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Analysis of solubility, absorption heat and kinetics of CO_2 absorption into 1-(2-hydroxyethyl)pyrrolidine solvent

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HIGHLIGHTS

- Reaction kinetics of 1-(2-HE)PRLD with CO_2 is presented using stopped-flow technology.
- CO_2 absorption heat of 1-(2-HE)PRLD is shown.
- The plot of the kinetics versus heat absorption is created.

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ABSTRACT

The CO_2 absorption performance of aqueous 1-(2-hydroxyethyl)pyrrolidine (1-(2-HE)PRLD) was studied with respect to kinetics (i.e., in terms of the pseudo-first-order rate constant (k_o) and second-order reaction rate constant (k_2), obtained using the stopped-flow apparatus). CO_2 equilibrium solubility and heat of CO_2 absorption were evaluated at the temperature range of 293–313 K in the 1-(2-HE)PRLD concentration range of 0.20–1.00 mol/L for kinetics and at 2 M for CO_2 solubility. The values of k_o were then represented using the base-catalyzed hydration mechanism, which gave an acceptable AAD of 10%. In addition, Brønsted plots of k_2 vs. pKa were developed to predict k_2 using pKa values of various tertiary amines. In addition, the CO_2 equilibrium solubility and CO_2 absorption heat were obtained in this work. Based on a comparison with other amines such as MEA, MDEA and 1DMA2P, 1-(2-HE)PRLD showed better performance in terms of CO_2 equilibrium solubility (DEAB > 1-(2-HE)PRLD > 1-(2HE)PP > 1DMA2P > MDEA > MEA > DEA), kinetics (MEA > DEA > DEAB > 1-(2-HE)PRLD > 1-(2-HE)PP > DMMEA > 1DMA2P > MDEA.) and CO_2 absorption heat (MEA > DEA > MDEA > DEAB > 1-(2-HE)PRLD > 1-(2HE)PP > 1DMA2P). Therefore, 1-(2-HE)PRLD could be considered as a good alternative solvent for CO_2 capture. A correlation between kinetics and heat of CO_2 absorption has been developed to guide the design of what can be considered to be ideal amine solvents for CO_2 capture.

1. Introduction

Among several technologies (e.g. absorption, adsorption, membrane separation, cryogenic distillation, and biotechnology) for CO_2 removal from flue gases, the reversible absorption of CO_2 using aqueous amine solutions is considered to be one of the most widely applied technologies due to its maturity, good economic effectiveness, and ability to deal with a wide variety of exhaust gas streams (Rinker et al., 2000; Sema et al., 2012b). The main challenge of this technology is that the energy consumption is too high. The process of CO_2 capture using conventional amines (e.g., MEA) consumes a large amount of energy, approximately 4.1 GJ/ton CO_2. (Li et al., 2016) The current commercial technologies indicate that the energy requirements have been reduced by more than 30% to approximately 2.6 GJ/ton CO_2 (Liang et al., 2015b). As is well known, the amine used in the process of CO_2 capture was considered to be the vital issue in reducing the energy requirement. With the development of new chemicals, the energy requirement of PCC could be expected to be reduced by 2.0 GJ/ton CO_2. Hence, in order to achieve this objective, there has been a strong drive to develop attractive solvents that fulfil the following basic requirements: large absorption capacity, fast absorption kinetics, and low regeneration energy.

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Nomenclature

A	Arrhenius constant (m^3/mol s)
E_a	activation energy (kJ/mol)
k_o	overall reaction rate constant (s^{-1})
k_2	second order reaction rate constant (m^3/kmol s)
k_{H_2O}	reaction rate constant of reaction 3 (m^3/kmol s)
k_{OH^-}	reaction rate constant of reaction 2 (m^3/kmol s)
K_i	chemical equilibrium constants for reaction i
$K_{a,Amine}$	dissociation constant of amine (mol/m^3)
r_{CO_2}	overall CO_2 absorption rate (kmol/m^3 s)
R	universal gas constant (0.008315 kJ/mol K)
T	temperature (K)

Greek letter

α	CO_2 loading of amine solution (mol CO_2/mol amine)

A fundamental consideration when selecting an amine for PCC is the performance of the amine across both the absorption and desorption regimes (Conway et al., 2012). For the absorption process, fast absorption kinetics is a vital factor as it directly correlates with the required physical size of the absorber; thus, an amine that reacts fast with CO_2 is advantageous. In addition, the energy requirement for the stripping process is important, as the cost of steam often accounts for over half of the running cost of the plant (Middleton and Eccles, 2013). Information about heat of CO_2 absorption (ΔH_a) in aqueous solutions of amines is of prime importance for designing unit operations of CO_2 removal because it is directly related to the steam requirements of the amine regeneration stage, although this is only one of the many components of the overall energy consumption. New solvents that have been screened include: 4-(diethylamino)-2-butanol (DEAB) by Sema et al. (2012a), 1-dimethyl-amino-2-propanol (DMA2P) by Kadiwala et al. (2012). 2-(1-piperazinyl)-ethylamine (PZEA) by Paul et al. (2009), 3-diethylamino-1,2-propanediol (DEA-1,2-PD) by Chowdhury et al. (2013), and 1-diethylamino-2-propanol (1DEA2P) by Liu et al. (2014a). All these amines were reported to exhibit good performance for CO_2 capture with respect to CO_2 solubility, kinetics, mass transfer and regeneration heat.

