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## Kinetics of carbon dioxide absorption by nonaqueous solutions of promoted sterically hindered amines

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### Abstract

The mechanism and kinetics of CO<sub>2</sub> capture using piperazine (PZ) promoted nonaqueous solutions of 2-amino-2-methyl-1,3-propanediol (AMPD) and 2-amino-2-ethyl-1,3-propanediol (AEPD) were investigated by stopped-flow technique. The termolecular mechanism was used to model the kinetics of the reactions. AMPD or AEPD like other sterically hindered amines absorbs CO<sub>2</sub> in an equimolar ratio that is significantly higher than that of monoethanolamine (MEA). However, the steric hinderance results in decreased reaction rate as in the case of AMPD and AEPD. The reaction can be promoted by addition of small amounts of cyclic polyamines, such as PZ or its derivatives. Our results show clearly that nonaqueous solutions of AMPD and AEPD can achieve reaction rates comparable to commercial systems by the addition of small amounts of PZ.

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## 1. Introduction

The increase in greenhouse gas emissions from fossil fuel combustion over the past century is known to be part of the cause of global warming [1]. Among greenhouse gases, CO<sub>2</sub> is the primary contributor to the problem due to its high abundance, and thus it is a major target for reduction. The conventional technology to capture CO<sub>2</sub> on large scale is the absorption/desorption process, in which aqueous solutions of alkanolamines (specifically, 30 wt. percent monoethanolamine (MEA)) are frequently used as solvents [2]. This process is energy-intensive and costly with other side effects, hence alternative and affordable solvents or technologies for CO<sub>2</sub> capture are desired. In principle, an optimized CO<sub>2</sub> absorber/desorber system should have high CO<sub>2</sub> loading to decrease the solvent circulation and high reaction rate to enhance CO<sub>2</sub> absorption rate so that the unit is compact. However, aqueous alkanolamine solutions have low CO<sub>2</sub> loadings (much less than theoretical maximum of 0.5 mol CO<sub>2</sub>/mole amine) due to stable carbamate formation [3]. In order to combat this deficiency, sterically hindered amines have been introduced which can have loadings as much as 1 due to unstable carbamate ion [4]. However, steric hinderance -while increasing the loading capacity- often decreases the rate of reaction with CO<sub>2</sub> [5-8]. In fact, it is rare to find a sterically hindered amine with sufficiently fast reaction and 2-amino-2-methyl-1-propanol (AMP) could be considered as the only exception. Another approach is to use highly active amine promoters such as cyclic diamines especially piperazine (PZ) to compensate the rate loss due to steric hinderance. Compared to MEA, PZ has a faster reaction rate, higher absorption capacity and higher resistance to thermal and oxidative degradation [9-11]. In addition, compared to aqueous systems, the use of nonaqueous systems (i.e., ethanol system or methanol system) is considered to be a promising alternative method for CO<sub>2</sub> capture, due to high solubility and capacity, low corrosiveness and low energy consumption for the regeneration of used solvents [12-15]. To that effect, solution of two sterically hindered amines namely, 2-amino-2-methyl-1,3-propanediol (AMPD) and 2-amino-2-ethyl-1,3-propanediol (AEPD) in ethanol (or 1-hexanol) was investigated and piperazine (PZ) was used as a promoter. Interest in AMPD and AEPD comes from the fact that both of them can be produced from renewable sources, that is from 1,2 propanediol which is abundant as a side product of biodiesel process. Recently, it was reported that biodiesel derived glycerol could be utilised as a renewable feedstock for replacing fossil-derived chemicals. Catalytic conversion of glycerol to value-added chemicals such as propanediols (1,2-PDO, 1,3-PDO) are of great importance [16,17]. As for the promoter, PZ and PZ derivatives are good candidates for promoting the reaction rate both in aqueous and nonaqueous systems when sterically hindered amines are employed for carbon dioxide capture [10].

