretical sorption capacity with a ratio of 1:1 M (Benamor et al., 2008), thereby reducing the required volume of amine. The disadvantage is a slower reaction rate rendering it not a suitable choice given the large required number of stages in the absorber and its associated costs (Benamor et al., 2008). In order to improve the adsorption, it has been suggested that blended amines are used (Chakravarty et al., 1985). Here, tertiary amines are often blended with faster reacting primary and/or secondary amines and/or piperazine to utilize their high loading capacity, low degradation rate and low regeneration energy. The addition of small amounts of promoters to conventional tertiary amines such as MDEA can enhance the rate of absorption of CO_2 to a large extent without appreciably changing the stripping characteristics (Chakravarty et al., 1985).

Amino acid salts, a class of chemical absorbents for CO_2 capture normally referred to as aqueous alkaline salts of amino acids, contain two important functional groups—namely, amine ($-NH_2$) and carboxylic acid ($-COOH$). However, taurine, which contains a sulfonic acid group instead of the carboxylic acid, can also be considered as an amino acid (Lerche, 2012) and is one of the popular amino acids that have been tested for CO_2 capture. Amino acids have been commercially employed in acidic gas treatment processes, such as the BASF Alkazid solvent and the Giammarco-Vetrocoke (GV) process, which uses carbonate solution as an absorbing solvent.

Potassium (K) and sodium (Na) are normally used as counter ions with amino acids to form salts. However, it was reported that K provides a higher reactivity toward CO_2 than Na (Majchrowicz et al., 2014). Amino acid salts have drawn significant attention from researchers in the field of CO_2 capture owing to their many advantages. Their volatilities are very low because of their salt nature, resulting in low solvent losses during the regeneration process, and because they already exist in nature, the use of amino acid salts is expected to be more environmentally friendly than the use of alkanolamine solvents (Aronu et al., 2010). In addition, they have a substantial resistance to oxidative degradation, making them a suitable choice in the treatment of flue gases containing large amounts of oxygen (Kumar et al., 2003a). However, amino acid salts have their own drawback. They precipitate at high concentrations or high CO_2 loading, resulting in a lower mass transfer rate and a possibility of damaging the process equipment (Kumar et al., 2003b).

Research groups from the University of Twente have extensively studied the use of amino acid salts for CO_2 absorption. The crystallization of products between CO_2 and amino acid salts was investigated by Kumar et al. 2003b). They reported that although the solid particles formed by the crystallization could cause some problems such as fouling and plugging in the process equipment and lowering the volumetric mass transfer coefficient, they also offer an opportunity to enhance the equilibrium conversions between CO_2 and amino acid salts in the liquid phase by removing the produced solid. Their study also showed that the produced crystallized solid was in the form of protonated amine. In another work, Kumar et al. (2003a) studied CO_2 solubility in a region where the crystallization occurred, and they showed that crystallization can increase the CO_2 absorption capacity of the potassium taurate solvents. A new process concept for the CO_2 capture based on the precipitation of the amino acid zwitterion species during the absorption of CO_2 was proposed by Sanchez Fernandez et al. (2013). Unlike the convectional CO_2 capture process, a separator was added after the absorption column to separate the crystallized products from the striper and hence recycled a part of the used solvent back to the absorber. Simulation results related to this process showed that the specific reboiler energy of this process is 2.4 GJ/tCO_2, which is approximately 35% lower compared with the MEA baseline. Additional studies on physico-chemical and transport properties were performed by the same research groups. This includes determinations of diffusion coefficients in amino acid salt systems (Hamborg et al., 2008) and N_2O solubility, viscosity and density in the potassium salt of amino acid salts (Holst et al., 2008).

Amino acid salts are known for having high surface tensions, which make them suitable absorbents in membrane gas absorption processes (MGA) that use the membrane as a phase barrier for the mass transfer between gas and liquid phases. Using amino acid salts, MGA can operate in the non-wetted mode, in this case, all membrane pores are filled with the gas and the overall mass transfer resistance is much lower compared to the partially wetted and wetted modes encountered when using amine absorbents, owing to their low surface tensions. The performance of the potassium salt of taurine in MGA was investigated by Kumar et al. (2002). The breakthrough pressures calculated from the Laplace—Young equation indicated that the membrane pores were difficultly wet when using amino acid salts. Long-term performance tests of mixed absorbents between MEA and sodium glycinate were performed by Rongwong et al. (2009). The applicability of 16 common amino acids to be used in the MGA process was investigated by Song et al. (2012). Their results showed that among all amino acid salts, the salts of serine resulted in the highest surface tension values and the lowest pore wettability.

Reaction kinetics, an indication of how fast the reaction between CO_2 and amine occurs, is one of the most important parameters for the design and the simulation of an absorption column. Various equipment and experimental techniques have been used to obtain reaction kinetic data. Examples of equipment types, their advantages and disadvantages have been reported by Sema et al. (2012). Different reaction mechanisms have been used to interpret the rate constants, ranging from simplified kinetics models (i.e., zwitterion, termolecular or base catalyzed hydration) to a more comprehensive numerically solved reaction kinetics model that considers the coupling among the chemical equilibrium, mass transfer and chemical kinetics of all possible reactions. Detailed reviews of these kinetic data and their corresponding reaction mechanisms have been reported by Blauwhoff et al. (1984), Versteeg et al. (1996), Vaidya et al. (2010), Sema et al. (2012) and recently by Couchaux et al. (2014) and Liang et al. (2015).

Despite the importance of amino acids, their use as reaction promoters in combination with alkanolamines has been overlooked by researchers; no similar work has been published in the open literature. Accordingly, the main aim of this current investigation is to present new experimental data on the kinetics of CO_2 with aqueous solutions of MDEA mixed with glycine using the stopped flow technique. The results obtained from the stopped flow experiments were modelled using the zwitterion mechanism for critical experimental variables such as temperature (ranging from 298 to 313 K) and amine total concentration (range between 0.25 and 2 M).

2. Reaction mechanism and rate models

2.1. Reaction rate models of CO_2 with MDEA

The overall reaction of aqueous CO_2 and MDEA solution can be written as follows (Donaldson and Nguyen, 1980):

$$CO_2 + R_1R_2R_3N + H_2O \xrightarrow{K_{MDEA}} R_1R_2R_3NH^+ + HCO_3^- \tag{1}$$