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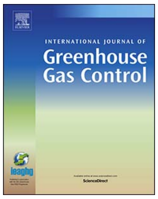

Reaction kinetics of carbon dioxide with aqueous solutions of L-Arginine, Glycine & Sarcosine using the stopped flow technique

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ABSTRACT

The use of amino acids as potential solvents for carbon dioxide (CO_2) capture has been considered by a number of researchers. However, very little is known about the kinetics and mechanism of amino acids-CO_2 reactions. In this work, we investigate the reactions of three amino acids (L-Arginine, Glycine and Sarcosine) with CO_2 in aqueous media using stopped-flow conductivity technique. The experiments were performed at temperatures between 293 and 313 K and amino acids concentrations were in the range of 0.05–0.2 molar. The overall rate constants (k_{ov}) was found to increase with increased amino acid concentration and solution temperature. Both zwitterion and termolecular mechanisms were used to model and interpret the data. However, the Zwitterion mechanism was found to be the preferred one. From the stopped-flow results at pH around 6, we found that neutral L-Arginine, Glycine and Sarcosine react with $CO_2(aq)$ with $k(M^{-1}\,s^{-1}) = 2.81 \times 10^{10}\exp(-\frac{4482.9}{T\,(K)})$, $k(M^{-1}\,s^{-1}) = 3.29 \times 10^{13}\exp(-\frac{8143.7}{T\,(K)})$ and $k(M^{-1}\,s^{-1}) = 3.90 \times 10^{13}\exp(-\frac{7991.0}{T\,(K)})$ respectively. The corresponding activation energies are 37.28 kJ mol^{-1}, 67.71 kJ mol^{-1} And 66.44 kJ mol^{-1} respectively. A comparison between the kinetics of the three amino acids showed that Arginine exhibits highest reaction rate with CO_2 followed by Sarcosine and then Glycine. The technique and results obtained from this work can be used as strong tools in the development of efficient new solvents for the removal of CO_2 from flue and industrial gases.

1. Introduction

Carbon dioxide is thought to be the most important contributor to global warming among other greenhouse gases (Figueroa et al., 2008). The reduction of carbon dioxide emissions is mandatory to keep CO_2 concentration at an acceptable level for human life. The technology of CO_2 post-combustion capture (PCC) is well recognised by governments and industry as an effective way of absorbing 80–90% of CO_2 emissions from fossil fuel-fired power plants (MacDowell et al., 2010). Captured CO_2 can be compressed and stored in depleted oil and gas fields, deep saline aquifers and unmineable coal seams, thereby reducing the amounts of CO_2 emitted to the atmosphere.

Remarkable progress in CO_2 capture processes using reactive chemical solvents have been observed in the last few decades. Alkanolamines, are well known solvents 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 choice in the industry for CO_2 removal owing to their established characteristics (Liang et al., 2016).

Monoethanolamine (MEA), a first-generation solvent, is known by its low production cost, high selectivity towards CO_2 and fast reaction rate with CO_2. This can reduce the absorber height and ensure a stable operation of the process. However, several drawbacks are linked to MEA, this include high energy requirements for solvent regeneration, lower absorption capacity compared to tertiary amines such as MDEA and its susceptibility to thermal and oxidative degradation, which forces periodic solvent make up to maintain stable absorption performance. Furthermore, the significant corrosion tendency of MEA results in considerable equipment maintenance costs.

Amino acid salts, represent a new class of chemical absorbents for CO_2 capture usually referred to as aqueous alkaline salts of amino acids. They contain two important functional groups-namely, amine ($-NH_2$) and carboxylic acid ($-COOH$). Taurine, which contains a sulfonic group instead of the carboxylic acid group is also considered as an amino acid (Lerche, 2012). It is one of the popular amino acids that have been

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Nomenclature

Arg	Arginine
Gly	Glycine
Sar	Sarcosine
AA	Amino acids
AAD	Average absolute deviation
k_2	Reaction rate constant of the formation of the intermediate zwitterion [m^3/mol s]
k_{-1}	Reaction rate constant of the consumption of the intermediate zwitterion [m^3/mol s]
k_b	Individual reaction rate constants according to zwitterion mechanism [m^3/mol s]
r_{CO2}	Reaction rate of CO_2 with amino acid [l/mol s]
k_{OV}	Overall reaction rates of CO_2 with amino acids [s^{-1}]
T	Temperature [K]
t	Time [s]
K_w	Water dissociation constant [–]
pK_a	Dissociation constants of amino acids [–]
$k_{ov\text{-}exp}$	Apparent rate constant [s^{-1}]
$k_{ov\text{-}pre}$	Predicted apparent rate constant [s^{-1}]
E_a	Activation energy [kJ/mol]
k_β	Catalytic contribution of amino acid in the reaction rate according to the zwitterion mechanism [$m^6\,kmol^{-2}\,s^{-1}$]
k_{hyd}	Contribution of hydroxyl ion in the reaction rate according to the zwitterion mechanism [$m^6\,kmol^{-2}\,s^{-1}$]
k_w	Contribution of water in the reaction rate according to zwitterion mechanism [$m^6\,kmol^{-2}\,s^{-1}$]
k	Rate expression of the amino acid [$M^{-1}\,s^{-1}$]

