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Measurement and modelling of the solubility of carbon dioxide in aqueous 1,8-p-menthane-diamine solution

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ABSTRACT

The solubility of CO_2 in aqueous 1,8-p-menthane-diamine (MDA) solution with substance concentrations of 0.625 and 1.25 mol · L^{-1} was measured at temperatures (313.15, 333.15 and 353.15) K with CO_2 partial pressures ranging from (0.55 to 776.0) kPa and CO_2 loading ranging from (0.120 to 1.97) mol CO_2 per mol MDA. The gas solubility results are expressed as the partial pressure of CO_2 (P_{CO_2}) against its mole ratio, *i.e.* α_{CO_2} (mol CO_2 per mol MDA). The chemical absorption reaction and thermodynamic model have been proposed. The physicochemical Kent–Eisenberg model was used to correlate all the experimental results of the solubility of CO_2 in the aqueous MDA solutions under investigation. The chemical equilibrium constants and model parameters were determined by fitting the VLE data.

1. Introduction

The greenhouse effect induced by CO_2 emissions has been receiving ever-increasing attention. The majority of industrial CO_2 emissions come from power plants using fossil fuels such as coal and natural gas. Amine scrubbing is probably the only technology for the post-combustion capture of CO_2 [1]. Monoethanolamine (MEA) solutions are widely used in CO_2 capture because of their fast reaction rate and low solvent cost. However, the loading capacity of MEA reduces because of the formation of stable carbamate [2,3]. Methyldiethanolamine (MDEA) has a higher loading capacity and lower absorption of heat, but it exhibits low reaction rates [4]. Recently, piperazine (PZ) has received increasing attention due to its higher loading capacity and better physical properties [5,6]. It is worthwhile to search for amines with better physical properties, higher loading capacities and faster reaction rates.

As shown in figure 1 1,8-p-menthane-diamine (MDA) comprises an alicyclic ring with two primary NH_2 groups. In the MDA molecule, the steric hindrance introduced by the bulky substituent adjacent to the amino group lowers the stability of the carbamate formation. The steric hindrance enables the MDA to yield a higher thermodynamic capacity and a faster reaction rate with CO_2 [7]. Furthermore, MDA has several special physical and chemical properties, including excellent antioxidant ability and high thermal stability. Kim *et al.* [8] reported that the CO_2 loading ratio of the MDA solution is higher than that of 2-amino-2-methyl-1-propanol (AMP), MDEA and MEA, and the regeneration heat of aqueous MDA is lower than that of aqueous MEA. Lee *et al.* [9] measured the absorption rate of CO_2 of an AMP solution with MDA as an additive; the obtained absorption rates were higher than those of MEA and AMP solutions. They concluded that MDA can be used as an excellent absorbent or additive for AMP for CO_2 capture. However, experimental data regarding the solubility of CO_2 in aqueous MDA solutions are insufficient and the equilibrium constants for MDA-CO_2–H_2O are not available. Measuring the fundamental (vapour + liquid) equilibrium (VLE) data and modelling the data for applications in industrial design and operation purposes can prove worthwhile.

In this work, we measured the solubility of CO_2 in aqueous MDA solutions with concentrations of (0.625 and 1.25) mol · L^{-1} at T = (313.15, 333.15 and 353.15) K over a pressure range of (0.55 to 776.0) kPa. The VLE data were regressed using the well-known Kent–Eisenberg (KE) model [10]. Thereafter, the sterically hindering effect is discussed by comparing the equilibrium constants.

2. Materials and methods

2.1. Reagents

The MDA was purchased from Rohm and Haas Chemicals LLC; by means of chromatographic analyses (Agilent 7890A, FID

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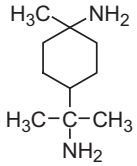

FIGURE 1. Molecular structure of MDA.

detector, HP-5 column), it was determined that the purity was more than 97%. The solution was prepared with deionised water. The gases and other reagent used in this experiment were listed in table 1.

2.2. Solubility measurement

2.2.1. Apparatus

The schematic representation of the apparatus used to measure the CO_2 solubility is shown in figure 2. The reactor (GCF-0.5, Dalian Automatic Control Equipment Factory, China) consisted of a cylindrical stainless steel tank (595 cm^3 by calibration) that was fitted with a magnetically coupled stirrer. A thermometer (TM-301, AS ONE Co., Japan) with an uncertainty of ±0.1 K was used to measure the temperature in the reactor. A pressure transducer (2600T, ABB Ltd., Switzerland) with an uncertainty of ±0.075% was used to measure the pressure in the reactor. A water bath (±0.1 K) was used to control the temperature of the reactor tank. A mass flow meter (CS200, SEVENSTAR Ltd., China) was used to control the total mass of CO_2 introduced into the reactor.

