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Comprehensive mass transfer and reaction kinetics studies of CO_2 absorption into aqueous solutions of blended MDEA–MEA

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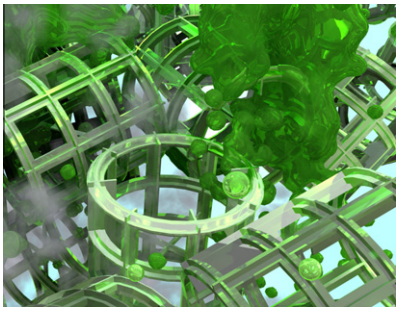
HIGHLIGHTS

- Mass transfer and reaction kinetics of MDEA–MEA was comprehensively studied.
- Considering effect of blended ratio, temperature, liquid flow rate, CO_2 loading.
- k_{MEA} was successfully extracted and in good agreement with the literature values.
- Reaction kinetics can successfully explain mass transfer behavior.

GRAPHICAL ABSTRACT

The graphic illustrates the CO_2 absorption inside packed column, where CO_2 contacts with reactive amine solvents. CO_2 is represented by the white cloudy gas, while reactive amine solvent is represented by the green liquid.
The graphic clearly and visually shows:

(i) CO_2 and reactive liquid solvent contact in the absorption packed column.
(ii) The packing generates more gas-liquid contact area by letting reactive liquid solvent spread over the packing and creating droplets of the reactive liquid solvent. The more contact area will lead to the higher CO_2 absorption performance.
(iii) The randomly alignment of the packing in the absorption packed column.
We believe this graphic will lead to the more understanding on CO_2 absorption behavior using reactive amine solvents in the packed column.



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ABSTRACT

In the present work, the reaction kinetics and mass transfer performance of CO_2 absorption into aqueous solutions of blended MDEA–MEA solutions were comprehensively studied. The reaction kinetics was investigated using a laminar jet absorber in terms of a second order reaction rate constant and enhancement factor. The mass transfer performance was evaluated experimentally in a lab-scale absorber packed with high efficiency DX structured packing in terms of CO_2 concentration profile and over all mass transfer coefficient ($K_G a_v$). The experiments were conducted over the MDEA/MEA concentrations of 27/3, 25/5, and 23/7 wt% MDEA/wt% MEA (which equivalent to MDEA–MEA molar ratios of 2.3/0.5, 2.1/0.8, and 1.95/1.16 M, respectively). It was found that k_{MEA} was successfully extracted and can be expressed as: $k_{MEA} = (5.127 \times 10^8) \exp\left(-\frac{3373.8}{T}\right)$. The results also show that the operating parameters (i.e., MDEA–

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MEA blended ratio, temperature, and CO_2 loading) affect both the reaction kinetics and mass transfer performance significantly. Lastly, the MDEA–MEA blended ratio of 1.95/1.16 provided the highest reaction kinetics and mass transfer performance among the three concentrations investigated in this study.

Nomenclature

C_e^*	equilibrium concentration of gas at interface, mol/L or kmol/m^3
C_j^0	bulk concentration for species j, kmol/m^3
d	jet diameter, m
D_i	diffusivity of chemical species i, m^2/s
E	enhancement factor
FEM	finite element method
G_I	gas flow rate, kmol/m^2 h
h	jet height, cm or m
He_{CO_2}	Henry's constant, kPa m^3/kmol
k_G	gas side mass transfer coefficient, kgmol/m^2 s kPa
k_L^0	liquid phase mass transfer coefficient for physical absorption of CO_2, m/s
$k_{2,i}$	second order forward rate coefficient for reaction i, m^3/kmol s
$k_{-2,i}$	second order reverse rate coefficient for reaction i, m^3/kmol s
K_i	chemical equilibrium constant for reaction i
K_G	overall mass transfer coefficient, kgmol/m^2 s kPa
$K_G a_v$	volumetric overall mass transfer coefficient, kmol/m^3 h kPa
L	liquid flow rate, cm^3/s or m^3/s
N	local CO_2 absorption rate per unit area, kmol/m^2 s
N_{ave}	average CO_2 absorption rate per unit area, kmol/m^2 s
P_{CO_2}	partial pressure of CO_2, kPa
R_A	rate of gas absorption, mol/s
t	time, s
T	temperature, K
u	velocity, m/s
x	penetration depth, m
y^*	mole fraction of solute A at interface
$Y_{A,G}$	mole ratio of solute A in the gas phase
Z	height of the column, m

