

High-Throughput CO₂ Solubility Measurement in Miscible and Liquid–Liquid Phase Separation Types of Amine Solvent Using Headspace Gas Chromatography

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Cite This: *Ind. Eng. Chem. Res.* 2024, 63, 5823–5832



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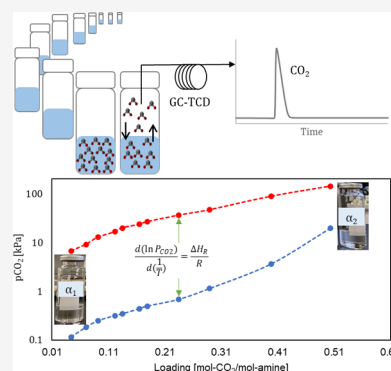
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ABSTRACT: CO₂ solubility is one of the key factors in evaluating not only the efficiency of the absorbent but also the energy consumption of the CO₂ capture process from flue gas. In this study, a system namely headspace gas chromatography (HS-GC), which is a combination of gas chromatography (GC-3200, GL Sciences) and a headspace autosampler (Turbomatrix HS16, PerkinElmer), was developed to measure the CO₂ solubility of amine solutions. The equilibrium time and calibration curve of this system were checked and compared with those of the literature data. The developed system showed high reproducibility with reference CO₂ solubility data of benchmark amine solutions. Distinct from conventional measurement methods of CO₂ solubility, high-throughput CO₂ solubility measurement by HS-GC shows its advantages such as a small amount sample requirement, rapid achievement of equilibration time, automation of sample exchange, and high reproducibility, which is superior in the amine solvent screening phase. Moreover, this system can evaluate new types of CO₂ capture solvents, including the phase separation solvent. By acquiring continuous data, the inflection point in the solubility curve indicated by phase separation was observed. The absorption heat estimated from those CO₂ solubility curves measured by this system also agrees well with the experimental data.

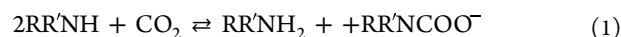


1. INTRODUCTION

In transitioning to a net zero world and keeping global warming down to no more than 1.5 °C (The Paris Agreement), CO₂ emissions are required to be reduced by 45% by 2030 and reach net zero by 2050. Hence, carbon dioxide captured and storage (CCS), carbon dioxide captured and utilization (CCU), and direct air capture (DAC) are expected as the counter-measure technologies against global warming. However, their energy consumption assessment is still in the primary stage. Therefore, energy savings of CO₂ capture technologies are required for their practical use. Typical CO₂ capture techniques include an absorbent method, an adsorbent method, and a membrane separation method. The absorbent method has already been used for commercial-scale applications such as the Petra Nova carbon capture project in Texas or demonstration projects such as the Tomakomai CCS project in Japan, etc.¹ Various absorbents are being developed to save energy.^{2,3}

In our laboratory, we developed a new phase-separation absorbent that changes from homogeneous to liquid–liquid phases after CO₂ absorption.^{4,5} This absorbent contains amine (2-(ethylamino)ethanol (EAE)), organic solvent (diethylene glycol diethyl ether (DEGDDE)), and water at a 30:60:10 weight ratio. After CO₂ is flown into the solution, the amine in the organic solvent reacts with CO₂ as in eq 1 to form

carbamate with a hydrophilic characteristic, whose hydrophobicity is far from that of the hydrophobic organic solvent (DEGDDE). As a result, the absorbent exhibits phase separation into two phases: a CO₂-lean phase with DEGDDE as the main component and a CO₂-rich phase with carbamate, amine, and water.



where R and R' are C₂H₅- and -CH₂CH₂OH, respectively.

Both phases are mixed well and sent to the regeneration tower. Here, the freed amine will be dissolved again into the CO₂-lean phase (DEGDDE phase), in which reaction 1 voluntarily moves to the left side. This means that ether boosts the regeneration of solvent. Consequently, this absorbent can be regenerated at a lower temperature compared to the conventional one (i.e., aqueous solvent of 2-aminoethanol (MEA) 30 wt %). To create an energy-saving

