Absorption of CO₂ in DMAEE-DGA-DBU Aqueous Solution

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Abstract. 39 sets of solutions were compounded from 2-[2-(Dimethylamino)ethoxy]ethanol (DMAEE), 2-(2-Aminoethoxy)ethanol (DGA) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). These solutions were tested relevant to the stirred reactor, at 303K~323K, 0.1MPa, to establish their absorption performance. An equation was utilized to model the absorption curve and the simulation results agreed well the experiments. The relevance of temperature and composition of solution with absorbed performance were revealed on the basis of comparison and analysis.

1 Introduction

There was increasing emission of carbon dioxide (CO₂) in the process of industrialization, which was causing a series of environmental issue[1]. To mitigate emissions problems, amine was used as absorber in post combustion CO₂ capture of power plants in recent decades[2]. In current research and application, the absorption performance of single amines was barely satisfactory such as conventional amines MEA and DGA, secondary amines MMEA and EMEA, and tertiary amines DEAE [3]. For example, MEA has fast absorption rates, but low absorption loading, high energy consumption, poor thermal stability and oxidation resistance. Therefore, it is important that study the physical properties of other novel reagents and analyze their feasibility in industrial applications to reduce the cost of CO₂ capture.

An enormous amount of amines had been being researched with stronger absorption capacity, faster rate of absorption and low energy consumption of regeneration [4]. DMAEE has similar properties to MDEA, but it has a lower viscosity than MDEA. Meng et al. suggested that DMAEE was a good substitute for MDEA[5]. Du et al. screened 36 kinds of novel reagents and found that DMAEE and DGA aqueous solution had the best resistance to high temperature oxidation[6]. Nevertheless, DMAEE also has common characteristic of other tertiary amine: the reaction rate of CO₂ absorbed is relatively slow. In order to make up for the deficiencies of DMAEE, DGA and DBU are added to the solution.

DGA has similar properties to MEA, but it has a stronger thermal stability than MEA[7, 8]. Al-Juaied et al.

reported that the pseudo-first-order (PFO) was satisfactory approximation for CO₂ absorption in DGA aqueous solution at the CO₂ loading less than 0.2 mol CO₂/mol DGA[9]. However, high concentration of DGA with a high viscosity increases operating costs and affects absorption performance. DBU exist lower viscosity than DGA. Zhao et al. reported that DBU could effectively catalyze the synthesis reaction involving CO₂ [10]. Moreover, He et al. investigated the behavior of DBU for different concentration in spraying scrubber and measured 5 vol.% DBU with the largest absorption loading[11].

Herein, this study presents one main absorbent and two rate promoters: DMAEE, DGA and DBU. The mass fraction of DMAEE is 0.3 and the mass fraction of DGA and DBU ranged from 0 to 0.15 and 0.025 to 0.075 in turn. These solutions are tested at 303.2K~ 323.2K, 0.1MPa, relevant to the stirred reactor, to establish their absorbed performance.

2 Experimental methods

2.1 Materials

The reagents of this experiment are displayed in Table 1. In which, MDEA, DMAEE, DGA and DBU were purchased from Aladdin reagent, China. It is not purified before experiment for them. The high purity water was used to mix DMAEE-DGA-DBU aqueous solution, which is made from the Heal Force ROE (Reverse Osmosis Electrodeionization)-100 apparatus.

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Table 1. Chemical specification

Chemical abbreviation	CAS	Purity	Source
MDEA	105-59-9	$x \geq 0.99$	Aladdin Industrial Inc.
DMAEE	1704-62-7	$x \geq 0.98$	Aladdin Industrial Inc.
DGA	929-06-6	$x \geq 0.98$	Aladdin Industrial Inc.
DBU	6674-22-2	$x \geq 0.99$	Aladdin Industrial Inc.
CO ₂	124-38-9	$x \geq 0.9999$	Baoding Jinglian Gas
H ₂ O		Electrical resistivity $> 15\text{M}\Omega$ cm at $T=298\text{K}$	Heal force ROE-100 apparatus

2.2 Equipment preparation

The installations and instruments in our research are similar to that employed by Fu et al.[12-14]. An electronic balance was used to determine the mass of all required reagents with a minimum range of 10^{-4}g . The other instruments of this work were shown in figure 1. In the whole research process, the experimental instruments were invariable to avoid errors.

