

The Kinetics of Carbon Dioxide Absorption by Blend of Aqueous Amine Solution of N-(2-hydroxyethyl) piperazine and Tris(hydroxymethyl) aminomethane

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ABSTRACT — Aqueous alkanolamine solutions have been extensively studied for acid gas removal processes. Research interest has recently shifted towards blends of solutions containing amine groups in search for adequate solvents. In this study, the kinetic rates of absorption of carbon dioxide in aqueous blend of amine solution of N-(2-hydroxyethyl) piperazine, (N-HEPZ) and tris(hydroxymethyl) aminomethane, (AHPD) at 298K (25°C) were investigated using direct stopped-flow technique in a concentration range of 0.0025 - 0.03kmol/m³ of N-HEPZ with blend of 1kmol/m³ of AHPD. The kinetic rates of absorption of CO₂ in aqueous blend of N-HEPZ and AHPD were not found in open literature, hence they were considered for the present study.

It was found that the reaction follows a single termolecular reaction mechanism. The reaction rate between CO₂ and aqueous blend of N-HEPZ and AHPD at 298 K was 12971 m³/kmol.S. The result obtained was comparable with published reaction rate data of single alkanolamines and other blends of aqueous solutions containing amine groups.

The present study shows that blended aqueous solution of N-HEPZ and AHPD is a potential candidate for consideration as alternative solvent for capture of carbon dioxide from exhaust gases.

Keywords — amine blends, carbon dioxide removal, stopped flow technique.

1 INTRODUCTION

The main aim of this research has been to contribute to the selection of optimal solvent for CO₂ capture from exhaust gases. Apart from technical and economical reasons for CO₂ removal from process gas stream, the problem of global warming has resulted in the environmental concern over a reduction of greenhouse gas emission from industrial sources. Among green house gases, carbon dioxide is the primary contributor to the problem due to its high abundance, and thus a major target for reduction. The conventional technology to capture CO₂ on large scale is the absorption – desorption process, in which (aqueous) solutions of alkanolamines are frequently used as solvents [1]. This process is energy intensive and costly with other side effects hence the need for alternative and affordable solvent or technology for CO₂ capture. Thus, the vital step in the carbon dioxide capture and sequestration process geared towards clean air environment and mitigation of global warming can be achieved if there is established economical affordable technology for CO₂ removal from industrial exhaust gases prior to its discharge to the environment than the conventional amine technology applied.

Since the Industrial Revolution, the amount of pollutants emitted into the air has dramatically increased because of the prevalence of fossil fuels. In 1961, an English scientist, Guy Stewart Callendar, confirmed that there is a progressive annual increase in concentration of carbon dioxide in the Earth's atmosphere [2]. The effect of greenhouse gases such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydro fluorocarbons (HFCs), perfluorocarbons (PFCs), chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) became well noted and efforts to reduce overall greenhouse gas (GHG) emissions began in the 1970s [3]. The contribution of all the gases to the overall greenhouse effect is based on its emission volume as well as their individual greenhouse potentials. Although, CO₂ has the least impact of all the GHGs, however, CO₂ is considered the most influential GHG because of its large emission volume (6.0 x 10⁹ - 8.2 x 10⁹ tonnes CO₂/year on a dry air basis) into the atmosphere [4]. Global CO₂ emissions have increased by over 70% between 1971 and 2002. If unabated, it is speculated that by the end of the century earth's average temperature could rise from 1.4 to 6°C as carbon emission reaches approximately 26Gt/year by 2100 [5]. Notwithstanding that the flue gas produced from the combustion of coal is typically composed of a mixture of gases, including CO₂, NO_x, SO_x, H₂S and N₂, with CO₂ comprising about 12% of the mixture [6], most researchers focus on CO₂ as it captures the largest portion of greenhouse gas emissions [7]. Apart from CO₂ emission control from power plant sources, Table 1 shows the major industrial processes where carbon capture technology can be applied.

