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# Performance evaluation on complex absorbents for $CO_2$ capture

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ABSTRACT

Piperazine (PZ) and phosphates as additives were added into an aqueous *N*-methylmonoethanolamine (MMEA) to form complex absorbents, respectively. Performances of $CO_2$ capture by the complex absorbents were evaluated in a bubble column reactor. Reaction mechanisms and activations of the additives were presented theoretically. Effects of type and concentration of additives, and gas flowrates on volumetric mass transfer coefficient were investigated, and effects of orifice size of the gas sparger and stirring rates on average absorption velocity were also discussed. Results show that $CO_2$ loadings of MMEA–PZ and MMEA–$K_3PO_4$ complex absorbents were larger than that of single MMEA and MEA absorbents. The MMEA–PZ complex absorbent gave a highest $CO_2$ loading in all complex absorbents. The overall mass transfer coefficient increased, subsequently reached a maximum and then decreased with the increase of $K_3PO_4$ concentration in the complex absorbent. The overall mass transfer coefficient increased with the increase of the gas flow rates. Average absorption velocities increased with the decrease of the orifice size and with the increase of the orifice numbers. The average absorption velocities in moderate intensity of stirring rates were higher than that in the high intensity of stirring rates.



## 1. Introduction

Greenhouse gases, including carbon dioxide, methane, nitrous oxide, ozone, water vapor, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride ($SF_6$), can significantly contribute to global warming. It has been known that global warming resulted in serious global environmental problems [1]. Various climate models estimated that average global temperature may rise by about 1.4–5.8 °C by the year 2100 because of the enhanced greenhouse effect [2]. Carbon dioxide ($CO_2$), accounting for over 50% in the amount of greenhouse gases and currently responsible for over 60% of the enhanced greenhouse effect, is the primary species of greenhouse gases. It has turned to be a worldwide issue to reduce $CO_2$ emission and decrease $CO_2$ concentration in the atmosphere. The bulk of the $CO_2$ emission comes mostly from the fossil fuel-based energy industries [3], such as coal-combusted power generating and petroleum and metallurgy processing that are the foundations of sustaining economic growth. The capture of $CO_2$ from the industrial sources seems to be an important measure for this issue. Therefore, low energy-consumption, available, efficient technologies have attracted significant attention for the capture and removal of $CO_2$ from gas mixtures produced by industrial sources.

Current separation and capture technologies based on a variety of physical and chemical processes include absorption, adsorption, conversion, cryogenic separation, and membrane techniques. Such processes have been used in the chemical industry and others. The chemical absorption is an efficient method for $CO_2$ capture, especially for capture of low concentration $CO_2$ in gas source [4–6]. Amine is one of efficient absorbents, which has caught more attention from researchers. Aqueous alkanolamines (mono-, di-, or tri-ethanolamine), such as monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), di-isopropanolamine (DIPA) and methyldiethanoamine (MDEA) are widely used in petrolic and chemical industries for acid gases removal. Recently, the complex absorbents (or blended absorbents) composed of two single absorbents (e.g. alkanolamines) with varying compositions have been used to improve the $CO_2$ adsorbing performances [7–10]. The principle of formulation is to combine the favorable characteristics of different absorbents, for instance, higher absorbing capacity, higher absorbing velocity, lower energy consumption, reduced corrosion, and lower oxidative degradation; and simultaneously their unfavorable characteristics are suppressed [10]. Therefore, the complex absorbents combine the advantages of single absorbents. As a rule, one component (i.e., a solute) in the complex absorbent is as an additive (or so-called an activating agent) to be added into another component as a main solvent. The main solvent is usually large in varying compositions of concentration compared with the additives. Product costs of the additives are generally higher than the main solvent. For example, piperazine (PZ) or 2-amino-2-methyl-1-propanol (AMP), as an additive, is added into methyldiethanolamine (MDEA) as a main solvent to form the MDEA-based blended absorbent [9]. Bubble columns have been widely used in industry for carrying out a variety of chemical reactions such as absorption and purification [11].

