



Experimental study of the kinetics of the homogenous reaction of CO₂ into a novel aqueous 3-diethylamino-1,2-propanediol solution using the stopped-flow technique



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HIGHLIGHTS

- Kinetics was experimentally studied using the stopped-flow technique.
- Establishing the VLE model and Brønsted relationship.
- DEA-1,2-PD has faster reaction rate than other conditional tertiary amines.
- The mechanism explains the full experimental data.

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ABSTRACT

In this work, the stopped-flow technique was used to determine the kinetic parameters in terms of pseudo first-order rate constants (k_0) for homogenous reaction of CO₂ into aqueous 3-diethylamino-1,2-propanediol (DEA-1,2-PD) solutions as temperature ranged from 293 to 313 K and amine concentrations ranged from 0.20 kmol/m³ to 1.00 kmol/m³. It was found that k_0 increased with increasing amine concentration and temperature. Both the base-catalyzed hydration and the termolecular models were applied to interpret the experimental data. The results showed that the predicted CO₂ absorption rates exhibited good agreement with experimental data with an absolute average deviation (AAD) of 5.7% and 3.8% with respect to base-catalyzed hydration and the termolecular model, respectively. Furthermore, the pKa of DEA-1,2-PD was experimentally determined over the temperature range from 298 to 318 K. The relationship between experimentally measured second-order reaction rate constants (k_2) and pKa was correlated using the Brønsted relationship. The results suggest that the Brønsted relationship for DEA-1,2-PD developed in this work can predict the reaction rate constant very well with an AAD of 0.8%.

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1. Introduction

The number of studies of the removal of carbon dioxide (CO₂) from gas streams generated by coal-fired power plants has exploded over the past two decades. The increased research attention comes as a result of the emerging problem of global warming

caused by the accumulation of greenhouse gases in the atmosphere. Carbon capture and storage (CCS), especially post-combustion capture (PCC) technologies, has been identified as a promising candidate for reducing the emission of CO₂, a major greenhouse gas. Normally, in processes using amine solvents, the capture and subsequent release of CO₂ requires large amounts of energy, owing to the reboiler duty for the desorption process. However, the captured CO₂ has important utilization value, for example in the food industry and, more importantly, in the oil and gas industry for CO₂-enhanced oil recovery (EOR). If this process is to be widely used, it is important that novel technologies be developed for it so that efficiency is high and energy consumption is minimized.

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Nomenclature

1DEA2P	1-diethylamino-2-propanol	K_i	chemical equilibrium constant for reaction i
1DMA2P	1-dimethylamino-2-propanol	$K_{a,DEA-1,2-PD}$	dissociation constant of conjugate acid of DEA-1,2-PD (mol/m^3)
3DMA1P	3-dimethylamino-1-propanol	MEA	monoethanolamine
A	Arrhenius constant ($\text{m}^3/\text{mol s}$)	MDEA	methyldiethanolamine
AAD	absolute average deviation	$M_{DEA-1,2-PD}$	molecular weight of DEA-1,2-PD
AEAA	2-((2-aminoethyl) amino) ethanol	M_{H_2O}	molecular weight of water
AMP	2-amino-2-methyl-1-propanol	$n_{0,DEA-1,2-PD}$	initial number of moles of DEA-1,2-PD.
AmH	amine	n_{HCl}	number of moles of HCl
B	base (amine, water or hydroxyl ion)	PZ	piperazine
DEA	diethanolamine	r_{CO_2}	overall CO_2 reaction rate ($\text{kmol/m}^3 \text{ s}$)
DEAB	4-diethylamino-2-butanol	R	universal gas constant ($0.008315 \text{ kJ/mol K}$)
DEA-1,2-PD	3-diethylamino-1,2-propanediol	T	temperature (K)
DEMEA	diethylmonoethanolamine	t	time (s)
DMMEA	dimethylmonoethanolamine	V_{total}	total liquid volume
E_a	activation energy (kJ/mol)	Y_{∞}	constant value of the signal (V) at equilibrium
k_0	observed pseudo first-order reaction rate constant (s^{-1})	$[\]$	concentration (Kmol m^{-3})
k_2	second-order reaction rate constant ($\text{m}^3/\text{kmol s}$)		
k_{H_2O}	reaction rate constant of reaction 8 ($\text{m}^3/\text{kmol s}$)		
k_{OH^-}	reaction rate constant of reaction 9 ($\text{m}^3/\text{kmol s}$)		
$k_{DEA-1,2-PD}^T$	termolecular reaction rate constant contributed by DEA-1,2-PD, ($\text{m}^6 \text{ kmol}^{-2} \text{ s}^{-1}$)	<i>Greek letters</i>	
$k_{H_2O}^T$	termolecular reaction rate constant contributed by H_2O , ($\text{m}^6 \text{ kmol}^{-2} \text{ s}^{-1}$)	ρ_{H_2O}	density of water