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Table 1. Major industrial processes that need a CO₂ removal plant [8]

Process/Industry	Common clean-up targets (% CO ₂)
Hydrogen Manufacture	<0.1 % CO ₂
Ammonia Manufacture	<16 ppm CO ₂ + CO
Natural gas Purification Pipeline Gas LNG feedstock	< 1 % CO ₂ <50 ppm CO ₂
Syn gas for chemicals (H ₂ /CO)	<500 ppm CO ₂
Coal Gasification	500 ppm CO ₂
Ethylene Manufacture	1 ppm CO ₂

In view of these aforementioned statistics, many scientists, industrialists and policy-makers observed that the efficient removal and subsequent sequestration of CO₂ from postcombustion emission streams is a major lead of the efforts aimed at stabilizing atmospheric CO₂ levels. The absorption technique for CO₂ in amines has been widely used over the past few decades. Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA) have been commonly used in natural gas sweetening and is considered as the most important and mature post-combustion CO₂ capture technology having been patented for natural gas sweetening since 1930 [1]. Although there has been development in the absorption technique and the availability of solvents for acid gas removal, there are certain issues that still need attention:

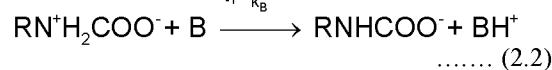
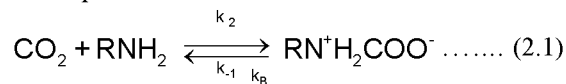
- Corrosion
- Solvent degradation
- Associated heat duty per CO₂ loading
- Economy of the absorption/stripping column

Inline to solve these problems, there is a need to investigate more reliable solvents having good physical and chemical properties such as high CO₂ loading capacities to reduce solvent circulation rates, low vapor pressures to minimize solvent loss, low to moderate viscosities for high design efficiency, thermal and chemical stabilities to reduce solvent reclaimer costs and high kinetic rates of absorption to minimize the size of absorption/stripping columns. Nowadays, there is a growing interest and research in using blends of amines instead of a single amine for gas sweetening processes. The concept of using amine mixture is based on utilizing and combining the advantages of the amines in the mixture, or of customizing the amine solution to a particular use. In these blends, one of the amine is sterically hindered so that its carbamate is unstable leading to free amine [9]. This leads to higher CO₂ pickup but usually the steric hinderance results in lower reaction rate. The decrease in reaction rate can be compensated by addition of a second amine.

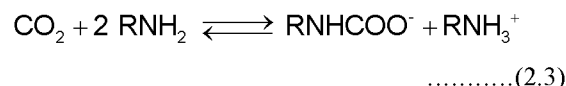
Blended amines results in observed pseudo-first-order rate constant values(*k_o*) that may be greater than the sum of the *k_o* values of the respective pure amines [10].

2 ANALYSIS

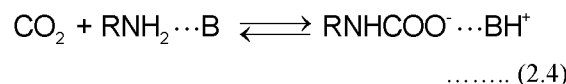
In a typical amine absorber-desorber system currently applied for CO₂ capture, the main operating cost is caused by the energy requirement of the reboiler which is proportional to liquid circulation rate and CO₂ loading [11]. In order to design the absorber on a rate-based modeling, kinetics of CO₂ – amine reactions should be known sufficiently accurately [12]. Therefore the mechanism of the reaction between CO₂ and aqueous solutions of amines has been studied experimentally by several researchers. Caplow and Danckwerts [13], [14] have both proposed a two-step mechanism, also known as the zwitterion mechanism, where a stable zwitterion intermediate is proposed to exist in solution, as in equations (2.1) and (2.2). In equation (2.2), the proton from the zwitterion is transferred to a base (B), which may be a water molecule, an additional amine, or any other basic species.



When the base is amine and the carbamate ion is stable, the overall reaction follows:



Using rate constant data, Crooks and Donnellan [15] suggested that the Danckwerts mechanism was unlikely, and rather proposed a single-step termolecular mechanism and was supported by Alper [16] as in equation (2.4). However, regardless of mechanism, a carbamate and a protonated base are the generally accepted products of this reaction.



