Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Experimental method for simultaneous and continuous measurement of absorption rate, viscosity and heat of reaction of carbon dioxide capture solvents

Junghwan Kim, Huiyong Kim, Jayeop Kim, Sung June Hwang, Kwang Soon Lee*

Chemical and Biomolecular Engineering Department, Sogang University, 35 Baekbeom-ro, Mapogu, Seoul 121-742, Republic of Korea

ARTICLE INFO

Article history:
Received 4 September 2017
Received in revised form 20 November 2017
Accepted 10 December 2017
Available online xxx

Keywords:
Carbon dioxide capture
Solvent screening
Wetted wall column
Simultaneous measurements
Continuous measurements

ABSTRACT

When screening solvents for carbon capture, a large amount of property data for each solvent in the CO_2-loaded state is required. In this paper, a novel experimental method is proposed that involves modifying a wetted wall column in order to simultaneously measure the absorption rate, viscosity, pH, and heat of reaction of carbon capture solvents while the CO_2 loading is increased continuously. The proposed method was applied to 30 wt% aqueous monoethanolamine and 30 wt% aqueous piperazine as solvents and found to produce measurement results that matched well with literature data.

Introduction

Reactive absorption is generally accepted as the most feasible technique among the various options for post-combustion CO_2 capture from large CO_2 emission sources such as power plants and industrial plants. The greatest challenge facing the absorption process before commercial deployment is further reduction of the energy demand [1–3]. A high-performance solvent is the key to the development of an energy-conservative process.

The development of a CO_2 capture solvent usually involves a screening process where various properties of many solvent candidates are measured, evaluated or derived, including CO_2 vapor–liquid equilibrium (VLE), absorption rate, heat of reaction, and viscosity. These properties should be measured for different CO_2 loadings. Thus, the measurement process is labor intensive and time consuming.

CO_2 absorption rate is measured using a wetted wall column (WWC) apparatus [4–8], although other measurement devices are sometimes used, such as a laminar jet [9], stopped-flow instrument [10,11], and stirred cell [12,13]. In the traditional WWC apparatus, the absorption rate is measured after the solvent reservoir is charged with 1–2 L of pre-loaded solvent to prevent the loading from varying during the measurement. Therefore, measurements for different CO_2 loadings at different temperatures require a rather large amount of solvent and a very long time.

Behr et al. [7] and Tunnat et al. [8] revised the traditional WWC experiment and operated the apparatus under a continuously increasing CO_2 loading. The solvent reservoir was charged with a small amount (approximately 130 mL) of solvent, and the outlet CO_2 concentration was measured continuously with time in order to estimate the transport of CO_2 to the solvent. However, they simply showed loading-dependent CO_2 flux data for various amine solvents instead of the mass transfer coefficient, which requires VLE information for computation.

The heat of reaction can be measured using a reaction calorimeter system [14] or estimated by applying the Gibbs–Helmholtz equation [15] to VLE data. A reaction calorimeter is a simple semi-bath reactor in which a solvent is pre-charged and CO_2 gas is continuously injected while the reactor temperature is regulated by a circulating cooling medium. Temperatures at various positions are accurately measured, and the heat of reaction is computed based on the heat and mass balance relationships. Reaction calorimeters from Mettler Toledo typically include 2000 cm^3 reaction vessels into which approximately 1500 mL of solvent is charged.

In this paper, we present a novel WWC-based experimental device with which absorption rate, heat of reaction, viscosity, and pH can be measured simultaneously as the CO_2 loading of the solvent is continuously increased. A set of experiments requires less than 150 mL of a solvent. The CO_2 absorption rate (mass

---

* Corresponding author.
E-mail address: kslee@sogang.ac.kr (K.S. Lee).

https://doi.org/10.1016/j.jiec.2017.12.012
1226-086X/© 2017 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

transfer coefficient) is calculated at each loading under the quasi-equilibrium assumption. The heat of reaction is estimated based on the heat and mass balance relationships and temperature measurements at the inlet and outlet positions of gas and solvent flows. The viscosity is calculated using a pressure drop measurement across a narrow tube and the Hagen–Poiseuille equation. Lastly, the pH is measured using a pH meter inserted in the solvent reservoir.

The proposed experimental technique was applied to 30 wt% aqueous monoethanolamine (MEA) and 30 wt% aqueous piperazine (PZ) as solvents. The absorption rate, heat of reaction, viscosity, and pH were measured as functions of loading and compared with literature data to validate the reliability of the proposed technique.

Description of the experimental apparatus

A schematic diagram of the proposed experimental apparatus is given in Fig. 1. The core part of the apparatus is contained in a constant-temperature air convection oven. A gas supply unit and a CO_2 sensor with auxiliary parts are installed outside the oven. A mixed gas with 15% CO_2 and 85% N_2 is fed through the mass flow controller (MFC, EL-Flow F-201CV from Bronkhorst) to the WWC at a rate of 4.75 standard liters per minute (SLM) after being fully moisturized in a water saturator. The exhaust gas from the WWC is dried completely in two desiccant units, and enters the nondispersive infrared (NDIR) sensor with 30% span from Edinburgh Gascard NG for the measurement of the CO_2 fraction in the exit gas. The CO_2 absorption rate and the CO_2 loading of the solvent are calculated using the CO_2 flow rate and concentration measurements.

The apparatus requires 120 mL of solvent, which is circulated around the WWC loop while the CO_2 loading is increased continuously. The solvent in the liquid reservoir is pumped at a rate between 130 and 200 mL/min using a gear pump (GA-V21 from Micropump), and it passes through the liquid oval flowmeter from FLOMEC, a short one-eighth-inch section of tube, and the WWC, and is returned to the reservoir. A differential pressure transmitter (DWS from Sensys) is installed across the one-eighth-inch tube section to measure the viscosity, and a pH electrode (InPro4800i from Mettler Toledo) is installed in the solvent reservoir. Thermocouples (TCs) calibrated within ±0.02 °C using a Fluke 7526A calibrator with a resistance temperature detector (RTD) reference sensor (Fluke 5622-10-M) are installed at the inlet and outlet positions of the gas and liquid streams of the WWC for the estimation of the heat of reaction.

The design of the WWC is the same as that reported by Dugas [4]. A double-layered tube made of SUS316 and Teflon for the outer and inner walls, respectively, is installed inside a cylindrical glass shell. Details of the shape and dimensions of each part are given in Fig. 2(a). The solvent enters the tube from the bottom, and then flows over the tube and downward on the outer surface of the SUS tube. The gas flows upward through the shell side. Fig. 2(b) presents the details of the viscosity measurement section. Measurements were taken once every second.

Data analysis for each measured property

Mass transfer coefficient based on CO_2 loading

Fig. 3 shows how the mass transfer coefficient was calculated. The procedure is basically the same as that with the batch WWC, except that the calculation is conducted continuously while the CO_2 loading is increased. Fig. 3(a) shows the results of real-time measurement of the CO_2 concentration of the gas stream at the inlet and outlet. CO_2 molar flux to the solvent can be calculated according to the following equation:

$$\dot{n}_{CO_2}\left[\frac{\text{mol}}{\text{m}^2\text{min}}\right] = \frac{PQ_G}{ART}\left(\frac{y_{in} - y_{out}}{1 - y_{out}}\right) \tag{1}$$

where y, A, Q_G, P, R, and T denote the CO_2 mole fraction, gas–liquid interfacial area (m^2), inlet volumetric gas flow rate (m^3/s), pressure (kPa), gas constant, and absolute temperature (K), respectively. A, which includes the bell-shaped top [4] and the effect of the liquid film thickness [16], was calculated and estimated to be 0.040–0.042 m^2 with a liquid flow rate in the 2.17×10^{-6} to 3.33×10^{-6} m^3/s (130–200 mL/min) range and viscosity in the 1–40 cP range.

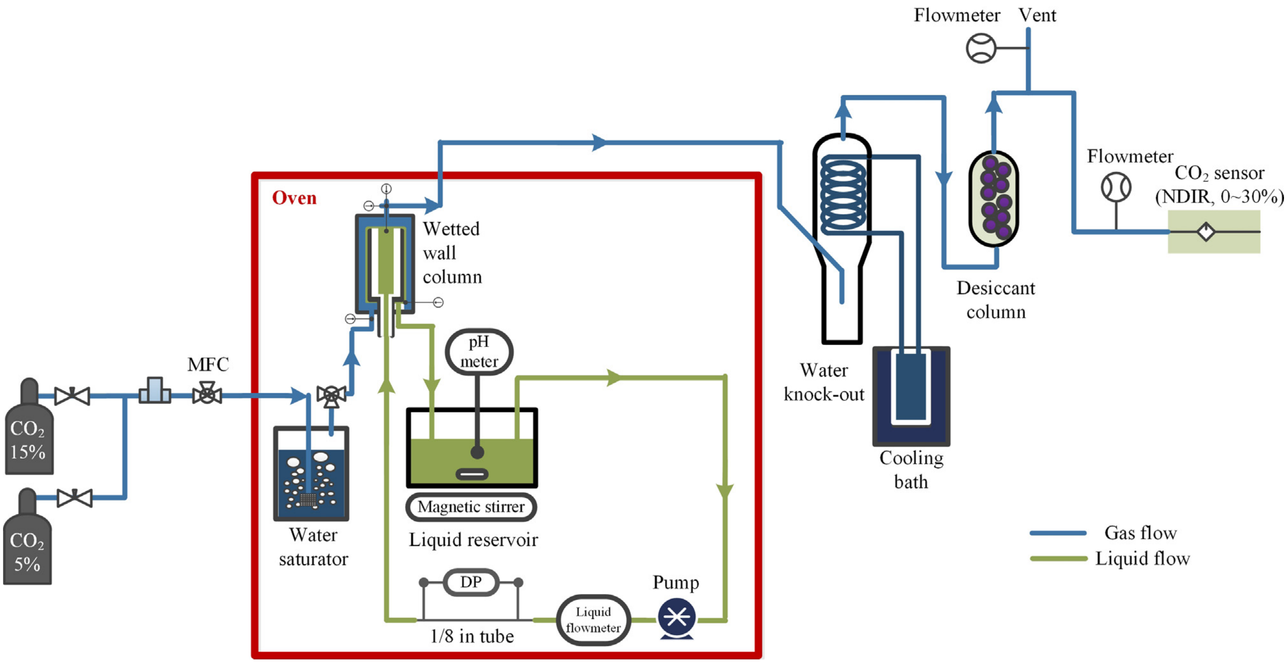

Fig. 1. Schematic diagram of the experimental apparatus.

Please cite this article in press as: J. Kim, et al., Experimental method for simultaneous and continuous measurement of absorption rate, viscosity and heat of reaction of carbon dioxide capture solvents, J. Ind. Eng. Chem. (2017), https://doi.org/10.1016/j.jiec.2017.12.012