Reaction kinetics is a critical parameter to predict the efficiency of the CO<sub>2</sub> absorption. There are several techniques for the investigation of reaction kinetics such as stirred cell, laminar jet absorber, wetted sphere and stopped-flow. Among these techniques, stopped-flow, a direct method, has been widely used due to its characteristics, such as the large coverage of reaction rates and reproduceable experiment data [18]. Therefore, in this work, the mechanism and kinetics of CO<sub>2</sub> capture using PZ as an activator to AMPD and AEPD in ethanol were investigated by stopped-flow technique. Termolecular mechanism was used to model the kinetics of the system as will be described within the following text.

## 2. Experimental Methods

### 2.1. Reagents

PZ of purity  $\geq 99.0\%$  was supplied by Sigma-Aldrich (St. Louis, MO). Sterically hindered amines, AMPD and AEPD of purities  $\geq 99.8\%$ , and ethanol of purity  $\geq 99.9\%$  were supplied by Merck (Darmstadt, Germany) and J.T. Baker, respectively. These reagents were used without further purification. Carbon dioxide with a purity of 99.9% was supplied by Linde (Munich, Germany). The experiments were carried out in ethanol using amines of concentrations 0.50 kmol/m<sup>3</sup> of AMPD and AEPD promoted by 0.05–0.25 kmol/m<sup>3</sup> of PZ, at 298 K.

## 2.2. Kinetic Measurements

The standard stopped flow apparatus (model SF-61SX2; Hi-Tech Scientific, Salisbury, UK) with a conductivity detector is a direct standard technique used for the kinetic study of amine–CO<sub>2</sub> reaction systems. The equipment is made up of four main units: a sample handling unit, a conductivity detection cell, an A/D converter, and a microprocessor unit. The entire flow circuit, with the exception of the stop/waste syringe, is enclosed in a thermostat and maintained at a constant temperature by an external water bath within  $\pm 0.1$  K. During an experimental run, a fresh solution of CO<sub>2</sub> was loaded into one syringe and a fresh solution of amine was loaded into the other. “Kineticasyst” software was used to activate the pneumatically controlled drive plate, which pushes the solutions accurately in equal volumes into the conductivity detection cell through a mixing loop. For each experimental run, equal volumes of solution were suddenly pushed into and mixed in the stopped flow mixer cell; the flow was stopped for the reaction to occur. In the conductivity cell, solutions react to generate ions that conduct electricity through platinum electrodes placed across the cell. The conductivity detection system directly measures the intrinsic rate of the rapid homogeneous reaction. The circuit measures the conductivity change and gives an output voltage directly proportional to the solution conductivity. The reaction software (kinetic studio) automatically calculates the observed pseudo–first-order-rate constant ( $k_o$ ) based on least square regression and displays the same at the microprocessor’s unit monitor. To satisfy the pseudo–first-order condition, concentration ratios of the amine mixture (AMPD or AEPD promoted by PZ) to that of CO<sub>2</sub> were maintained at about 10:1 for all the experiments. Further details of the equipment and the experimental procedure can be found elsewhere [5,10,12].

## 2.3. Reaction Mechanism

Generally, the reactions between amines and CO<sub>2</sub> have two established mechanisms that can be used to satisfactorily describe their kinetics with respect to carbamate formation, which is the main reaction of CO<sub>2</sub> absorption [19]. The mechanisms are known as zwitterions, as proposed by Caplow [20] and Danckwerts [21], and the termolecular mechanism, as proposed by Crooks and Donnellan [22]. Based on the termolecular mechanism, it was assumed that there is a loosely bound encounter complex formed as initial products in the reaction, not the zwitterion (Fig. 1).

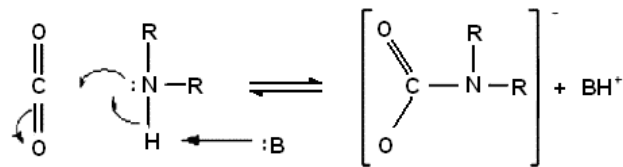


Fig. 1. Schematic drawing of a single-step termolecular reaction mechanism [22].