If the amine is sterically hindered, then the carbamate ion is unstable and the following reaction also takes place [9];

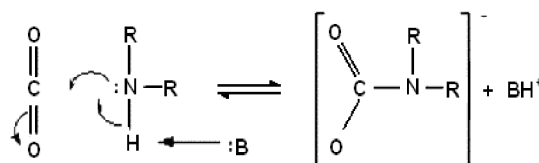
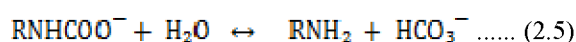


Fig. 1. Schematic drawing of single-step termolecular reaction mechanism [15]

Furthermore, mechanistic insights into the CO₂-amine reaction system have been made possible through computational chemistry by works of da Silva and others. Da Silva and Svendsen [17] used ab initio calculations and continuum solvation models in providing evidence that supports the single-step termolecular reaction mechanism as in equation (2.4) and also stated that if a zwitterion intermediate exist, it is likely to be short-lived [18], [19]. Moreover, using density functional theory (DFT) coupled with free energy perturbation methods, they have shown that carbamate stability can be reasonably modeled [17]. Arstad et al. [20] in their work used molecular orbital (MO) theory and DFT to provide mechanistic insight into the CO₂-amine reaction, highlighting the catalytic effect that water or alkanolamines may have on the reaction kinetics.

Termolecular reaction mechanism (Fig. 1) leads to a reaction rate of:

$$r_{\text{obs}} = k_o[\text{CO}_2] \dots\dots\dots (2.6)$$

Where:

$$k_o = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{RNH}_2] + k_{\text{RNH}_2}[\text{RNH}_2]^2 \dots (2.7)$$

Now, considering a mixture of two amines say A₁ and A₂:

$$k_o = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{A}_1] + k'_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{A}_2] + k_{\text{A}_1}[\text{A}_1]^2 + k_{\text{A}_2}[\text{A}_2]^2 + k_{\text{A}_1-\text{A}_2}[\text{A}_1][\text{A}_2] \dots\dots\dots (2.8)$$

Assuming water concentration remains constant, $k = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$ and $k' = k'_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$; Eq. (2.8) gives:

$$k_o = k[\text{A}_1] + k'[\text{A}_2] + k_{\text{A}_1}[\text{A}_1]^2 + k_{\text{A}_2}[\text{A}_2]^2 + k_{\text{A}_1-\text{A}_2}[\text{A}_1][\text{A}_2] \dots\dots\dots (2.9)$$

$$k_o = \{k + k_{\text{A}_1}[\text{A}_1]\}[\text{A}_1] + \{k' + k_{\text{A}_2}[\text{A}_2]\}[\text{A}_2] + k_{\text{A}_1-\text{A}_2}[\text{A}_1][\text{A}_2] \dots\dots\dots (2.10)$$

The concentrations of amines A₁ and A₂ can be varied one at a time; if one is varied, the other should be constant in the mixture.

Assuming $[\text{A}_1] = [\text{A}_1]_0 = \text{Constant}$

$$k_o = k_{\text{A}_2}[\text{A}_2]^2 + k_4[\text{A}_2] + k_3 \dots (2.11)$$

Where: $k_3 = \{k + k_{\text{A}_1}[\text{A}_1]_0\}[\text{A}_1]_0 \dots (2.12)$

$$k_4 = k' + k_{\text{A}_1-\text{A}_2}[\text{A}_1]_0 \dots\dots\dots (2.13)$$

Here, taking A₁ as AHPD which is a sterically hindered amine and A₂ as N-HEPZ which reacts with CO₂ at a very high rate, equation (2.11) gives:

$$k_o = k_{\text{N-HEPZ}}[\text{N-HEPZ}]^2 + k_4[\text{N-HEPZ}] + k_3 \dots\dots\dots (2.14)$$

