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CO₂ CAPTURE BY ABSORPTION IN ACTIVATED AQUEOUS SOLUTIONS OF N,N-DIETHYLETHANOLOAMINE

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Abstract: The CO₂ absorption process using aqueous amine solutions has been the most promising technique used for the removal of CO₂ from gas streams in energy sector. In recent years, many researchers tested solutions which are composed of several compounds: a slow reacting tertiary amine- and a fast amine acting as an activator. In this paper, the CO₂ absorption rate in an aqueous solution of N,N-diethylethanolamine (DEEA) and activated solutions DEEA is investigated experimentally. The activators considered are sterically hindered amines: 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1,3-propanediol (AMPD) and N-methyl-1,3-propanediamine (MAPA) from the group of polyamines. The experiments were conducted over the temperature range of 303-333 K and the total amine concentration of 2 M. From the CO₂ absorption experiments into mixed aqueous solutions of DEEA and MAPA, it was found that the addition of small amounts of MAPA into aqueous DEEA solutions has a significant effect on the enhancement of the CO₂ absorption rate. The application of hindered amines: AMP or AMP as activators resulted in a marginally improvement of the absorption rate of CO₂.

Keywords: CO₂ capture, absorption kinetics, N,N-diethylethanolamine, amine blends

Introduction

The absorption of CO₂ in the amine solutions is one of the most effective method of capturing carbon dioxide from flue gases produced during the combustion of conventional fuels in the energy sector [1]. Nowadays, aqueous monoethanolamine (MEA), which is a primary amine, has been most commonly used for gas purification [2-4]. Primary and secondary amines react to form carbamates via a fast reaction with CO₂. However, the heat of absorption associated with the carbamate formation is high. Consequently, this results in high solvent regeneration costs [5-7]. Numerous studies are performed to replace the MEA solution with new solvents which are relatively easy to regenerate and have a high capacity to absorb CO₂. These requirements are met by tertiary amines which do not form carbamates by reaction with CO₂, have a low heat of absorption, and greater absorption capacity than the primary and secondary amines. Their disadvantage is a low CO₂ reaction rate. There is a growing interest in recent times to use blended amine solvents, which

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consist of a mixture of an activator with a tertiary amine. Some of the hindered amines proposed for CO₂ absorption are 2-amino-2-methyl-1-propanol (AMP) and amino-2-methyl-1,3-propanediol (AMPD), which can be used as additives to reduce the cost of regeneration of absorbing solution or N-methyl-1,3-propane-diamine (MAPA), a reactive polyamine, in order to accelerate the overall absorption rate, while taking advantage of a tertiary amine as a base solvent [8].

The aim of this paper was to measure the CO₂ absorption rate in aqueous N,N-diethylethanolamine (DEEA) solutions and determine the kinetics of the reaction of CO₂ with DEEA. Additionally, a quantitative assessment of the impact of activators: AMP, AMPD and MAPA on the overall CO₂ absorption rate into DEEA blended solutions was made. The other authors [9] proved that the concentrated solution of DEEA+MAPA forms a two-phase system under certain conditions and may be a preferred alternative to the commonly used MEA in terms of the energy demand for desorption. The performance of DEEA+AMP and DEEA+AMPD blends has not been investigated so far.

The selected literature data on the kinetics of the CO₂ reaction with DEEA, which is a tertiary amine are given in Table 1. The k_1 presented in Table 1 is expressed according to the reaction mechanism described by Eq. (6).

Table 1

The kinetic rate constants of CO₂ in aqueous DEEA at 303 K

k_1 [m ³ /(mol·s)]	Experimental technique	Literature
0.070	Stirred cell reactor	[10]
0.059	Stirred cell reactor	[11]
0.115	Stopped flow	[12]

CO₂ absorption in aqueous amine solution is accompanied by several chemical reactions which are responsible for the CO₂ capacity and the mass transfer rate.