In this mechanism, the bonding between amine and CO<sub>2</sub> and the proton transfer take place simultaneously, involving only a single step as illustrated in Fig. 1 and represented by Eq. (1). Here, carbamate formation involves the transfer of a proton from the amine functionality.



It is noted that for sterically hindered amines the carbamate ion is unstable, leading to the following reaction [10]



The observed carbon dioxide absorption rate in amine solutions is given as

$$r_{obs} = k_o [\text{CO}_2] \quad (3)$$

The observed pseudo–first-order reaction rate constant ( $k_o$ ) in aqueous systems is given as

$$k_o = k_{H_2O} [H_2O] [RNH_2] + k_{RNH_2} [RNH_2]^2 \quad (4)$$

According to Eq. (1), in nonaqueous systems such as in ethanol (EtOH),  $k_o$  will be

$$k_o = k_{EtOH} [EtOH] [RNH_2] + k_{RNH_2} [RNH_2]^2 \quad (5)$$

Now, considering a mixture of a sterically hindered amine (SHA) and piperazine (PZ) in ethanol (EtOH),

$$k_o = k_{EtOH} [EtOH] [HA] + k'_{EtOH} [EtOH] [PZ] + k_{PZ} [PZ] + k_{SHA} [HA] [HA] + k_{SHA-PZ} [HA] [PZ] \quad (6)$$

Considering that EtOH concentration remains constant for dilute nonaqueous amine solutions, then, introducing constants  $k$  and  $k^*$ , where

$$k = k_{EtOH} [EtOH] \quad (7)$$

$$k^* = k'_{EtOH} [EtOH] \quad (8)$$

Thus

$$k_o = k [HA] + k^* [PZ] + k_{PZ} [PZ] + k_{SHA} [HA] [HA] + k_{SHA-PZ} [HA] [PZ] \quad (9)$$

Since in our experiments the concentration of the sterically hindered amine used (AMPD or AEPD) was always kept constant ( $[HA] + [HA]_0 = \text{constant}$ ), new rate constants  $k_1$  and  $k_2$  can be defined. The observed pseudo–first-order reaction rate constant ( $k_o$ ) for our system simplifies as

$$k_o = k_1 + k_2 [PZ] + k_{PZ} [PZ]^2 \quad (10)$$

### 3. Results and Discussion

The reaction kinetics of AMPD or AEPD and PZ blends in ethanol were investigated. Experiments were carried out at constant AMPD (or AEPD) concentration ( $0.50 \text{ kmol/m}^3$ ) while PZ concentration was varied ( $0.05\text{--}0.25 \text{ kmol/m}^3$ ) keeping the temperature constant at  $298 \pm 0.1 \text{ K}$ . Table 1 and Fig. 2 show the experimentally obtained pseudo–first-order reaction rate constants for both sterically hindered amines dissolved in ethanol and when PZ was used as the promoter. It is clearly seen that the rate can be promoted significantly by the addition of small amounts of PZ and the dependency is nonlinear.

Table 1. Observed pseudo-first-order reaction rate constants in ethanol at 298 K.

AMPD or AEPD (kmol/m <sup>3</sup> )	PZ (kmol/m <sup>3</sup> )	$k_o$ (AMPD) (s <sup>-1</sup> )	$k_o$ (AEPD) (s <sup>-1</sup> )
0.50	0.00	11.0	9.6
0.50	0.05	204.4	243.9
0.50	0.10	564.0	648.4
0.50	0.15	974.1	900.9
0.50	0.20	1304.9	1378.5
0.50	0.25	1647.9	1870.8