3 MATERIAL AND METHOD

Reagent grade N-HEPZ and AHPD (purity of the amines ≥99%) were obtained from SigmaAldrich. The rates of reactions of blends of the pure amines (N-HEPZ and AHPD) with CO₂ (purity of ≥99.9%) in ultrapurified water were measured over a temperature of 298 K using a standard stopped-flow apparatus (Hi-Tech Scientific, UK, Model SF-61SX2). The experimental set-up of the stopped-flow apparatus consists of a conductivity detection system, which could be used to measure directly the intrinsic rate of a rapid homogeneous reaction (here, between aqueous solutions of CO₂ and mixture of N-HEPZ and AHPD). All parts of the flow circuit were thermostated and the temperature control was better than ±0.1 K. Also, in the experimental set-up, the amine and CO₂ solutions were placed in sealed drive syringes. In each experimental run, equal volumes of the solutions of amine blend and carbon dioxide were mixed in the stopped-flow mixer. The concentration of amine blend was always much in excess of that of CO₂ (usually the molar ratio was about 20:1). The product formation was monitored by fast conductimetry. Fig. 2 shows the stopped-flow equipment schematically and other pertinent details of which can be found elsewhere [16], [21]. Fig. 3 shows the complete view of the equipment set-up.

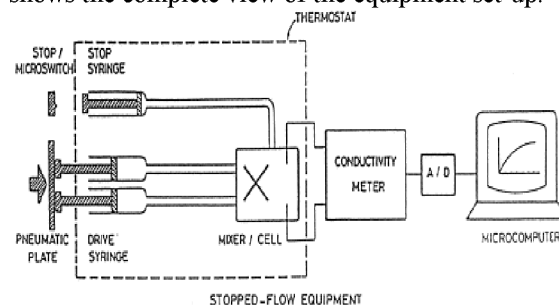


Fig. 2. Stopped flow intrinsic reaction kinetics system using fast conductimetry



Fig. 3. The stopped-flow equipment set-up

4 RESULTS AND DISCUSSION

Stopped-flow data gave very satisfactory pseudo-first order plots according to equation (2.6). Since the reaction between OH⁻ and CO₂ was not detected by the conductivity measurements, the fitted rate constant corresponded directly to k_o in equation

(2.6). Under the temperature studied (298K), AHPD concentration in the amine blend was constant. Thus, increase in N-HEPZ concentration in the amine mixture resulted in the increase in observed pseudo-first-order reaction rate constants (k_o) as expected. In Fig. 4, the observed reaction rate constant k_o obtained is plotted as a function of N-HEPZ concentration.

Table 2 shows the experimental data, that is k_o as a function of N-HEPZ concentration at 298K as plotted in Fig. 4. Using the least-square-method, empirical power law kinetics was fitted to these data and fractional order of 1.19 was obtained. This order for the concentration range of this study indicates that the termolecular reaction mechanism may be appropriate for this chemical reaction.

Table 2. Reaction rate data for CO₂– aqueous (AHPD+N-HEPZ) blend system

[AHPD] (kmol/m ³)	[N-HEPZ] (kmol/m ³)	k_o (298K) (S ⁻¹)
1.00	0.0025	51.04
1.00	0.005	100.55
1.00	0.01	192.7
1.00	0.02	554.33
1.00	0.03	1005.96

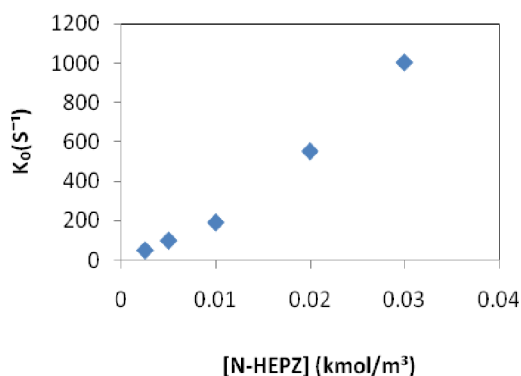


Fig. 4. Effect of N-HEPZ concentration on k_o values at 298K ([AHPD] = 1.00kmol/m³)

These experimental data were fitted to equation (2.14) by using the Nelder-Mead simplex algorithm of the unconstrained minimization technique as shown in Figures 5 and 6. Table 3 shows the summary of results, while Table 4 shows the literature data for CO₂ absorption by different solvents using stopped flow method.