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 use carbonate solution as an absorbing solvent. Siemens Energy tested a commercial absorbent based on a functional amino acid salt solution in an industrial-scale pilot plant in Germany at 298 K and 313 K. Compared to MEA solution, the amino acid salt solution has near-zero fugitive emissions, less corrosion in equipment materials and very little oxygen degradation (Jockenhoevel et al., 2009; Jockenhövel and Schneider, 2011). Amino acid salts have drawn significant attention from researchers in the field of CO_2 capture owing to their attractive characteristics (Kumar et al., 2003a,d,e; van Holst et al., 2009; Vaidya et al., 2010; Simons et al., 2010; Sodiq et al., 2014; Shen et al., 2016; Benamor et al., 2016). Amino acids are known to have low volatility which results in low solvent losses during the regeneration process (Aronu et al., 2010), substantial resistance to oxidative degradation, making them a suitable choice in the treatment of flue gases containing large amounts of oxygen. They bind readily with CO_2 due the presence of a polar side chain within their structure (Chatterjee et al., 2016). 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., 2003c). Kumar et al. (2003a), Kumar et al. (2003d) measured the solubility of CO_2 in taurate solution at 298 K and 313 K at CO_2 partial pressures ranging from 0.1 to 6 kPa. They also investigated the kinetics of CO_2 absorption in taurate and glycine solutions at temperatures using a stirred-cell reactor and determined their respective reaction rate constants. Portugal et al. (2007) compared the overall kinetic constant of CO_2 absorption in glycinate and MEA solutions, and found that the absorption rate of CO_2 in glycinate solution is faster than that in MEA solution. Knuutila et al. (2011) used a laboratory-scale pilot plant to study the CO_2 absorption kinetics of sarcosinate solution. Although the absorption rate of sarcosinate solution is faster than MEA, they found that sarcosinate requires a higher reflux ratio and desorption temperature than MEA in the reboiler and stripper for CO_2 desorption. van Holst et al. (2009) investigated the apparent rate constants for several amino acid salts at 298 K to find suitable absorbents for CO_2 capture. They found that amino acids solutions such as glycinate, prolinate, sarcosinate and taurate exhibit relatively high reaction rate constants that are similar to monoethanolamine (MEA) solutions. Wei et al. (2014) investigated the salt of potassium taurate as potential solvent for use as a high-temperature absorbent for post- combustion CO_2 capture. They found that CO_2 solubility of taurate solutions, measured using a stirred-cell reactor, is comparable to that of alkanolamines at high temperatures. Thee et al. (2014) studied the kinetics of CO_2 capture with potassium carbonate solutions promoted with various amino acids: Glycine, sarcosine and proline using a wetted-wall column for concentrations up to 2.0 M and temperatures from 40 to 82 °C. Their results showed that the addition of 1.0 M glycine, sarcosine and proline accelerates the overall rate of absorption of CO_2 into a 30 wt% K_2CO_3 solvent by a factor of 22, 45 and 14, respectively. Benamor et al. (2016) studied the reaction kinetics of CO_2in aqueous blends of N-methyldiethanolamine and glycine using the stopped flow technique and found out that the addition of small amounts of Glycine to MDEA, considerably enhances its reaction rate with CO_2. The molecular structure of Glycine, Arginine and Sarcosine are shown in Fig. 1.

Several alternative techniques are available for the investigation of reaction kinetics, this include stirred cell, stirred semi-batch, laminar jet absorber, falling film, wetted sphere and stopped-flow technique (Sema et al., 2012). Among these techniques, stopped-flow, which is a direct method, has been widely used due to its large coverage of reaction rates and reproducible results (Couchaux et al., 2014). Furthermore, the stopped-flow technique is very useful for screening novel solvents due to its requirement for very small solvent quantities and its experimental procedure (Vaidya and Kenig, 2007). Therefore, in this study, the reaction kinetics of three amino acids with CO_2 were investigated using the stopped-flow technique.

With the exception of the works of Guo et al. (2013) and Xiang et al. (2012), no prior studies have considered the reactions between glycine and CO_2 and that of Sarcozine and CO_2. However, no kinetic data are available for the reaction of Arginine and CO_2. The main aim of this current work is to investigation the kinetics and mechanisms of aqueous CO_2 reactions with solutions of neutral forms of L-Arginine, Glycine & Sarcosine using stopped flow conductivity technique under different experimental conditions such as temperature, ranging from 298 to 313 K and amine total concentration varying between 0.05 and 0.2 M. The obtained experiments experimental results were modelled using the zwitterion and termolecular mechanisms and the corresponding rate constants and their associated activation energies were evaluated. Furthermore, a comparison between the kinetics of the three the amino

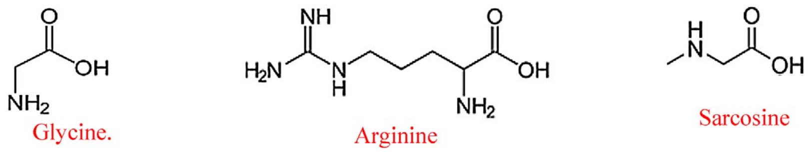

Fig. 1. Molecular structure of amino acids used in this study.