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**Nomenclature**

| | |
|---|---|
| $a$ | specific interfacial area ($m^{-1}$) |
| $C$ | concentration (kmol $m^{-3}$ or mol $L^{-1}$) |
| $d$ | bubble diameter (m or mm) |
| $D$ | diffusion coefficient ($m^2\ s^{-1}$) |
| $E$ | enhancement factor for chemical reaction |
| $G$ | gas flow rate ($m^3\ s^{-1}$ or L $min^{-1}$), |
| $H$ | Henry constant |
| $Ha$ | Hatta number |
| $K$ | overall mass-transfer coefficient (m $s^{-1}$) |
| $k$ | individual mass-transfer coefficient (m $s^{-1}$), or reaction rate constant ($m^3\ mol^{-1}\ s^{-1}$ or $s^{-1}$) |
| $k_La$ | volumetric mass transfer coefficient ($s^{-1}$) |
| $k^0_L$ | physical mass transfer coefficient ($s^{-1}$) |
| $L$ | $CO_2$ loading of liquid phase (mol $L^{-1}$) |
| $\bar{R}$ | average absorption velocity (mol $L^{-1}\ s^{-1}$) |
| $t$ | time (s) |

*Subscripts*

| | |
|---|---|
| A | gas component |
| $a$ | additive |
| g | gas phase |
| L | liquid phase |
| ov | overall |

*Greek letter*

| | |
|---|---|
| $\varepsilon$ | gas hold-up |

Because they can offer favorable performances such as a simple structure without moving parts, high gas/liquid contact areas, good mass/heat transfer rates, and large liquid hold-ups [12]. Mass transfer in bubble columns has been extensively investigated [13–14].

MMEA is a kind of the secondary amine, which molecule structure is shown in Fig. 1. It was selected as a main solvent for the complex absorbents because it is commercially available, low product cost and lower corrosiveness due to weaker alkalinity compared with MEA. The reaction schemes of $CO_2$ captured by various alkanolamines such as MEA, DEA, TEA, MDEA, diglycolamine (DGA), DIPA, and AMP, have been proposed in literature [15–16]. In this work, MMEA blended with other alkanolamines such as bis-amino amine PZ (its molecule structure is shown in Fig. 1) or phosphates was used as $CO_2$ absorbents to form novel composite solutions, which was expected to have a higher $CO_2$ reaction rate and loading capacity. Therefore, the alkanolamine composite solution would result in substantial lower solution circulation rates while it was compared with a unique amine solution. Both lower circulation rate and resulted lower pumping energy cost would lead to a reduction of regeneration energy requirement.

In this work, Piperazine (PZ) and phosphates as additives were added into the aqueous MMEA to form the MMEA-based complex absorbents, respectively. $CO_2$ capture performances of the complex absorbents were evaluated in a bubble column reactor. Reaction mechanism and activation of the additives were schemed theoretically. Effects of type and concentration of additives, and gas flowrate on absorption performance were investigated, and effects of orifice size and stirring rates on average absorption velocity were also discussed.

## 2. Theory section

### 2.1. Reaction scheme and mechanism

Zwitterion mechanism is the recently most widely accepted mechanisms for primary and secondary amines reacting with $CO_2$ [10]. Following reactions occur in the solution:

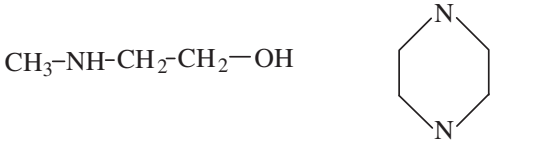


**Fig. 1.** Molecule structures of MMEA and PZ

$$R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH^+COO^- \quad (1)$$

$$R_1R_2NH^+COO^- + B \rightleftharpoons R_1R_2NCOO^- + BH^+ \quad (2)$$

where B is a base present in the solution. The zwitterionic mechanism indicates that, an amine reacts with $CO_2$ to form a zwitterion, successively a base (B) makes the zwitterion deprotonate to form carbamate. B could be $R_1R_2NH$,$OH^-$, or $H_2O$.

In addition, $CO_2$ also reacts with the hydroxide ions present in solution:

$$CO_2 + OH- \rightleftharpoons HCO_3^- \quad (3)$$

The contribution of reaction of Eq. (3) to the overall reaction rate can be considered negligible. On the one hand, alkanolamines are weak bases [6]. They hydrolyze to create a little $OH^-$ ion. On the other hand, a great deal of molecule is $R_1R_2NH$ in the solution. $CO_2$ collides with $R_1R_2NH$ rather than $OH^-$. Hereby, reaction of Eq. (3) was negligible in the contribution to the overall reaction rate. Amines protonation, bicarbonate and carbonate formation, and water dissociation are also negligible as a result of they are not dominant in the aforementioned system.

### 2.2. Activation scheme and mechanism

When phosphates as additives are added into the aqueous MMEA, following multilevel hydrolytic reactions would occur in the solution.

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \quad (4)$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \quad (5)$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \quad (6)$$

Phosphates and their hydrolytes in the solution could serve as the B. Accordingly, the additives would impact the reaction between MMEA and $CO_2$. B could be $PO_4^{3-}$, $HPO_4^{2-}$, or $OH^-$.

As PZ as an additive is added into the aqueous MMEA, the following reactions could occur in the solution: