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Comprehensive mass transfer and reaction kinetics studies of a novel reactive 4-diethylamino-2-butanol solvent for capturing CO_2

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HIGHLIGHTS

- Mass transfer and reaction kinetics of DEAB was comprehensively studied.
- Reaction kinetics can successfully explain mass transfer behavior.
- Solvent concentration, temperature, CO_2 loading effect kinetics and mass transfer.
- DEAB has a good potential to be used as the alternative solvent for capturing CO_2.

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ABSTRACT

In the present work, the reaction kinetics and mass transfer performance of CO_2 absorption into aqueous solutions of DEAB were comprehensively studied. The reaction kinetics was investigated using a laminar jet absorber in terms of a reaction rate constant (k_{DEAB}) and enhancement factor (E). The mass transfer performance was evaluated experimentally in a lab-scale absorber packed with high efficiency DX structured packing in terms of overall mass transfer coefficient ($K_G a_v$). It was found that k_{DEAB} was successfully extracted and can be expressed as: $k_{DEAB} = (4.01 \times 10^{13})\exp(-7527.7/T)$. Regarding to the reaction rate constant, the reaction kinetics of DEAB can be ranked as PZ $\gg$ MEA $\gg$ DEAB $\sim$ AMP $\sim$ DEA $>$ MDEA. Also, the predicted CO_2 absorption rates obtained from the developed reaction rate/kinetics model are fit favorably with the experimental results with an absolute average deviation (AAD) of 6.5%. For the mass transfer study, the $K_G a_v$ can be ranked as: MEA $>$ DEAB $>$ MDEA, which is corresponding well with the reaction kinetics results. In addition, the predictive correlation for $K_G a_v$ of DEAB has successfully been developed. The predicted results were found to fit reasonably well with the experimental results with an AAD of 14.6%.

1. Introduction

Recently, global warming and climate change problems have begun to receive considerable attention globally. It is generally accepted that human activities have raised the accumulative concentration of greenhouse gases (GHGs) in the atmosphere, resulting in the increasing of earth surface temperature, which directly affects human activities in many ways through the rapid melting of polar ice caps, the presence of heat waves, drought, and severe weather (Houghton et al., 1990; IEA, 2005). Among the GHGs, carbon dioxide (CO_2) is considered to be a major contributor due to its abundance at about 77% (Houghton et al., 1990). At present, more than 100 countries have agreed to mitigate the global warming and climate change problems by reducing the CO_2 emissions by 50% in 2050. With this goal, the increasing of earth surface temperature will be limited at 2 °C or below. In order to accomplish this goal, the CO_2 emissions need to be reduced at least 25% by 2020 (Meinshausen et al., 2009).

The absorption of CO_2 into reactive solvents is one of the most promising technologies for capturing CO_2 because of its maturity, cost effectiveness, and capability of handling large amounts of exhaust stream (Kohl and Nielsen, 1997). One of the key parameters of this technology is to use an effective solvent, which should have fast reaction kinetics, high mass transfer performance, high absorption capacity, low energy requirement for regeneration, low degradation

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rate, and low corrosiveness (Astarita et al., 1983; Kohl and Nielsen, 1997; Sema et al., 2012a). At the International Test Centre for CO_2 Capture (ITC), 9 novel reactive solvents (namely, 4-diethylamino-2-butanol, 4-morpholino-2-butanol, 4-isopropylamino-2-butanol, 4-piperidino-2-butanol, 1-dimethylamino-2-methyl-3-pentanol, 1-diethylamino-2-methyl-3-pentanol, 1-dimethylamino-4,4-dimethyl-3-pentanol, 4-propylamino-2-butanol, and 4-ethylmethyl-amino-2-butanol) were developed based on a systematic modification of the structure of amino alcohols by an appropriate placement of the substituent, especially hydroxyl function, relative to the position of the amino group, in order to promote CO_2 capture performance (Tontiwachwuthikul et al., 2008). Among the 9 solvents, 4-diethylamino-2-butanol (DEAB), which is considered as a tertiary amine, shows the best performance in terms of absorption capacity and cyclic capacity (Tontiwachwuthikul et al., 2008; Maneeintr et al., 2009). The absorption capacity of DEAB is competitive with that of piperazine (PZ) and higher than those of 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA), monoethanolamine (MEA), and diethanolamine (DEA) (Sema et al., 2011). Also, it was found that the energy requirement for regeneration of DEAB is lower than those of MDEA, DEA, and MEA, respectively (Maneeintr et al., 2009; Sema et al., 2011). However, several fundamental knowledge of DEAB (such as, reaction kinetics and mass transfer performance) need to be investigated to get a full picture of how DEAB can be used effectively because both reaction kinetics and mass transfer performance are required for effective design and simulate the absorption column (Astarita et al., 1983; Kohl and Nielsen, 1997; Sema et al., 2012a).