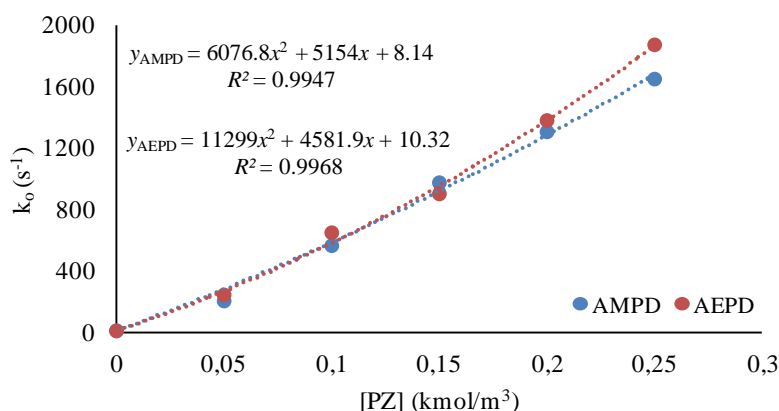


Fig. 2. Observed pseudo-first order rate constant as a function of PZ concentration in ethanol at 298 K.

The forward reaction rate constants ( $k_1$ ,  $k_2$  and  $k_{PZ}$ ) can be evaluated according to Eq. (10), which was derived from termolecular reaction assumption. The equations of nonlinear regressions of the curves for AMPD and AEPD were found as:  $y_{AMPD} = 6077x^2 + 5154x + 8.14$  and  $y_{AEPD} = 11299x^2 + 4582x + 10.32$ , respectively (Fig. 2). The quality of the fitting judged by the coefficient of correlation ( $r^2$ ) value was 0.996 on average. Table 2 shows the derived reaction rate constants for both AMPD and AEPD according to Eq. (10).

Table 2. Evaluated rate constants according to Eq. (10) in ethanol at 298 K

Sterically hindered amine (SHA)	$k_1$ (s <sup>-1</sup> )	$k_2$ (m <sup>3</sup> /kmol.s)	$k_{PZ}$ (m <sup>6</sup> /kmol <sup>2</sup> .s)
AMPD	8.1	5154.0	6076.8
AEPD	10.3	4581.9	11299.0

Aqueous MEA generally acts as the benchmark chemical solvent for carbon dioxide capture and is still of great value both in industrial application and research. Currently a number of pilot plants deploy MEA at different concentrations to test its performance and evaluate its potential for implementation [2]. Additionally this testing helps to justify and act as a comparison for the performance of novel solvents under development. Previously, Alper [5] and Ali [23] reported the value of second order forward reaction rate constant ( $k_2$ ) of aqueous MEA at 298 K

using the stopped-flow as  $5545 \text{ m}^3/\text{kmol.s}$  and  $5520 \text{ m}^3/\text{kmol.s}$ , respectively. A value of  $5868 \text{ m}^3/(\text{kmol.s})$  at 298 K was also obtained by Hikita et al. [24] using another direct technique, rapid mixing. When we compare the values of second order rate constants of nonaqueous solutions of AMPD and AEPD promoted by PZ with those reported values for commercially used aqueous MEA, the results show clearly that the nonaqueous solutions of sterically hindered amines AMPD and AEPD -which have high  $\text{CO}_2$  loadings- can achieve reaction rates comparable to commercial systems by the addition of small amounts of PZ.

The values as given in Table 2 were substituted into Eq. (10) to obtain corresponding calculated  $k_o$  values at 0.05–0.25  $\text{kmol}/\text{m}^3$  PZ. Thereafter, the values of experimental and calculated  $k_o$  for AMPD and AEPD were compared in a parity graph as shown in Fig. 3, which gave good parities for both.

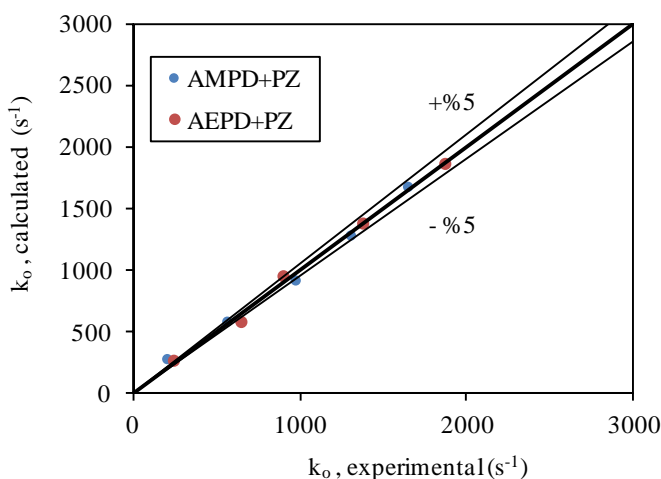


Fig. 3. Comparison of calculated and experimentally measured observed rate constants for AMPD and AEPD.