2.2.2. Absorption procedure

The CO_2 absorption experiment was carried out as follows. First, the concentration of the studied aqueous solution of MDA were prepared by mass using an analytical balance (Mettler ML104, ±0.0001 g). 100 mL (298.15 K) aqueous MDA solution was placed in the reactor. A vacuum pump was used to remove the remaining air; then, N_2 gas was introduced into the reactor. The pressure in the reactor was maintained to be stable after stirring at a speed of 150 rpm for approximately 1 h. Then, the VLE in the reactor was achieved, and the pressure was recorded as P_{N_2}. The CO_2 gas was introduced into the gas container via the mass flow meter, and the volume of the standard state introduced into the reactor was recorded. The temperature in the reactor was then adjusted to the desired level. The VLE was achieved again after approximately 10 h, and the equilibrium pressure in the reactor was recorded as P_T.

The Peng–Robinson cubic equation of state (P–R EOS) [11] was used to represent the non-ideal gas. The original equation can be expressed as

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}. \quad (1)$$

Here, v represents the molar volume of a gas at a particular pressure and temperature, which can be calculated using the P–R EOS if the volume, pressure and temperature of the gas phase of the system are already known. The number of moles of gas in the system (n) can be calculated as

$$n = V/v, \quad (2)$$

where V is the system volume occupied by the gas phase. The moles of the gas introduced into the reactor measured by the mass flow meter are defined as n_{in}. With the assumption that the gas phase obeys Dalton's law, when the VLE is achieved in the reactor, the partial pressure of CO_2 (P_{CO_2}) can be determined using

$$P_{CO_2} = P_T - P_{N_2}. \quad (3)$$

According to the P–R EOS, the number of moles of CO_2 in the reactor is n_{CO_2}. The moles of CO_2 absorbed in 100 mL of MDA (n_{ab}) at the pressure P_{CO_2} can be calculated as

$$n_{ab} = n_{in} - n_{CO_2}. \quad (4)$$

Using the moles of CO_2 dissolved in MDA (n_{ab}) and the total moles of MDA introduced into the reactor (n_{amine}), the CO_2 loading capacity (α_{CO_2}) in the liquid phase can be defined as

$$\alpha_{CO_2} = \frac{n_{ab}}{n_{amine}}. \quad (5)$$

The uncertainty in the measured temperature, pressure and volume were ±0.1 K, ±0.075% and ±0.5%, respectively. The uncertainty in determining the MDA concentration was estimated as ±1%. From Eqs. (3)–(5), the uncertainty of CO_2 loading can be determined using the following equation:

$$\alpha_{CO_2} = \frac{n_{in} - n_{CO_2}}{n_{amine}}. \quad (6)$$

The contributions of Δn_{in} and Δn_{CO_2} account for the uncertainties in the measured temperature, pressure and volume. The contribution of Δn_{amine} can be attributed to the MDA concentration. The uncertainty of α determined from the above uncertainties was estimated as ±3.5%.

To verify the uncertainty of the experiment, the solubility of CO_2 in 30 wt% (4.95 mol · L^{-1}) MEA solution was measured at T = 313.15 K and the obtained results were compared with the literature data [12,13] (figure 3).

The experimental VLE data used for correlation are listed in tables 2 and 3.

TABLE 1
Source and purity of chemicals used in this work.

Chemicals	Source	Mass fraction purity
MDA	Rohm and Haas Co.	>0.97
MEA	Sigma–Aldrich	⩾0.99
N_2	Qianxi Gas Co.	⩾0.999
CO_2	Qianxi Gas Co.	⩾0.999

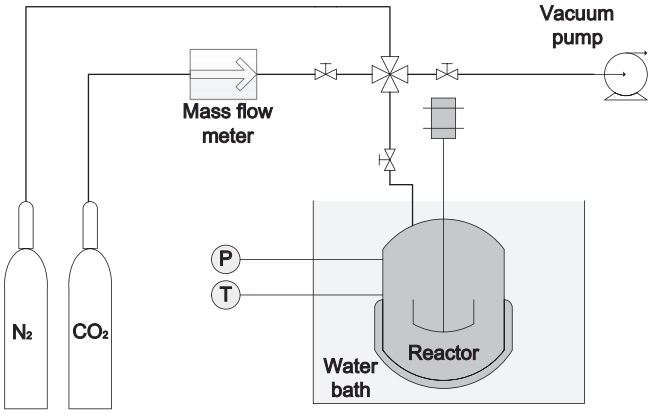

FIGURE 2. Schematic diagram of the experimental equipment.

2.3. Thermodynamic framework

Numerous ionic species exist in the liquid phase and certain chemical equilibrium constants are unknown; therefore, the physicochemical KE model [10] was used in this study to correlate the VLE data. This model was developed by Hu and Chakma [14], who