



A study of structure–activity relationships of commercial tertiary amines for post-combustion CO₂ capture



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HIGHLIGHTS

- Ethyl group is beneficial for tertiary amines of CO₂ absorption.
- The existence of side carbon chain may promote the activity of tertiary amine.
- Hydroxyl group reduces the equilibrium CO₂ solubility, k_2 and pKa.
- Heterocyclic structure decrease the equilibrium CO₂ solubility, k_2 and pKa.
- Hydroxyl group results in higher CO₂ absorption heat.

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ABSTRACT

This work examined the relationship between the structure of various commercial tertiary amines and their activity in CO₂ absorption/desorption in terms of rate of CO₂ absorption, equilibrium CO₂ loading, pKa and heat of CO₂ absorption in order to establish possible guidelines for selection of tertiary amine components for amine blends. Results show that any electron donating group linked directly to the nitrogen atom increases their reactivity with CO₂. In addition, the presence of steric hindrance effect and good water solubility also show enhancements in activity. In contrast, the existence of a hydroxyl group leads to a decrease in all the activity of the tertiary amine. The heat of CO₂ absorption of tertiary amines, which is closely related to the regeneration energy, can be reduced by decreasing the number of hydroxyethyl groups or by positing the hydroxyl group at the proper carbon relative to the nitrogen atom.

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1. Introduction

Global warming poses one of the most serious global challenges, which may be blamed for disasters such as glacier melting, severe weather, storms and droughts. These make it necessary to prevent global warming and the rising average temperature. The contributor to global warming is greenhouse gas (GHG) emissions, and the most abundant GHG due to human activities is carbon dioxide (CO₂). With the rapid development of global economies, increasingly large amounts of fossil fuel is used especially for producing electricity and other forms of energy [1,2]. The large consumption of fossil fuel leads to the release of large amounts of CO₂ into air which leads to increasing concentration of CO₂ in the atmosphere. Since CO₂ has a stable chemical structure and

hardly reacts with other materials in the atmosphere to cause its decay, it is not possible to use natural means to cause its elimination. Consequently, it becomes necessary to find other efficient methods to either remove it from or prevent further emission into the atmosphere. One of the most mature technologies for capture of CO₂ to prevent its release into the atmosphere is post-combustion capture from large point industrial sources using chemical solvents such as aqueous amines.

A large number of amine-based solvents have been investigated for their performance in CO₂ absorption in terms of CO₂ absorption rate, CO₂ solubility and heat of regeneration. Monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) are examples of conventional primary, secondary and tertiary amines, respectively, which are commercially available and have been used as common absorbents in industrial CO₂ capture processes. However, there are still some drawbacks in their use as absorbents. Depending on the type, such drawbacks include

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Nomenclature

DMEA	dimethylmonoethanolamine	k_2	second-order reaction rate constant ($\text{m}^3/\text{mol s}$)
DEEA	diethylmonoethanolamine	T	temperature (K)
TEA	triethanolamine	P_{CO_2}	CO_2 partial pressure
TREA	triethylamine	α	CO_2 loading
MDEA	N-methyldiethanolamine	Q	reboiler duty
1DMA2P	1-dimethylamino-2-propanol	ΔH_{des}	desorption heat
3DMA1P	3-dimethylamino-1-propanol	$-\Delta H_{\text{abs}}$	absorption heat
1-(2-HE)-PRLD	1-(2-hydroxyethyl)-pyrrolidine	$Q_{\text{H}_2\text{Ogen}}$	the heat required to generate water vapor
1-(2-HE)-PP	1-(2-hydroxyethyl)-piperidine	Q_{sen}	the sensible heat
DEAB	4-diethylamino-2-butanol		
DEA-2P	1-diethylamino-2-propanol		