Among various CO_2 capture technologies for PCC, which include absorption, cryogenics distillation, and membrane separation, chemical absorption with amines is the most widely used technology. This is due to advantages in terms of the feasibility and maturity of the technology, and its operation cost and efficiency [1]. One of the most important factors for the development of this technology is the selection and/or development of effective solvents. These solvents are required to have good performance in many aspects, such as fast reaction rates, high mass transfer coefficient, high absorption capacity, low heat duty for regeneration, not easily degraded, and low corrosiveness [2,3].

Tertiary amines, which are considered to be reasonable solvents for blending with primary and secondary amines due to their high absorption capacity and low energy requirement for regeneration, have received increased attention recently. Tontiwachwuthikul et al. [4] developed a new tertiary amine, 4-diethylamine-2-butanol (DEAB) which exhibited good performance for CO_2 capture and has attracted the attention of many researchers. In earlier work, Sema et al. [5] and Liu et al. [6] researched the reaction kinetics of CO_2 with DEAB, using a laminar jet absorber and the stopped-flow technique, respectively. The results showed that the reaction rate of CO_2 absorption into DEAB was faster than for diethylmonoethanolamine (DEMEA), dimethylmonoethanolamine (DMMEA), and MDEA in terms of the forward rate constant k_2 . Moreover, it was also found that DEAB has a higher CO_2 absorption capacity and lower energy requirement for regeneration than conventional tertiary amines such as MDEA.

Recently, Chowdhury et al. [7] conducted a performance comparison study of 24 tertiary amines for CO_2 capture that included synthetic amines, conventional widely used amines and some novel amines. Absorption rate, CO_2 absorption capacity, cyclic CO_2 capacity, and heat of reaction were experimentally determined for each absorbent. The results were compared to MDEA and seven amine absorbents with faster kinetics, higher cyclic capacities and lower reaction heat were identified. 1-diethylamino-2-propanol (1DEA2P), one of the tested amines, whose chemical structure is similar to that of DEAB, was then comprehensively investigated for its reaction kinetics by Liu [8], using the stopped-flow

technique. The 1DEA2P molecule contains a 2-propanol group in the place of the 2-butanol group in DEAB. According to the work of Liu, the capacity of CO_2 absorption into 1DEA2P was higher than that of MEA, MDEA, AMP and DEAB at 313 K but the CO_2 absorption rate in 1DEA2P was found to be slower than that in DEAB. The results correspond to the work of Couchaux et al. [9], who focused their discussions on pK_a and the reaction mechanism as well as the kinetics of a series of similarly structured amines.

DEA-1,2-PD, another new tertiary amine of the seven amines identified by Chowdhury, whose chemical structure is similar to that of 1DEA2P and DEAB, showed excellent enhancement of absorption rate and CO_2 absorption capacity compared with MDEA as well as better performance in terms of the reaction rate and cyclic capacity than the other six amines. One more hydroxyl group is attached to the hydroxyalkyl in the DEA-1,2-PD molecule than that in 1DEA2P, providing for a reduction of the partial pressure and increasing the water solubility of the DEA-1,2-PD. It was also found that less energy was required for the regeneration of DEA-1,2-PD than for 1DEA2P, MDEA, DEA and MEA. However, no investigation of the kinetics parameters or the vapor-liquid equilibrium (VLE) model of CO_2 absorption into DEA-1,2-PD solutions had been carried out. Hence, a broad knowledge of these parameters of DEA-1,2-PD is essential in order to get a full picture of the performance of DEA-1,2-PD solvent.

On the other hand, reaction kinetics is also an essential parameter required for simulation of the absorption process and design of the absorption column [5]. So, in this work, the stopped-flow technique, a direct method, was applied to measure the kinetics data of DEA-1,2-PD. Many amine systems [10–15], including primary amine, secondary amine, tertiary amine, and the mixture of these amines, have been successfully studied through the stopped-flow technique because of its advantages. It was found that the experimental kinetics values obtained from the stopped-flow technique compared favorably with those obtained from the indirect techniques. For example, Saha and Bandyopadhyay [16] who investigated the kinetics of AMP at 294–318 K by gas absorption study using a wetted-wall column found that the reaction was first order in amine. Their results agreed closely with those of Alper [10] which

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