High Throughput CO_2 Solubility Measurement in Amine Solution using HS-GC

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Abstract

CO_2 solubility is one of the key factors in evaluating the energy consumption of the CO_2 capture process from flue gas or air. High-throughput CO_2 solubility measurement techniques such as small samples, rapid equilibration time, automated sample change, and high reproducibility are important, especially in the amine screening phase. We have developed a measurement apparatus of CO_2 solubility in amine solutions using headspace gas chromatography (HS-GC). We used a GC-3200 gas chromatograph (GL Sciences) with a Turbomatrix HS16 headspace autosampler (Perkin Elmer) and a thermal conductivity detector. The equilibrium time and calibration curve were checked first. Developed apparatus showed high reproducibility with reference CO_2 solubility data in amine solution. Using HS-GC system, we have been evaluating new type of CO_2 capture solution including phase separation solvent, water-lean solvent and polyamine solutions.

1. Introduction

CCS (Carbon dioxide captured and storage), CCU (Carbon dioxide captured and Utilization) and DAC (Direct Air Capture) are expected as a counter-measure technology against global warming. These technologies include capturing CO_2 from combustion exhaust gas or the atmosphere. Therefore, energy saving of CO_2 capture technology is required for practical use of this technology. Typical CO_2 capture techniques include an absorbent method, an adsorbent method, and a membrane separation method. The absorbent method has many researches and practical applications, and is adopted by in the Petra Nova carbon capture project in Texas and Tomakomai CCS project in Japan, etc [1]. Various absorbents are being developed to save energy.

One of the indicators of absorbent development is CO_2 solubility. Most of the CO_2 recovery energy is dominated by the heat load in the reboiler, which consists reaction heat, sensible heat of absorbent, steam latent heat. These energies can be estimated from the CO_2 solubility data. The heat of reaction can be estimated from the change in equilibrium pressure at a certain solubility as shown by the Gibbs-Helmholtz equation. The sensible heat of absorbent can be calculated from the difference between rich loading and lean loading from the equilibrium solubility, and the heat exchanger temperature setting. The latent heat of vaporization can be estimated by Raoul's law at the tower top temperature. Goto et al. reported that CO_2 capture energy estimated from summation of each energy is close trend with bench scale energy analysis [2]. Therefore, CO_2 solubility is important for screening for an absorbent. More detailed tower design, mass balance, and heat balance can be obtained by determining reaction equilibrium parameters in the process simulator using CO_2 solubility data.

Examples of the CO_2 solubility measuring method include a method of measuring by a batch-type vapor-liquid equilibrium device as shown in et al.[3], A method of measuring by a flow-type method [4], and a method of measuring by Headspace GC [5]. Both the batch-type and the flow-type require equilibration time, sample replacement, equipment cleaning, etc., and it takes time in the initial screening stage. Therefore, we established a solubility measurement method by the HS-GC method. We also report the evaluation results of the new absorbent solution by this apparatus.

2. Experimental

CO_2 solubility measurement was conducted by Headspace GC. We used a GC-3200 gas chromatograph (GL Sciences) with a Turbomatrix HS16 headspace autosampler (Perkin Elmer) and a thermal conductivity detector. The measurement procedure is briefly explained as follows. First, a desired concentration of amine solution was prepared, then CO_2 was dissolved in this prepared sample. The CO_2 concentration in the sample was determined using TOC (total organic carbon). The desired CO_2 concentration sample was prepared by mixing the CO_2 loaded and unloaded samples. These samples were enclosed in a headspace vial. Next, the gas phase of the vial was analyzed according to the Headspace-GC setting conditions. The partial pressure of CO_2 in the gas phase was obtained from the peak area of CO_2. The relationship between peak area and partial pressure was pre-determined from the relationship between MDEA: N -methyl diethanolamine area values with accurate CO_2 solubility data. To confirm the reliability of the measurement, MEA: 2-aminoethanol (30 wt%) [3] and MDEA (2, 4 mol/kg) [5], which are typical amines, were measured.

3. Results and discussion

3.1. Effect of equilibration time

Prior to the measurement, the headspace GC method had to determine the equilibrium time, which means the time to achieve vapor-liquid equilibrium in the vial. To check the equilibrium time, its dependence for GC area was measured. Figure 1 shows the relationship between equilibrium time and area. The equilibrium was reached in about 30-40 minutes.

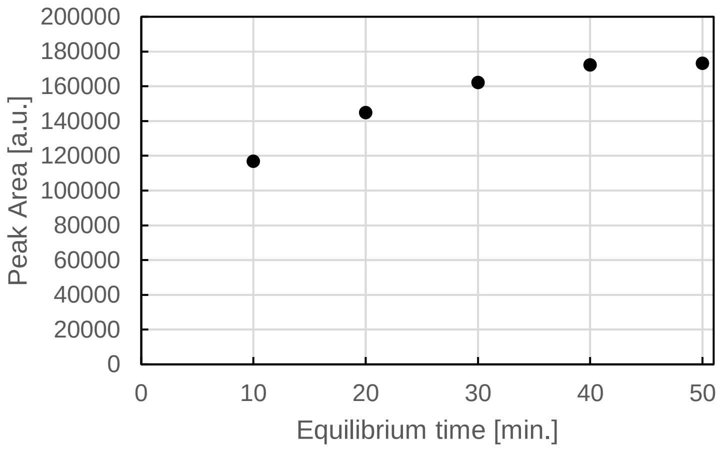

Fig.1 Relationship between equilibrium time and peak area (4 mol/kg MDEA)

3.2. CO_2 solubility of amine solution

Figure 2 shows the results of equilibrium solubility measurement of MDEA and MEA and comparison results of literature values. The isothermal data can be measured 10 points in 6 hours. The flow-type CO_2 solubility measurement conducted in our laboratory takes 2 to 6 hours to measure one point, which can greatly improve the efficiency. As shown in the figure, the agreement of the literature data is also high.

Currently, we are conducting a highly efficient screening for CO_2 absorbents by linking predictions from molecular structures, machine learning, and the results of this high-speed CO_2 solubility measuring apparatus.

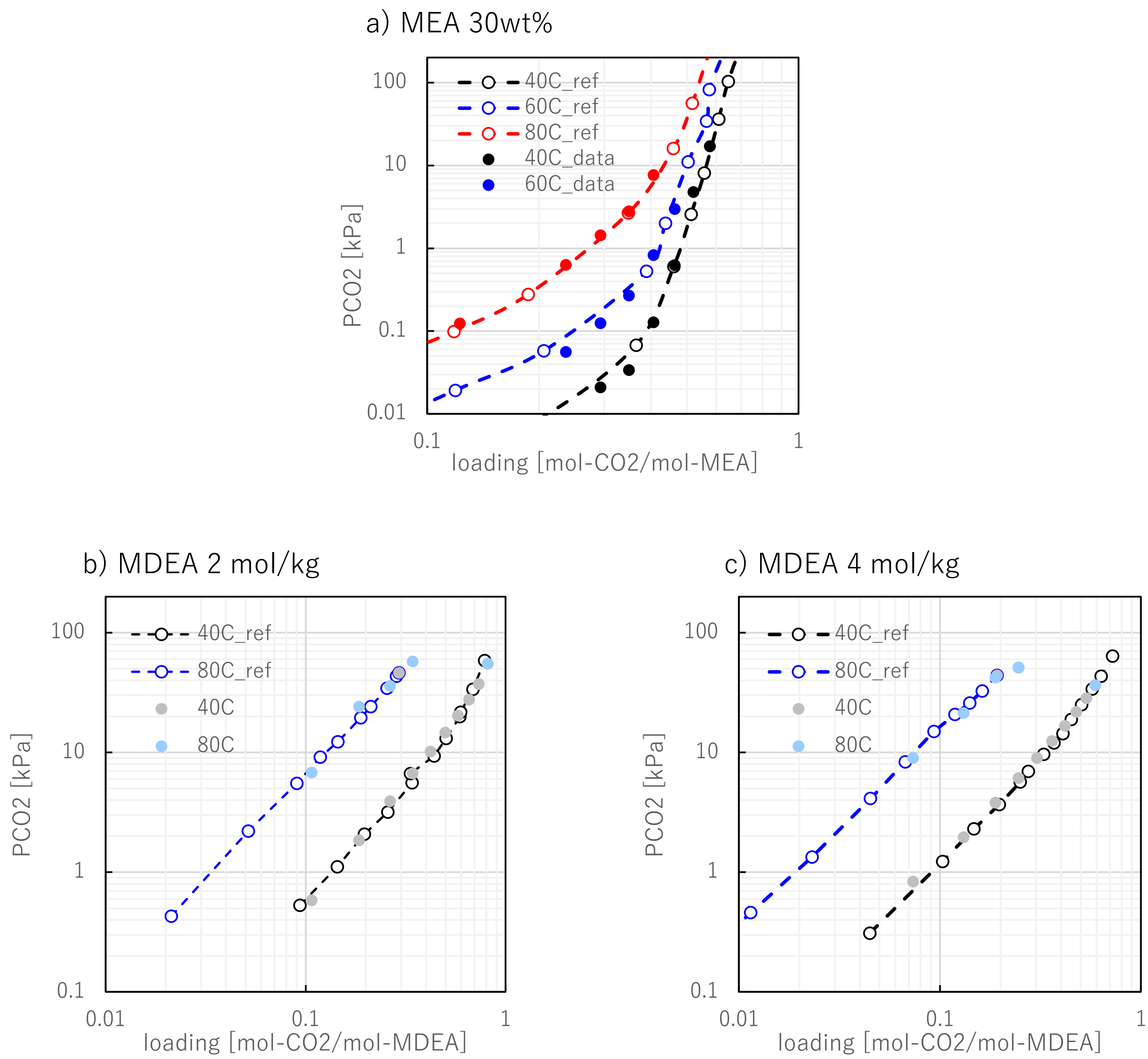

Fig. 2 Comparison of CO_2 solubility data between our data and references MEA (30 wt%) [3] and MDEA (2, 4 mol/kg) [5]

6. Conclusion

To develop a high-throughput CO_2 solubility measurement apparatus in amine solution, we verified the Headspace-GC system. It showed a high agreement with the literature data, and also showed that it was possible to measure at shorter measurement time compared with the conventional batch-type and flow-type measurement.

Currently, we are evaluating the newly developed absorbent solution by this Headspace GC method. We are also building a new system with a detector suitable for measuring ppm level CO_2 suitable for DAC.

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References

[1] D. Rassool, C. Consoli, A. Townsend, H. Liu, Glob. CCS Inst. (2020).

[2] K. Goto, H. Okabe, F.A. Chowdhury, S. Shimizu, Y. Fujioka, M. Onoda, Int. J. Greenh. Gas Control. 5 (2011) 1214–1219.

[3] F.-Y. Jou, A.E. Mather, F.D. Otto, Can. J. Chem. Eng. 73 (1995) 140–147.

[4] H. Yamada, F.A. Chowdhury, K. Goto, T. Higashii, Int. J. Greenh. Gas Control. 17 (2013) 99–105.

[5] V. Ermatchkov, Á. Pérez-Salado Kamps, G. Maurer, Ind. Eng. Chem. Res. 45 (2006) 6081–6091.