1-(2-Hydroxyethyl)pyrrolidine (1-(2-HE)PRLD) is a new cyclic tertiary amine that has drawn considerable attention because of its good behaviour in CO_2 capture. Chowdhury et al. (2013) reported that 1-(2-HE)PRLD exhibited a higher CO_2 cyclic capacity than MDEA (currently the most used commercial tertiary amine). Also, according to Chowdhury et al. (2013), 1-(2-HE)PRLD exhibited a relatively higher absorption rate in comparison with another tertiary amine (dimethylmonoethanolamine (DMMEA)). In order to develop a reliable and systematic design of PCC systems using any potential solvents, knowledge of the absorption/desorption parameters of the solvent for CO_2 capture (e.g., CO_2 absorption kinetics, CO_2 solubility, heat of CO_2 absorption and mass transfer characteristics) is required. This implies that for 1-(2-HE)PRLD to be evaluated for its potential as an alternative solvent, such parameters must be evaluated. In addition, the knowledge of these parameters can be used to judge if 1-(2-HE)PRLD can be a standalone alternative solvent or a component in a blended solvent.

In this work, the kinetics data of CO_2 absorption in aqueous 1-(2-HE)PRLD solution were experimentally measured using the stopped-flow apparatus over a temperature range of 293–313 K and a 1-(2-HE)PRLD concentration range of 0.20–1.00 mol/L. All the experimental kinetic results were analyzed with respect to a pseudo-first-order rate constant (k_o) and a second-order reaction constant (k_2), which was derived through establishing a Brønsted-based relationship of pKa and k_2 for 1-(2-HE)PRLD in order to predict the values of k_2. In addition, CO_2 equilibrium, solubility, and heat of CO_2 absorption in 1-(2-HE)PRLD were also measured. Furthermore, a comparison of reaction kinetics, CO_2 equilibrium solubility and heat of CO_2 absorption was made between 1-(2-HE)PRLD and conventional amines as well as with other alternative amines in order to evaluate the possibility of 1-(2-HE)PRLD being recommended as a potential solvent for CO_2 capture.

2. Theoretical basis for estimation of parameters

The base-catalyzed hydration mechanism originally proposed by Donaldson and Nguyen (1980) was employed to interpret the reaction process with respect to the reaction of tertiary amines with CO_2. As suggested in this mechanism, the tertiary amine just acts as a base that catalyzes the hydration of CO_2 without direct reaction with CO_2. On the base of the base catalyzed hydration mechanism, the reaction of tertiary amine-H_2O-CO_2 can be expressed in Eqs. (1)–(6):

The base catalyzed hydration mechanism used can be described as:

$$Amine + H^+ \overset{K_1}{\leftrightarrow} AmineH^+ \tag{1}$$

$$Amine + CO_2 + H_2O \overset{K_2,k_2}{\leftrightarrow} AmineH^+ + HCO_3^- \tag{2}$$

$$CO_2 + OH^- \overset{K_3,k_{OH^-}}{\leftrightarrow} HCO_3^- \tag{3}$$

$$CO_2 + H_2O \overset{K_4,k_{H_2O}}{\leftrightarrow} H_2CO_3 \tag{4}$$

$$HCO_3^- \overset{K_5}{\leftrightarrow} H^+ + CO_3^{2-} \tag{5}$$

$$H_2O \overset{K_6}{\leftrightarrow} H^+ + OH^- \tag{6}$$

where *Amine* is a tertiary amine, K_i are the chemical equilibrium constants for reaction i, k_2 represents second order reaction rate constant of reaction (2) (m^3/kmol s), and k_{OH^-} and k_{H_2O} are reaction rate constant of reaction (3) (m^3/kmol s), and reaction rate constant of reaction (4) (m^3/kmol s), respectively.

2.1. Reaction kinetics

On the basis of reactions (2)–(4), the overall reaction rate of CO_2 absorption (r_{CO_2}; kmol/m^3 s) can be presented as:

$$r_{CO_2} = k_o[CO_2] = \{k_2[Amine] + k_{OH^-}[OH^-] + k_{H_2O}[H_2O]\}[CO_2] \tag{7}$$

where k_o is the observed pseudo-first-order reaction rate constant (s^{-1}), [ ] represents concentration (kmol/m^3).

Because of its slow reaction rate in comparison with reactions (2) and (3) due to its slow reaction rate in terms of mass transfer in comparison with those reactions, the contribution of reaction 4 can be neglected. (Hagewiesche et al., 1995; Henni et al., 2008; Kadiwala et al., 2012; Littel et al., 1999). Therefore, the expression of r_{CO_2} can be expressed as the following equation:

$$r_{CO_2} = k_o[CO_2] = \{k_2[Amine] + k_{OH^-}[OH^-]\}[CO_2] \tag{8}$$