2.3 Experimental setup

To verify the accuracy of experimental installation, the absorption capacity of CO₂ in MDEA aqueous solution was tested (40 wt%, temperature at 313.2 K), then compared with the previous reports in the research of Zhang et al.[15] (40 wt%, temperature at 313.15 K). The experimental result indicated that the correlation between our study ($\alpha = 0.60$) and the work of Zhang et al. ($\alpha = 0.59$) is satisfactory. The deviation of them is only 1.7%. After selecting the equipment, the uncertainties for temperature, w_{MDEA} and pressure are respectively 0.1 K, 0.0001 and 5 kPa in subsequent experiments.

The diagrammatic sketch of this work is displayed in figure 1. According to schematic diagram, installations were connected. The reaction temperature was regulated by control panel of water bath with a minimum range of 0.1K. Magnetic stirring speed was set to 1300 revolutions per minute. During the test, after decompression of the relief valve, CO₂ was inlet into the one mass flow controller (MFC, temperature T_0) to accurately control flow rate of gas (v_0), after that entered the reactor and reacted with the aqueous solution. The residual and volatilized gas firstly flowed into a desiccator to remove the steam, and then into the CO₂ analyzer and the mass

flow meter (MFM, temperature T_1). The concentration of partial pressure of CO₂ (C_i) was gauged by the analyzer, and the flow rate (v_i) of residual CO₂ was determined by the mass flow meter. The data of C_i , v_i and the corresponding time t_i were simultaneously and synchronously saved by the workstation (record once per second). The experiment was stopped when C_i is equal to C_0 . The absorptive volume (Q) of CO₂ can be computed from:

$$Q = \int_0^t v_i - v_0 dt \approx v_0 C_0 t \cdot \frac{273.15}{T_0} - \sum_{i=0} v_i C_i n t \frac{273.15}{T_1} \quad (1)$$

where t is the time of achieving absorptive equilibrium.

The moles of CO₂ can be estimated from:

$$n = \frac{Q / 22.4 \times 44}{m_i} \times 100 \quad (2)$$

in which m_i is the weight of fresh aqueous solution without absorption of gas.

3 Results and discussions

3.1 Absorption capacity

Figure 2 reflects the time dependence of the mass of the absorbed CO₂ (m) in DMAEE aqueous solution and the comparison with that in MDEA aqueous solution. One can obvious get information from this figure that DMAEE is superior to MDEA in absorption capacity. The deviation of absorption capacity between DMAEE aqueous solution ($m=9.93\text{g CO}_2$ per 100g aqueous solution) and MDEA aqueous solution ($m=8.79\text{g CO}_2$ per 100g aqueous solution) is 12.97%, at given mass fraction of DMAEE ($w=0.4$), mass fraction of MDEA ($w=0.4$) and temperature ($T=313.2\text{ K}$).

Figure 1. Schematic diagram for experiments **Figure 2.** Time dependence of absorption capacity. Symbols: ■MDEA, ●DMAEE.

The absorption mass of CO₂ in DMAEE-DBGA-DBU aqueous solutions were tested at 0.1MPa with temperatures ranging from 303.2K to 323.2K. The mass of the absorbed CO₂ is displayed in Table 2. At stated temperature and given w_{DMAEE} , the mass of the absorbed CO₂ increases almost linearly with w_{DGA} and w_{DBU} . One may discover from the table that at given w_{DMAEE} , w_{DGA}

and w_{DBU} , the absorption capacity decreases with increasing temperature. While the total gas pressure unchanged, the partial pressure of water vapor increases and the partial pressure of CO₂ decreases with increasing of temperature. Moreover, the promotion effect of DBU and DGA declines with increasing temperature.