The following reactions occur when CO₂ is absorbed in aqueous solutions:



Equation (1) describes the physical dissolution of gaseous CO₂ into a liquid.

All amines undergo the protonation reaction:



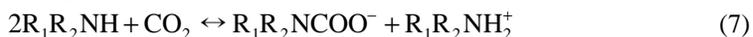
Other reactions are distinct for different kind of amines (tertiary, primary and secondary, polyamines and sterically hindered amines).

Tertiary amines (R₁R₂R₃N) participate in a base-catalyzed CO₂ hydration leading to formation of bicarbonate ions and the protonated amine [8]:



The main advantages of tertiary amines are their relatively CO₂ loading capacity of about 1 (mol of CO₂/mol of amine) and a small enthalpy of reaction with CO₂. However, the formation of bicarbonate ion is relatively slow which limits the CO₂ absorption rate.

The primary and secondary alkanolamines (R₁NH₂; R₁R₂NH) react directly and reversibly with CO₂ forming stable carbamates (R₁NHCOO⁻; R₁R₂NCOO⁻):



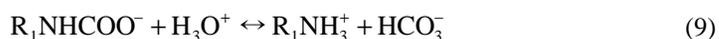
The formation of carbamate increases the reaction rate but limits the loading to 0.5 (mol of CO₂/mol of amine). The formation of carbamate is associated with a high heat of reaction, contributing to higher energy consumption for reversing the CO₂ reaction with amine.

A sterically hindered amine is defined structurally as:

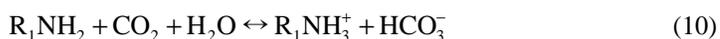
- a primary amine in which the amino group is attached to a tertiary carbon atom;
- a secondary amine in which the amino group is attached to a secondary or a tertiary carbon atom [13, 14].

In the present work, two sterically amines *i.e.* 2-amino-2-methyl-1-propanol (AMP) and amino-2-methyl-1,3-propanediol (AMPD) are tested as activators of tertiary DEEA.

The major reactions between a sterically hindered amine and CO₂ are the formation of carbamate and bicarbonate, as described in Eqs. (8) and (9) [15]:



Formation of carbamate is unfavorable and relatively slow due to the increased hindrance around the amino group. This finding was supported by several authors [15-17]. The authors indicated that hindered carbamate is thermodynamically unstable and in the CO₂ loaded amine solution there is much less carbamate formed than bicarbonate and carbonate species. Therefore, the reaction mainly proceeds via bicarbonate production according to:



As a result, the overall reaction rate for sterically hindered amines is usually smaller than for primary and secondary amines, and higher than for tertiary amines.

Polyamines have at least two amine functionalities and can be expected to have a high capacity for binding CO₂ and a high reaction rate. The mechanism of the CO₂ reaction with polyamines cannot be generalized as it depends on the structure of the specific amine. N-methyl-1,3-propane-diamine (MAPA) used in this study has got two amine groups. In the present case, CO₂ reacts simultaneously with both amine groups, forming primary (MAPACOO_p⁻) and secondary (MAPACOO_s⁻) carbamates.

Experimental set-up and methodology

In this work, the absorption kinetics of CO₂ in N,N-diethylethanolamine (DEEA) aqueous solutions and in DEEA mixed with hindered amines containing a primary amino group (AMPD, AMP) and a polyamine (MAPA) was studied. The molecular structures of the amines investigated in this work are shown in Figure 1.

The chemicals used were: DEEA (Alfa, > 99%), AMPD (Sigma-Aldrich, > 99%), AMP (Sigma-Aldrich, > 97%), MAPA (Sigma-Aldrich, > 98%). Experimental conditions are presented in Table 2.

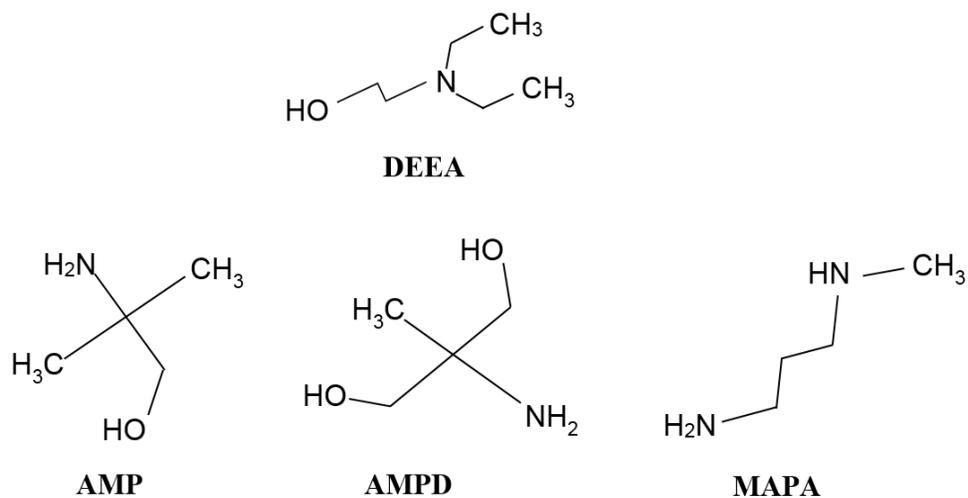


Fig. 1. Chemical structures of studied amines

Table 2

Parameters of CO₂ absorption experiments

The composition of the aqueous solutions	Concentration [M]	<i>T</i> [K]
DEEA	2	303, 318, 333
DEEA+AMP	1.5+0.5	303
DEEA+AMD	1.5+0.5	303
DEEA+MAPA	1.8+0.2	303



Fig. 2. The CPA 201 reactor (Syrris Ltd)

The measurements of the kinetics of CO₂ in standalone DEEA aqueous solutions and activated DEEA solutions were carried out in a fully automated reaction calorimeter (CPA 201, SyrrisLtd), which is a cylindrical, double-walled glass vessel with a plane, horizontal gas-liquid interface (Fig. 2). The reactor was equipped with baffles, gas and liquid phase stirrers that are mounted on the same shaft. A Peltier element that is mounted inside the bottom of the reactor enables effective heating and cooling of the system with an accuracy of $\pm 0.1^\circ\text{C}$. All operating conditions including a gas pressure, a reactor temperature, a stirring speed and the heat flow rate were recorded every 2 seconds. The present reaction calorimeter is analogous to the measurement system used in our previous studies [10].

Studies of the absorption kinetics of CO₂ in aqueous DEEA solutions and DEEA blends with AMP, AMPD and MAPA are based on the fall-in-pressure technique during the batch absorption of CO₂. The measurements were carried out in isothermal conditions. The experiments for 2 M DEEA solutions were conducted at the temperature range of 303-333 K. The solution concentrations for activated amine were the following: 1.8 M DEEA + 0.2 M MAPA, 1.5 M DEEA + 0.5 M AMP and 1.5 M DEEA + 0.5 AMPD. Measurements for activated amine solutions were carried out at 303 K.

The procedure was the same as described in detail in other works [10, 18]. The pure CO₂ was introduced into the reactor in a very short time. The liquid was previously loaded, degassed and thermostated at the desired temperature. The absorption was initiated by switching on the stirrers. The process was monitored by recording the pressure decrease vs time. The CO₂ absorption rate (N_{CO_2} [mol m⁻²s⁻¹]) was calculated from the experimental data by the mass balance in the reactor gas phase according to:

$$N_{\text{CO}_2} = -\frac{v_G}{R T A} \frac{dp_{\text{CO}_2}}{dt} \quad (11)$$

where v_G is a gas phase volume in the reactor [m³], A is a gas-liquid interfacial area [m²], R is a gas constant [J/(mol·K)], T is a temperature [K], p_{CO_2} is a CO₂ partial pressure [Pa], t is a time [s].