Additional similar experiments were carried out using 1-hexanol instead of ethanol. Rate constants were also evaluated in a similar fashion. As shown in Table 3, there is a progressive increase in the  $k_o$  values with increasing PZ concentration at a given AEPD concentration.

Table 3. Observed pseudo-first-order reaction rate constants in hexanol at 298 K.

AEPD ( $\text{kmol}/\text{m}^3$ )	PZ ( $\text{kmol}/\text{m}^3$ )	$k_o$ (AEPD) ( $\text{s}^{-1}$ )
0.50	0.00	5.99
0.50	0.05	179.54
0.50	0.10	476.66
0.50	0.15	837.99
0.50	0.20	1057.24
0.50	0.25	1592.02

Fig. 4 shows the experimentally obtained pseudo-first-order reaction rate constants for AEPD dissolved in hexanol and when PZ was used as the promoter.

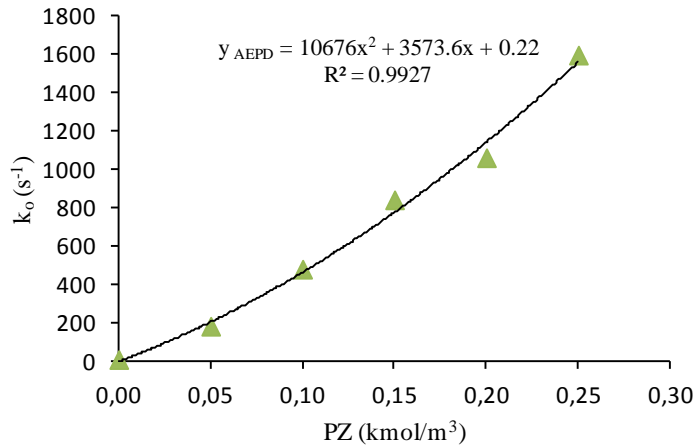


Fig. 4. Observed pseudo-first order rate constant as a function of PZ concentration in hexanol at 298 K.

The termolecular reaction mechanism was utilized through applying Eq. (10). Table 4 shows a summary of the obtained kinetic data for AEPD and PZ blends in hexanol.

Table 4. Evaluated rate constants according to Eq. (10) in hexanol at 298 K

Sterically hindered amine (SHA)	$k_1$ (s <sup>-1</sup> )	$k_2$ (m <sup>3</sup> /kmol.s)	$k_{PZ}$ (m <sup>6</sup> /kmol <sup>2</sup> .s)
AEPD	0.22	3573.6	10676.0

Further, cyclic absorption/desorption experiments were carried out in a stirred gas-liquid reactor when the solvent component was 1-hexanol. Further details of the equipment and experimental procedure can be found in elsewhere [25,26]. Cumulative plot of the CO<sub>2</sub> absorption/desorption with respect the time for AEPD-PZ-Hexanol system is shown in Fig. 5.

