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Solubility and viscosity for CO_2 capture process using MEA promoted DEAE aqueous solution

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ABSTRACT

The saturated solubility of CO_2 in monoethanolamine (MEA) promoted 2-diethylaminoethanol (DEAE) aqueous solution was investigated at temperatures ranging from (303.2 to 323.2) K. The mass fraction and temperature dependences of the saturated solubility and CO_2 loading are illustrated. The viscosities of both CO_2-unloaded and CO_2-loaded DEAE–MEA aqueous solutions were measured and then calculated by using the Weiland equation. The effects of temperature, mass fraction and CO_2 loading on viscosities are demonstrated.

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1. Introduction

The greenhouse effect and the acid rain caused by the emissions of carbon dioxide (CO_2) have attracted increasing attentions worldwide and the reduction of CO_2 has become a global issue [1–3]. Many technologies, including chemical absorption, physical adsorption, membrane separation, oxygen combustion of fuel [4,5], are currently employed for the separation of CO_2 from gas streams. Among these technologies, amine-based absorption technologies are considered to be the most robust and able to be used on a large scale for post-combustion CO_2 capture [6–8]. Alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA), have been widely applied to remove the acid gases in industrial processes [6,9].

In recent decades, interest increased rapidly in the use of mixed amine absorbents, especially the blends of primary-tertiary amines (*e.g.*, MEA–MDEA) or secondary-tertiary amines (*e.g.*, DEA–MDEA). The blending amines combine the high equilibrium capacity and low enthalpy of the tertiary amine with the high reaction rate of the primary or secondary amine [10,11]. The primary or secondary amine plays a role as activator. For example, MEA is considered as the promising additive to MDEA aqueous solution because it can absorb CO_2 and forms intermediate very quickly, and then the intermediate transfers CO_2 to MDEA [12]. Thus, small amount of MEA can significantly accelerate the absorption rate of CO_2 in

MDEA aqueous solution under appropriate temperatures. By far, adding small amount of MEA to an aqueous solution of MDEA has found widespread application in the removal of CO_2 [13–17]. The absorption performance of MEA-tertiary amine aqueous solution depends on the characteristics of both MEA and tertiary amine, *e.g.*, high reaction rate of MEA, high cyclic capacity and low enthalpy of tertiary amine. Development of new absorbents with higher absorption rates, higher absorption capacities, higher cyclic capacities and lower reaction enthalpies has attracted great attention for reducing CO_2 emission.

Recently, Chowdhury *et al.* [18] investigated the absorption characteristics of 24 tertiary amine absorbents and compared their performances with that of the conventional tertiary absorbent MDEA. Via laboratory experiments, seven tertiary amines with potential application in CO_2 capture were screened out. In particular, amine 2-diethylaminoethanol (DEAE) shows good chemical stability, higher CO_2 loading capacities, higher cyclic capacities yet lower heats of reaction than MDEA. Puxty *et al.* [19] studied the CO_2 absorption performance in 76 amines including DEAE. The trend of initial CO_2 absorption rate was given as DEAE > MDEA. By far, there are many studies concerning the thermodynamics and kinetics of solutions containing DEAE. Lebrette *et al.* [20] and Maham *et al.* [21] investigated the volumetric properties of DEAE aqueous solutions over the entire composition range at different temperatures. Benitez-Garcia *et al.* [22] measured the effect of basicity on the absorption of CO_2 in tertiary amines aqueous solution at $T = 298$ K. Kim and Savage [23] studied the absorption rates of CO_2 in DEAE aqueous solutions at 323 K and showed that the

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second-order kinetic rate constant increased with increasing basicity. Xu *et al.* [24] used 1,4-butanediamine (BDA) promoted DEAE aqueous solution to capture CO_2 and found that the addition of BDA into DEAE aqueous solution did accelerate the absorption rate. Littel *et al.* [25] investigated the kinetics of the absorption of CO_2 in DEAE aqueous solutions at $T = (293$ to $333)$ K, and deduced that the reaction order is around 1.0 for all the investigated temperatures. Vaidya and Kenig [26] studied the absorption rate of CO_2 in PZ promoted DEAE aqueous solutions at $T = (298$ to $308)$ K. Their results showed that small amount of PZ can significantly enhance the absorption rate. Konduru *et al.* [27] studied both the equilibrium and kinetic characteristics of the carbonated DEAE-PZ aqueous solutions. They concluded that CO_2–DEAE–PZ system belongs to the fast pseudo-first-order reaction regime system and determined the second-order rate constant.

Besides the absorption rate, the solubility of CO_2 is also an important parameter for the estimation of the absorption capacity of absorbent. However, studies concerning the saturated solubility of CO_2 in MEA–DEAE aqueous solutions under wide temperature and concentration ranges are rarely reported by far. Moreover, the solubility of CO_2 is closely related to solution viscosity, because viscosity significantly affects the liquid film coefficient for mass transfer [14,28–30]. Previous work [31,32] showed that the addition of activator into amine aqueous solution +sometimes leads to abnormalities in absorption capacity, especially in the case of high solution viscosity, because high viscosity of the solution leads to a less diffusion coefficient of the gas in the solution, thus hinders the absorption. From these views, it is very necessary to study the viscosities of MEA–DEAE aqueous solutions and illustrate the effect of viscosity on the solubility and CO_2 loading capacity.

The viscosities of binary solutions of DEAE and water have been measured and the results over comprehensive ranges of compositions and temperatures have been reported in the literatures [20,21,33]. However, the studies concerning the viscosities of carbonated DEAE–MEA aqueous solutions are rare so far.

The main purposes of this work are (1) to determine experimentally the solubility of CO_2 in MEA promoted DEAE aqueous solution and illustrate its mass fraction dependence; (2) to determine experimentally the viscosities of carbonated DEAE–MEA aqueous solution and then calculate it with Weiland equation [34], so as to demonstrate the effects of temperature, CO_2 loading, mass fractions of DEAE and MEA on viscosity.

2. Experimental

2.1. Materials

DEAE and MEA were used without further purification. The sample description is shown in table 1. Aqueous solutions of DEAE–MEA were prepared by adding the high purity water made from the Heal Force ROE (Reverse Osmosis Electrodeionization)-100 apparatus.

2.2. Apparatus and procedure

The solubility was measured by the equipment composed of one high-pressure CO_2 tank, one mass flow controller (MFC), one

mass flow meter (MFM), one absorption bottle, one constant temperature water bath, one desiccator and one CO_2 analyzer (Advanced Gasmitter by Germany Sensors Europe GmbH, the accuracy is ±2%). The schematic diagram of the experiment is shown in figure 1. The flask was immersed into the thermostatic bath and the temperature of the solution can be regulated within 0.1 K. During the experiment, CO_2 from a high-pressure tank (concentration $C_0 \geqslant 0.9999$, temperature T_0) was inlet into the MFC to maintain a constant flow rate (v_0) and then into the absorption bottle and absorbed by the solution. The residual and unabsorbed gas firstly flowed into the CO_2 analyser (temperature T_1) and then into the mass MFM. The CO_2 concentration (C_i) was measured by the CO_2 analyser, and the flow rate (v_i) was measured by the MFM. C_i, v_i and the corresponding time t_i were simultaneously recorded by the computer (interval time $\Delta t = 1$ s). The solution was saturated when C_i is close to 100%. The volume (V) of the absorbed CO_2 can be calculated from:

$$V = v_0 C_0 t \times 273.15/T_0 - \sum_{i=1} v_i C_i \Delta t \times 273.15/T_1 \qquad (1)$$

in which t is the total absorption time.

The CO_2 solubility can be calculated from:

$$n = \frac{V/22.4 \times 44}{m} \times 100 \qquad (2)$$

in which m is the total mass of CO_2 unloaded DEAE–MEA aqueous solution.

To verify the reliability of the equipment, the saturated CO_2 loading in MEA aqueous solution (30 wt%, 0.1 MPa, $T = 313.2$ K) was measured. The uncertainties for temperature, w_{MEA}, pressure and CO_2 loading are respectively 0.1 K, 0.0001, 5 kPa and 0.03 $molCO_2$ per molMEA. Our result ($\alpha = 0.58$) is close to the value ($\alpha = 0.59$) reported in the work of Shen *et al.* [37]. We also measured the CO_2 loading in DEAE aqueous solution (61 wt%, 0.1 MPa, $T = 313.2$ K) and compared with the value reported in the work of Arshad *et al.* [38] (61.087 wt%, 97 kPa, $T = 313.15$ K). The uncertainties for temperature, w_{DEAE}, pressure and CO_2 loading are respectively 0.1 K, 0.0001, 5 kPa and 0.03 $molCO_2$ per molDEAE. The deviation between our result ($\alpha = 0.76$) and that from the work of Arshad *et al.* [38] ($\alpha = 0.798$) is 5%.

Once the carbonated solution was prepared, varying proportions of the unloaded and loaded solutions were mixed together to produce a set of samples. CO_2 loading is defined as $\alpha = n_{CO_2}/(n_{DEAE} + n_{MEA})$ [34,39], in which n_{CO_2} is the mole of loaded CO_2, and n_{DEAE} and n_{MEA} are respectively the moles of DEAE and MEA in the unloaded aqueous solutions. A certain amount of CO_2 escaped when the loaded solution was mixed with the unloaded solution and the atmospheric CO_2 and humidity had some effects on the CO_2 loading and solution concentration. The CO_2 loadings of some diluted samples were checked by using the analytical method based on the precipitation of $BaCO_3$ [14,40]. The estimated uncertainty in the CO_2 loading was less than 2%.

The viscosities of the carbonated DEAE–MEA aqueous solutions were measured by using the NDJ-5S digital rotational viscometer produced by Shanghai Changji Geological Instrument factory. The measurement ranges and measurement error are respectively (0.1 to 10^5) mPa · s and ±1% (for a Newtonian fluid).

TABLE 1
Sample description.

Substance	Source	Mole fraction purity (as stated by the supplier)	CAS No.	Density/(g · cm^{-3}) at $T = 303.15$ K
MEA	Aladdin reagent	$x \geqslant 0.995$	141-43-5	1.0077 [35]
DEAE	Aladdin reagent	$x \geqslant 0.99$	100-37-8	0.87575 [36]
Carbon dioxide	Jinglian Gas	$x \geqslant 0.9999$		
Water	Heal force ROE-100apparatus	Electrical resistivity > 15 MΩ · cm at $T = 298$ K		