Greek letters

μ	liquid viscosity, g/cm s
α	CO_2 loading, mol CO_2/mol amine
τ	contact time, s

1. Introduction

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. Among the GHGs, carbon dioxide (CO_2) is considered to be the major contributor due to its abundance [1]. Recently, more than 100 countries have agreed to mitigate the global warming and climate change problem 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 [2].

The absorption of CO_2 into reactive chemical solvents is one of the most promising technologies for capturing CO_2 due to its maturity, cost effectiveness, and capability of handling large amounts of exhaust stream [3,4]. However, it is generally accepted that energy penalty for solvent regeneration for CO_2 absorption process is large. In order to reduce the cost of CO_2 capture, the reduction of energy requirement for regeneration is crucial since it contributes to about 70% of the operating cost [5]. One of the key parameters for reducing regeneration cost is to use an effective solvent, which requires low energy for regeneration. In addition, the solvent should have fast reaction kinetics and high absorption capacity. Charkravarty et al. [6] first proposed a blended amines system by adding small amounts of primary (or secondary) amine to tertiary amine such as blended methyldiethanolamine (MDEA)–monoethanolamine (MEA) and blended MDEA–diethanolamine (DEA). The blended amines system was suggested in order to capitalize the performance of tertiary and primary (or secondary) amines on the low energy requirement for regeneration and high absorption capacity of tertiary amine, and the fast reaction kinetics of primary (or secondary) amine [5].

By comparing blended MDEA–MEA and MDEA–DEA solutions, it was observed by Dawodu and Meisen [7] that the equilibrium solubility of CO_2 in the blended MDEA–MEA is higher than that of MDEA–DEA at low CO_2 partial pressure. In addition, it was also found that the mixing ratio plays an important role on the equilibrium solubility of blended MDEA–MEA solutions in that the equilibrium solubility of CO_2 was found to be increased as the ratio of MEA in the blended solutions increased over the low CO_2 partial pressure range of less than 100 kPa. However, at the high CO_2 partial pressure, the equilibrium solubility of CO_2 in the blended MDEA–MEA solutions was found to be decreased as the ratio of MEA in the blended solutions increased [8,9]. The simple reaction rate of CO_2 absorption into the blended MDEA–MEA and MDEA–DEA at mixing ratio of 50 wt%/5 wt% at 296 K using stirred cell reactor was done by Gonzalez-Garza et al. [10] and Rivera-Tinoco and Bouallou [11]. They concluded that the CO_2 absorption rate of the blended MDEA–MEA is faster than that of MDEA–DEA. It is because MEA has faster reaction kinetics than that of DEA [12]. Thus, the blended MDEA–MEA would be considered to be suitable for the low pressure CO_2 capture such as flue gas from coal-fired power generation plant.

Another two important parameters for the amine based CO_2 capture process are reaction kinetics and mass transfer coefficient in packed column because they (i) directly affect the height of the absorption column and (ii) required for designing and simulating the absorption process [5,13]. Therefore, the studies on (i) reaction kinetics and (ii) mass transfer in packed column were widely investigated.

One of the very first investigations on reaction kinetics of CO_2 absorption into blended MDEA–MEA was done by Critchfield and Rochelle [14] using a stirred cell reactor. They successfully predicted the mass transfer rate from shuttle mechanism. Also, Versteeg et al. [15] performed the absorption experiment in the stirred cell reactor for several blended amines, including MDEA–MEA. The parallel reversible reaction based on both film and penetration theories were used to model the absorption process. They found that the predicted results from the developed model were in