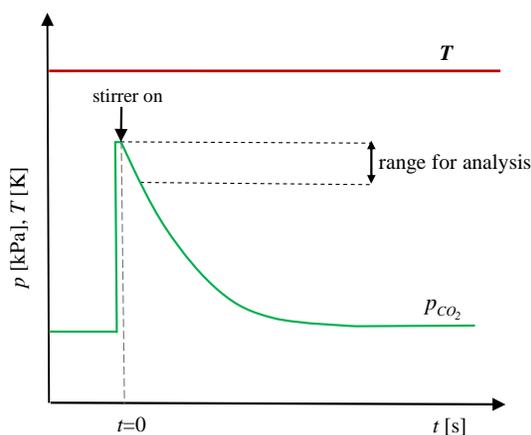


Fig. 3. Experimental procedure (fall in pressure technique) - for batchwise mode of operation with respect to the gas phase

In the present experiments, the initial CO₂ partial pressure was below 60 kPa. All experimental runs were performed at a constant stirring speed of 120 rpm. The typical run of the absorption experiment is shown in Figure 3. As can be seen, after switching on the stirrer, the pressure in the reactor begun to decrease due to absorption of CO₂ into the solvent. We analyzed the first 30 seconds of the run since we calculated the CO₂ absorption rate at the initial stage of the process, when the liquid bulk was not loaded with CO₂.

Results and discussion

Studies of the absorption kinetics of CO₂ in 2 M DEEA solutions were conducted at the temperature range of 303-333 K in order to determine the kinetics of a chemical reaction in the liquid phase. The reaction of CO₂ in aqueous solutions of N,N-diethylethanolamine proceeds according to equation (12)



DEEA promotes the CO₂ hydrolysis reaction, which results in bicarbonate formation under the mechanism of base-catalyzed hydration as described in the Theory section.

According to Kierzkowska-Pawlak and Chacuk [19], the total rate of the forward reaction of CO₂ in aqueous tertiary amines solutions is mostly interpreted using a second order rate expression:

$$r_{\text{CO}_2\text{-DEEA}} = k_1[\text{DEEA}][\text{CO}_2] = k_{ov}[\text{CO}_2] \quad (13)$$

where $r_{\text{CO}_2\text{-DEEA}}$ is a reaction rate [$\text{mol}\cdot\text{m}^{-3}\text{ s}^{-1}$], k_{ov} denotes the overall reaction rate constant (observed pseudo-first order [s^{-1}]) which is expressed by Eq. (14), $[\text{CO}_2]$ is a molar concentration of CO₂ [kmol/m^3], $[\text{DEEA}]$ is a molar concentration of N,N-diethylethanolamine [kmol/m^3].

$$k_{ov} = k_1[\text{DEEA}] \quad (14)$$

where k_1 is a second order rate constant [$\text{m}^3\text{mol}^{-1}\text{s}^{-1}$].

The rate of CO₂ mass transfer in the conducted experiments can be expressed as [10, 11]:

$$N_{\text{CO}_2} = \sqrt{k_{ov}D_{\text{CO}_2}}[\text{CO}_2]_i \quad (15)$$

where D_{CO_2} is a CO₂ diffusion coefficient in the liquid phase [m^2s^{-1}], $[\text{CO}_2]_i$ is the interfacial concentration of CO₂ and can be obtained from Henry's law:

$$[\text{CO}_2]_i = \frac{P_{\text{CO}_2}}{He_{\text{CO}_2}} \quad (16)$$

where He_{CO_2} is a Henry's laws constant of CO₂ in the solvent [$\text{kPa}\cdot\text{m}^3/\text{mol}$].

It should be noted that Eq. (15) can be only applied for the fast, pseudo-first-order reaction regime where the absorption rate does not depend on the hydrodynamic conditions [10].

Hence, the rate of mass transfer can be expressed as follows:

$$N_{CO_2} = \frac{\sqrt{k_{ov} D_{CO_2}}}{He_{CO_2}} p_{CO_2} \quad (17)$$

The solubility of CO₂ can be estimated indirectly from the so-called “CO₂/N₂O analogy” [10]. The diffusion coefficient of CO₂ (D_{CO_2}) and the values of Henry’s law constant of CO₂ (He_{CO_2}) in an amine aqueous solution were estimated from the correlations previously used by Kierzkowska-Pawlak [10].

The results of CO₂ absorption rate in 2 M DEEA solutions measured under different partial pressures of CO₂ at the temperature range of 303–333 K allowed to determine the observed reaction rate constants (k_{ov}) from Eq. (17). The second order kinetic rate constants (k_1) were calculated from Eq. (14) using the estimated values of k_{ov} .

Regression of k_1 values obtained at different temperatures gave the following Arrhenius equation:

$$k_1 = 9.66 \cdot 10^5 \exp\left(\frac{-4953}{T}\right) \quad (18)$$

The k_1 rate constants evaluated in the present study were compared with the literature data in Figure 4.

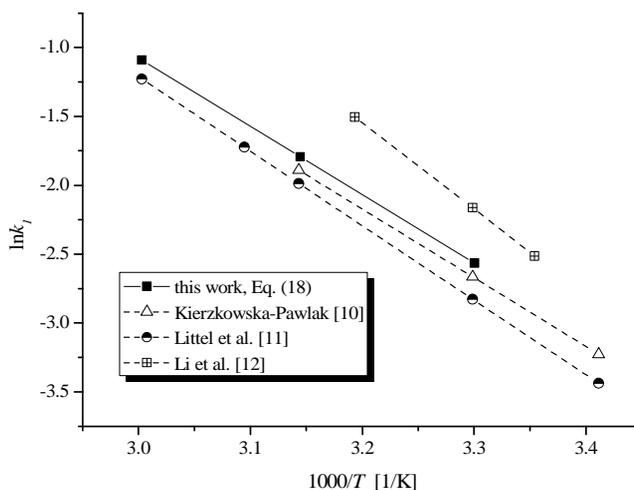


Fig. 4. Comparison of the obtained k_1 [$m^3 mol^{-1} s^{-1}$] rate constants for the CO₂ reaction in aqueous DEEA with literature data

As can be seen, the kinetics results vary between different researchers. The large discrepancy is observed when comparing the obtained k_1 with the values of Li et al. [12], determined by using a different measurement technique (the stopped flow method). This method differs from the commonly used ones since the mass transfer from gas to liquid was not considered in it. The values of k_{ov} were determined automatically by fitting the

exponential function to the measured conductance of the solution over the whole time span of the reaction taking place entirely in the liquid phase. Such a simplified interpretation may be one of the reasons for the observed inconsistency. However, the second order rate constants determined in this study show good agreement with the data of Littel et al. [11], who performed the measurements by using the similar experimental technique as in this work. Furthermore, the present results are also very similar to our previous data determined in the analogous measurement system [10]. The good compatibility of literature data [10, 11] with the current study confirmed the correctness of the performed experiments and data analysis.

Table 3
The pseudo-first-order reaction rate constant (k_{ov}) for AMP, AMPD, MAPA and DEEA at 303 K

Amine	Concentration [M]	k_{ov} [1/s]	Experimental technique	References
AMP	0.5	364	Stirred-cell reactor	[20]
AMPD	0.5	73	Wetted wall column	[2]
MAPA	0.2	9451	String of discs contactor	[21]
DEEA	2	154	Stirred-cell reactor	this work
	1.8	138		
	1.5	115		

The results of the experimental CO_2 absorption rates in the blended DEEA solutions with MAPA, AMP and AMPD are shown in Figure 5. In order to interpret the obtained data, a summary of a literature review for the observed reaction rate constants (k_{ov}) for all investigated amines is given in Table 3.

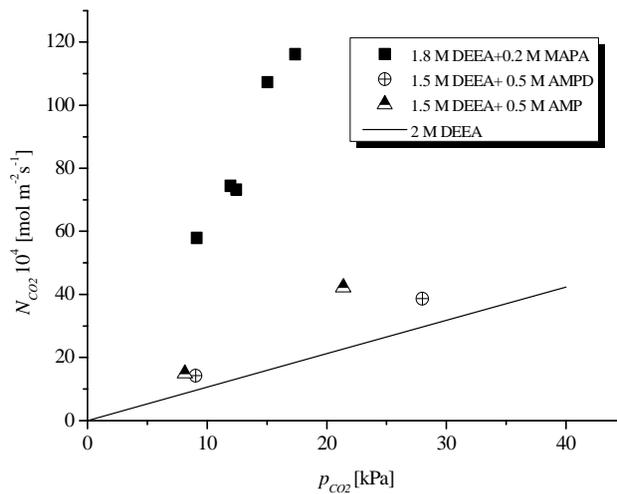


Fig. 5. CO_2 absorption rate into aqueous DEEA solutions activated with AMP, AMPD and MAPA at 303 K

According to the experimental data presented in Figure 5, the CO₂ absorption rates in DEEA activated solutions are higher than that in the standalone DEEA for the same overall amine concentration. Furthermore, the enhancement of MAPA on mass transfer is much larger than that of AMP and AMPD. The absorption rate determined in the mixture of 1.8 M DEEA+0.2 M MAPA was about 5-fold higher than the rate for the 2 M DEEA. Activating a tertiary amine solution with AMP at a concentration of 0.5 M, which reacts quickly with CO₂ forming unstable carbamates, resulted in a 1.4-fold enhancement of CO₂ absorption rates, while the effect of addition of AMPD was less pronounced.

The observed trends can be explained by comparing the individual overall rate constants for DEEA, MAPA, AMP and AMPD at 303 K, which were estimated for the applied concentrations. Obviously, the effect of MAPA resulted in a substantially enhancement of the CO₂ absorption rate since the k_{ov} of MAPA with CO₂ is considerably higher than that of AMP and AMPD. The overall reaction rate constant of AMP is over twice as that of AMPD, and therefore, the activated DEEA+AMP solution induced a larger enhancement as compared with the DEEA+AMPD activated solution.

The analysis of the activated mechanism was proposed by Lu et al. [22]. According to the so-called “shuttle mechanism”, a fast reacting activator rapidly reacts with CO₂ near the gas-liquid interface. The reaction product (e.g. the carbamate) diffuses into the liquid bulk and it dissociates, converting its CO₂ into carbonate and releasing H⁺, and the activator is regenerated. The H⁺ ion reacts with DEEA in the liquid bulk, and the regenerated activator returns to the liquid film near the gas-liquid interface to react with freshly-absorbed CO₂. The action of the activator is as a carrier of CO₂, which accelerates the CO₂ mass transfer rate.

Conclusions

The kinetics of CO₂ reaction with DEEA and activated solutions DEEA were studied in this work. The present results of the second-order rate constant of CO₂ reaction in DEEA aqueous solutions showed good agreement with the data of Littel et al. [11] and Kierzkowska-Pawlak [10] who determined the kinetics by using a similar experimental technique. However, the second-order rate constants that were measured by Li et al. [12] by using the stopped flow technique are higher than the present values.

The rates of CO₂ absorption in different amine blends were examined and it was found that MAPA is the best activator for DEEA solutions. The absorption rate of CO₂ in a solution of 1.8 M DEEA + 0.2 M MAPA was about 5-fold higher than in the 2 M DEEA solution. By using AMP and AMPD as activators, no significant acceleration of the CO₂ mass transfer was observed. The present work shows that DEEA+MAPA blend can be an attractive solvent for CO₂ capture from the flue gases.

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