The process of CO_2 absorption in a packed column depends mainly on the contact between CO_2 and reactive solvent. Inside the absorption column, the packing provides a contact area, which separates the liquid flow into droplets (Kohl and Nielsen, 1997). This increases the amount of liquid surface area that is exposed to the gas phase. Aroonwilas and Tontiwachwuthikul (1998), Aroonwilas et al. (1999), and deMontigny et al. (2001) have shown that structured packing offers a superior performance compared to random packing. In addition, Fernandes et al. (2009) studied structured packing and found that the high surface area of this packing increases the mass transfer efficiency. The mass transfer performance of CO_2 absorption of MEA, AMP, DEA, diisopropanolamine (DIPA), MDEA, MEA–MDEA, DEA–MDEA, MEA–AMP, and DEA–AMP were studied in structural packed column by Aroonwilas and Veawab (2004). They found that the mass transfer performance in terms of relative column height requirement can be ranked as: MEA > MEA–AMP > DEA–AMP ~ DEA ~ AMP > MEA–MDEA > DEA–MDEA > DIPA > MDEA. They suggested that the reaction kinetics of CO_2 absorption plays an important role in the mass transfer behavior. For the single amine system, the mass transfer behavior can be explained using the reaction kinetics in terms of second order reaction rate constant (k_2), which can be ranked as: MEA > DEA > AMP > DIPA > MDEA. The mass transfer behavior of blended amine system was explained using mass transfer index and overall reaction rate constant (k_{ov}), which can be ranked as: MEA–AMP > DEA–AMP > MEA–MDEA > DEA–MDEA (Aroonwilas and Veawab, 2004).

A laminar jet absorber can provide very accurate and reliable kinetics data because the interfacial area is known accurately and the physical absorption rates have been shown to agree with Higbie's penetration theory prediction (Astarita et al., 1983; Aboudheir et al., 2003, 2004). One of the very first numerical comprehensive reaction rate/kinetics models of CO_2 absorption in aqueous amine solutions was developed by Hagewiesche et al. (1995). They studied the absorption of CO_2 in aqueous solutions of blended MEA–MDEA using a laminar jet absorber based on Higbie's penetration theory. However, the experiments were performed at only 313 K. Later, a more comprehensive kinetics models for CO_2 absorption into loaded aqueous amine solutions of MEA, DEA, AMP, MEA–AMP, MEA–MDEA, and MDEA–PZ were developed by Aboudheir et al. (2003), Jamal et al. (2006), Idem et al. (2009), and Edali et al. (2009, 2010). In their studies, the experimental kinetics data were obtained at various temperatures, amine concentrations, CO_2 loadings, and contact times. Moreover, the chemical equilibrium, the mass transfer, and the chemical kinetics of all possible reactions were taken into account in their comprehensive models. In the works of Idem et al. (2009), Edali et al. (2009, 2010), two numerical techniques, which are the finite difference method (FDM) based on the Barakat–Clark scheme and the finite element method (FEM) based on COMSOL software, were used for solving the reaction rate/kinetics models. They found that both FDM and FEM provide very accurate predicted CO_2 absorption rates. Also, no significant difference between the results obtained from FDM and FEM were observed. Therefore, they suggested that the FEM based on COMSOL software could be used for the numerical solution of the partial differential-algebraic equations because coding the program of the numerical scheme can be eliminated.

In the present work, the reaction kinetics and mass transfer performance of DEAB were comprehensively studied at DEAB concentrations of 1.0, 1.5, and 2.0 M. These ratios were selected because DEAB provides very high CO_2 absorption capacity (competitive with PZ) as mentioned in Tontiwachwuthikul et al. (2008), Maneeintr et al. (2009), Sema et al. (2011); thus, low DEAB concentration can achieve satisfactory CO_2 absorption capacity. For the mass transfer performance in packed column, the experiments were done in a laboratory-scale absorption column with DX structured packing (27.5 mm ID from Sulzer Chemtech Canada, Inc.) at atmospheric pressure. The mass transfer performance was investigated in terms of overall mass transfer coefficient ($K_G a_v$). The CO_2 absorption rate was experimentally measured using laminar jet absorber. The reaction kinetics was then interpreted in terms of reaction rate constant and enhancement factor. These kinetics parameters were then used to explain the mass transfer behavior in packed column.

2. Materials and methods

2.1. Chemicals

DEAB was synthesized according to the procedure described by Tontiwachwuthikul et al. (2008) in the solvent synthesis laboratory in the International Test Centre for CO_2 Capture (ITC) at the University of Regina. The purity of synthesized DEAB was determined by GC–MS and found to be 95%. Aqueous DEAB solutions of desired concentrations were prepared by adding a known amount of de-ionized water and predetermined amounts of DEAB. For the absorption experiment in a laminar jet absorber, 99.9% CO_2 was supplied by Praxair Inc., Regina, Saskatchewan, Canada. For the mass transfer experiment in packed column, premixed 15% CO_2 balanced with nitrogen (N_2) was also obtained from Praxair Inc, Regina, Saskatchewan, Canada.

2.2. CO_2 absorption rate

The CO_2 absorption rate was measured using the laminar jet absorber. A detailed description of the laminar jet absorber and its operation can be seen in Al-Ghawas et al. (1989) and Aboudheir et al. (2004). The laminar jet absorber was validated with water for the diffusivity of CO_2 at 298 K, which was found to be 1.97×10^{-5} cm/s (while Al-Ghawas et al. (1989) and Aboudheir et al. (2004) found to be 1.95×10^{-5} cm/s and 1.96×10^{-5} cm/s, respectively). Also some CO_2 diffusivity measurements were