amine losses caused by volatilization and degradation, high energy consumption for CO_2 regeneration, severe corrosion of pipes, low rates of absorption, etc. [3]. These problems increase the cost of CO_2 capture as well as affect the capture operation thereby tending to limit the usage of amines. According to Shakerian et al. [4], only a few solvents are available to facilitate the capture of CO_2 on a large scale. Thus, finding amines that show high CO_2 absorption rate and capacity, as well as requiring less energy for regeneration for industrial application is considered as a significant contribution which can improve post-combustion CO_2 capture [5]. In particular, primary and secondary amines have faster reaction rates with CO_2 than tertiary amines while tertiary amine shows higher solubility for CO_2 because of these amines use different reaction pathways when they react with CO_2 . Also, tertiary amines are attractive as absorbents because they act as catalyst to solely generate bicarbonates instead of carbamates when they react with CO_2 [6–9] thereby resulting in low heat duty for solvent regeneration. The stoichiometric absorption of CO_2 for tertiary amines can reach 1 mol CO_2 /mol amine when the bicarbonate is formed with CO_2 while the stoichiometry of a single reaction that forms a carbamate for primary and secondary amines is limited to only 0.5 mol CO_2 /mol amine [10]. A new class of amines called sterically hindered amines has been shown to have high reaction rate with CO_2 as well as high CO_2 loading capacity. This is because the steric effect reduces the stability of carbamates formed by reaction of the amine with CO_2 [11,12]. As is well known, the cost for providing energy to regenerate rich amines takes roughly 70–80% of the operating cost of the CO_2 capture process [13], which makes regeneration energy consumption to be a vital obstacle for wide application of amine-based CO_2 capture [14,15]. The energy requirement for stripping is made up of three parts: heat of CO_2 desorption, water vaporization heat and sensible heat. For the MEA absorption system, the high CO_2 reaction heat with MEA (85.6 kJ/mol CO_2) is related to the high energy requirement for stripping [16]. Although DEA shows a lower heat of reaction with CO_2 (76.3 kJ/mol CO_2), but the energy required to break the stable carbon–nitrogen bond of carbamate is still huge [16]. However, because aqueous tertiary amine forms a bicarbonate instead, it is much easier to separate CO_2 from their rich amines with less energy requirement [17]. On the other hand, the low CO_2 absorption rate of tertiary amines is the main limitation for the application of tertiary amines as the sole solvent for industrial CO_2 absorption processes.

Currently, many efforts have been made on amine screening to figure out an ideal amine. According to Li et al. [18], a total of 1297 patents are involved in CO_2 capture as solid sorbents, solvents or membranes of which approximately 37.5% are solvents (involving novel solvents and mixed solvents) [18]. Most screening works require a large amount of experimental data as well as specialized apparatus to evaluate amine performance for CO_2 capture, which

can be time-consuming and requiring substantial material resources. Consequently, a pre-evaluation of amines for CO_2 capture is very necessary in order to determine the potential commercial amine components for blending or for synthesis of novel amines. This pre-evaluation method should be established with guidelines that relate an amine performance to its molecular structure.

Extensive research has been conducted to study the characteristics of absorbents. According to Chakraborty et al. [19], the methyl group substitution at the α carbon changes the electronic environment of nitrogen. The interaction of π and π^* methyl group orbitals with the nitrogen lone-pair orbital decreases the charge at the donor site, nitrogen, which makes it a softer base thereby weakening the N–H bond of the amine [19]. Puxty et al. [20] screened amines with good performance for CO_2 absorption capability from 76 novel amines. This author pointed out that a hydroxyl group within 2 or 3 carbons of the nitrogen while it is free to move improves the capability of CO_2 absorption. It has been suggested that a stable intramolecular hydrogen bond exists between nitrogen and the hydroxyl group to form a five or six member ring structure, thereby destabilizing the formation of the carbamate, and resulting in higher CO_2 absorption ability [20]. Singh et al. showed structure-activity relationships for amine-based CO_2 absorbents which takes into account the effect of chain length, side chain, and number of functional groups. Much of the research has mainly focused on primary and secondary amines [21,22]. Chowdhury et al. screened tertiary amine-based CO_2 absorbents (i.e. dimethylamino-2-propanol (1DMA2P), diethylamino-2-propanol (DEA-2P), dimethylethanolamine (DMEA), etc.) with respect to absorption/desorption rates, vapor-liquid equilibrium and heat of reaction from twenty-five tertiary amines [23]. Accordingly, there exists a relationship between amine molecular structure and CO_2 absorption activity. Terrence and Donaldson [6] provided a mechanism for tertiary amine reacting with CO_2 where the pair of unshared electrons on the nitrogen atom enables the amine to act as general base catalysts for other reactions (Fig. 1). Therefore, it is clear that chain length, existence of functional groups, and position of the functional group in the amine determine the activity of the amine in reacting with CO_2 by changing the electronic environment of the nitrogen atom.

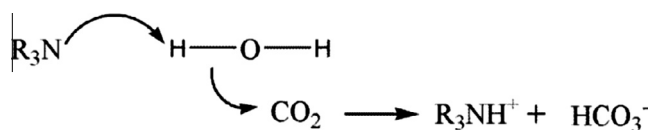


Fig. 1. Base catalysis mechanism for tertiary amine solvents reacting with CO_2 .

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