Table 2. Maximum absorption amount (m) of CO₂ in DMAEE-DGA-DBU aqueous solution under different mass fraction of DMAEE (w_{DMAEE}), DBU (w_{DBU}) and DGA (w_{DGA}).

w_{DMAEE}	w_{DBU}	w_{DGA}	$m/(\text{gCO}_2 \text{ per } 100\text{g aqueous solution})$		
			$T=303.2\text{K}$	$T=313.2\text{K}$	$T=323.2\text{K}$
0.30	0.00	0.00	8.41	8.06	7.17
		0.00	8.90	8.49	7.68
		0.05	9.27	8.79	7.97
	0.025	0.10	9.91	9.01	8.16
		0.15	10.26	9.38	8.47
		0.00	9.47	8.81	7.84
	0.05	0.05	10.40	9.35	8.23
		0.10	10.60	9.43	8.46
		0.15	10.81	9.53	8.57
	0.075	0.00	9.86	8.92	8.15
		0.05	10.56	9.53	8.42
		0.10	10.80	9.61	8.50
		0.15	11.16	9.71	8.67

3.2 Absorption Curve Model

Zhong et al. measured chemical reaction rate of CO₂ with DETA and MIPA using the PFO model [16]. Sun et al. used PFO model to describe the absorbed characteristics of CO₂ by 1-methoxyethyl-3-methyl imidazolium glycinate[17]. The pseudo-first-order function is expressed as:

$$\frac{d\alpha_t}{dt} = k_1(\alpha_e - \alpha_t) \quad (3)$$

where α_e and α_t are the absorption loadings at equilibrium and a given time, $k_1(\text{s}^{-1})$ is the pseudo first - order kinetic constant. the value of k_1 increases with decreasing of the time required to achieve chemical equilibrium. With the boundary conditions of $t=0$, $\alpha_t=0$ and $t=\infty$, $\alpha_t=\alpha_e$, function (3) can be expressed as:

$$\alpha_t = \alpha_e(1 - e^{-k_1 t}) \quad (4)$$

The absorptive weight of CO₂ at stated certain points (q_t) can be estimated from:

$$q_t = \frac{44 \times 100}{m} \times C \cdot \alpha_t = \frac{4400}{m} \times q_e(1 - e^{-k_1 t}) \quad (5)$$

where C is the total moles of amine in the aqueous solution, and q_e is maximum absorption amount of CO₂. Absorption capacity data were obtained once per second in each absorption experiments. Nonlinear fitting was performed by using equation (5) through orthogonal distance regression. The model parameters q_e and k_1 can be obtained by fitting to the experiment.

Figure 3 reflects the time dependence of the weight of absorbed CO₂ in different mass fractions of DGA aqueous

solution. One finds that at given w_{DMAEE} and w_{DBU} , the absorption rate rise with the mass fraction of DGA. The correlation between calculated and experimental data is satisfactory. The deviation of fitting D calculated by equation (6) is less than 3.5%.

Figure 3. The influence of mass fraction of DBU on the absorption rate of CO₂ in DMAEE-DGA-DBU aqueous solutions.

Symbols:

- $w_{DMAEE}/w_{DGA}/w_{DBU}=0.30/0/0$;
- $w_{DMAEE}/w_{DGA}/w_{DBU}=0.30/0/0.025$;
- ▲ $w_{DMAEE}/w_{DGA}/w_{DBU}=0.30/0.05/0.025$;
- ▼ $w_{DMAEE}/w_{DGA}/w_{DBU}=0.30/0.10/0.025$;
- ◆ $w_{DMAEE}/w_{DGA}/w_{DBU}=0.30/0.15/0.025$.

Main plot, $T=323.2\text{ K}$; Auxiliary plot, $T=303.2\text{ K}$; Lines: fitting lines.

$$D = \sum_{i=1}^t \left| 1 - q_{i,cal} / q_{i,exp} \right| \times 100\% / t \quad (6)$$

where $q_{i,exp}$ is absorption capacity data by experiment; $q_{i,cal}$ is absorption capacity data by calculation. Moreover, one can obvious find the rule that the absorptive kinetic descends with increasing of reaction time at given reagent ratio from the figure(3). Furthermore, from the main plot and auxiliary plot, one can find that DGA has a significant contributory effect on absorption both at 303.2K and 323.2K.

4 Conclusions

Absorption characteristics of DMAEE-DBU-DGA aqueous solution are tested in this research. The thermodynamics and kinetics of the process of CO₂ capture were investigated by controlling the temperature and reagent ratio. After comparison and analysis, our results show that:

- DMAEE is superior to MDEA in absorption capacity and rate;
- The correlation between calculated of PFO model and experimental data is satisfactory;
- The addition of DGA and DGA can improve the rate of absorption at ordinary temperature, 0.1MPa.

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