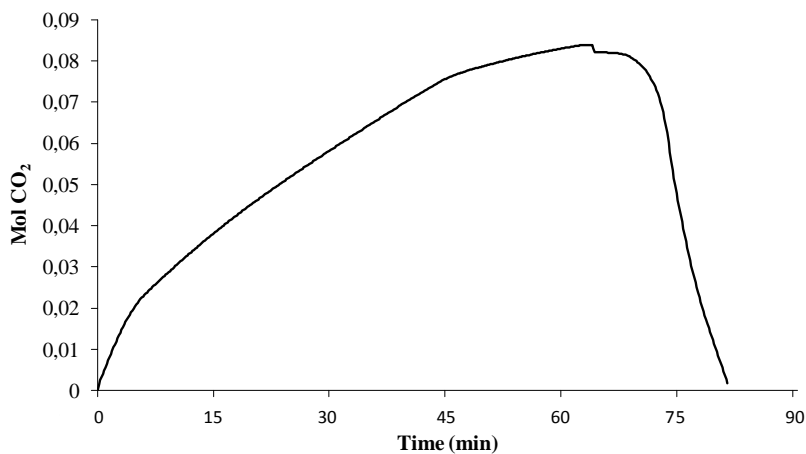


Fig. 5. Cumulative plot of the CO<sub>2</sub> absorption/desorption with respect the time for AEPD-PZ-Hexanol system

FTIR (Fourier transform infrared spectroscopy) analyses were also carried out to examine the regenerability of the AEPD-PZ-Hexanol system. The FTIR spectrum of the fresh solvent, solvent after the absorption and solvent after the desorption is shown in Fig. 6. As seen in Fig. 6, the characteristic fingerprint peaks of C=O bond with different sizes of loaded-CO<sub>2</sub> solution were observed at a wavelength of 1600–1700 cm<sup>-1</sup>. The area under this peak was expanded during absorption. After desorption, the C=O bond fingerprint peaks tightened and spectrum very similar to that of the lean solvent was obtained.

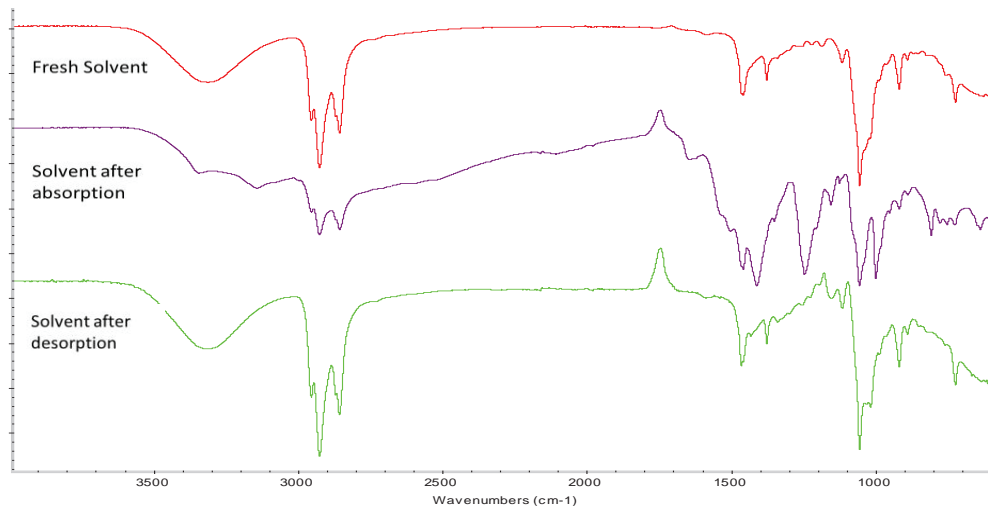


Fig. 6. FTIR spectra of the AEPD-PZ-Hexanol system

Desorption experiments showed that the solvent can be regenerated at about 363 K far below the boiling point of the solvent. That is, there seems to be no need for solvent evaporation as it is carried out in a conventional reboiler. Consequently, it is conceptually envisaged that a simple heated flash tank could replace the conventional stripper column leading towards a desorberless process intensified applications.

#### 4. Conclusion

The kinetics of the reactions between CO<sub>2</sub> and nonaqueous solutions of sterically hindered amines AMPD and AEPD promoted by PZ were investigated by stopped-flow technique and modelled by termolecular mechanism. Our results show clearly that the nonaqueous AMPD and AEPD -which have high CO<sub>2</sub> loadings- can achieve reaction rates comparable to commercial systems such as aqueous MEA by the addition of small amounts of PZ. Nevertheless, having a process in a nonaqueous environment eliminates several problems associated with using MEA such as corrosion, formation of heat stable salts and oxidative degradation are mitigated.

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