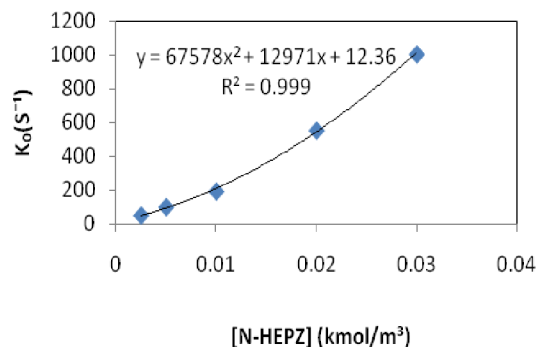


Fig. 5. k_o (S⁻¹) Vs [N-HEPZ] (kmol/m³) for CO₂– Aq. (AHPD+N-HEPZ) blend system at 298K

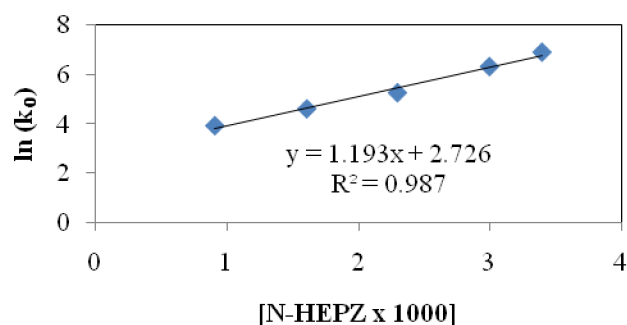


Fig. 6. $\ln(k_o)$ Vs \ln [N-HEPZ x 1000] for CO₂– Aq. (AHPD+N-HEPZ) blend system at 298K

Table 3. Summary of reaction rate parameters for CO₂–Aq. blend of N-HEPZ with AHPD system

Temp (K)	Power law order	k_3 (S ⁻¹)	k_4 (m ³ /kmol.s)	k_{N-HEPZ} (m ⁶ /kmol ² .s)
298	1.19	12.36	12971	67578

Table 4. Literature data for CO₂ absorption by different solvents in aqueous solution using stopped flow method

Ref.	Temp (K)	MEA (mol/m ³)	k ₂ (m ³ /mols)	E (kJ/mol)
Crooks & Donnellan [15]	288 – 308	0 – 60	4.48 (at 298K & 60 mol/m ³)	\
Alper [16]	288	0 – 450	2.867	46.7
	298		5.545	
Ali [10]	298	5 – 35	5.52	46.6
	303		7.53	
Li [22]	298	9.8 – 58	5.12	\
DEA – CO₂ absorption data				
Ali [10]	298	66.4 – 518.4	0.81	32.30
	303		1.00	
Amine blends – CO₂ absorption data				
Ali et al. [23]	303	400 mol/m ³		\
		AMP-MORPH	13.36	
		AMP-MEA	10.38	
		AMP-MMEA	9.75	
This work (2011)	298	1.0025-1.03 kmol/m ³		\
		AHPD + N-HEPZ	12.97	

5 CONCLUSION

The chemical reaction between aqueous blend of N-HEPZ and AHPD with CO₂ was found to follow a single termolecular reaction mechanism. It was found that the reaction rate of the amine mixture is comparable to those of MEA which is the commonly used alkanolamine for commercial CO₂ capture from exhaust gases. However, since AHPD is a sterically hindered amine, its carbamate is unstable leading to a theoretical CO₂ pickup which is higher than 0.5 mol CO₂/mol amine. While this is a superior property to conventional amines such as MEA, the low reaction rate is compensated by the addition of N-HEPZ.

Our result therefore shows that blended aqueous solution of N-HEPZ and AHPD is a potential candidate for consideration as alternative solvent for capture of carbon dioxide from exhaust gases requiring smaller reboiler duty in the desorber.

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