Received: September 18, 2023

Revised: February 19, 2024

Accepted: February 23, 2024

Published: March 19, 2024



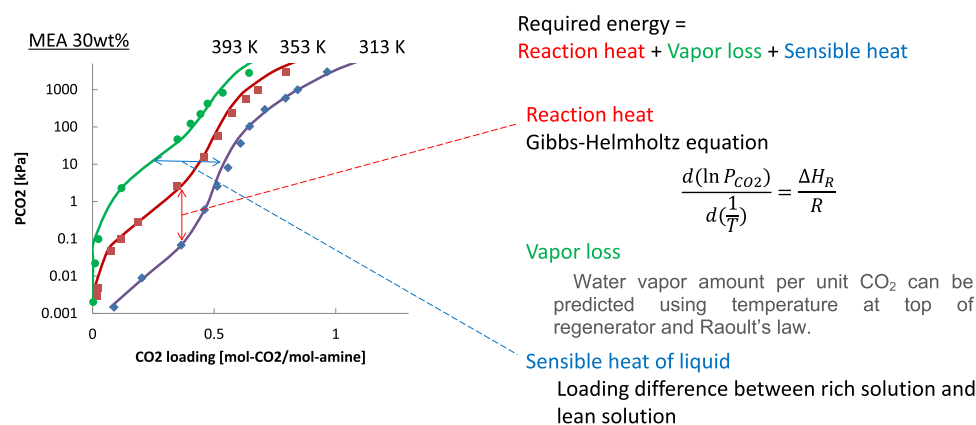


Figure 1. Main components for estimating the CO₂ capture energy can be calculated from the CO₂ solubility data.

absorption process, a heat pump was also used to recover the absorption heat. The phase separation solvent with a heat pump system demonstrated an energy consumption of around 1.6 GJ/ton-CO₂, indicating that this is an absorbent that saves energy.^{6,7} The physical characteristics of this absorbent such as CO₂ solubility,⁸ density, viscosity,⁹ and heat of absorption¹⁰ have been measured for process design. In addition, we have reported the development of in situ composition analysis technology by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR),¹¹ insight into the microscopic structure by small-angle X-ray scattering (SAXS),¹² and the methods to predict phase-separated absorbent by the conductor-like screening model for real solvents (COSMO-RS) method.^{13,14}

In absorbent development, the CO₂ solubility is an important indicator to evaluate its CO₂ capture efficiency. Moreover, the CO₂ capture energy (mentioned as the required energy in this paper) can be estimated from this CO₂ solubility data. Tower design, mass balance, and heat balance can be obtained by determining reaction equilibrium parameters in the process simulator using CO₂ solubility data. CO₂ captures energy by calculation in a test plan and its energy under practical operation agrees well with the report of Goto et al.¹⁵ Therefore, CO₂ solubility is an important parameter in absorbent screening.

Here, we explain how to obtain the required energy from the CO₂ solubility data. Most of the required energy is dominated by the heat load in the reboiler, which consists of reaction heat, the sensible heat of absorbent, and steam latent heat.¹⁶ These energies can be estimated from the CO₂ solubility data, explained in Figure 1.

The reaction heat or absorption heat is the heat generated when dissolved CO₂ reacts with an amine. It can be measured experimentally by calorimetry.^{17–20} Direct calorimetry provides accurate values on the enthalpy of absorption of CO₂ and amine and the influence of temperature on the absorption heat. In flow calorimetry (method (1)), CO₂ is added to increase the loading from 1 to loading 2. In this case, the amount of CO₂ absorbed is the difference between the two loadings. The absorption heat can be calculated by integral in loading but differential in temperature. Calorimetry in method (1) requires equilibrium time, and only one point of data can be obtained. The change of absorption heat between the two loadings cannot be observed. In reaction calorimetry (method (2)), CO₂ is added in several steps while the reactor temperature is kept constant. The absorbed CO₂, as a result, is differential in

the whole loading range. The absorption heat is calculated by differential in both temperature and loading. In our previous work, continuously measured calorimetry was used to measure absorption heat over a range of loading as in method (2).¹⁰ Besides calorimetry, the absorption heat can be obtained via temperature-dependent solubility (or CO₂ solubility curves), i.e. from the change in equilibrium pressure at a certain solubility as shown by the Gibbs–Helmholtz equation (eq 2). Because $\ln P_{\text{CO}_2}$ has a linear relation with $1/T$, this method does not show the temperature dependence of the reaction. To assess a solvent efficiency, not only its cyclic capacity but also its absorption heat should be considered. Nevertheless, the absorption heat estimated by the CO₂ solubility curves meets the fast criterion with acceptable results in evaluating the CO₂ absorption efficiency of an absorbent.

$$\frac{d(\ln P_{\text{CO}_2})}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_R}{R} \quad (2)$$

The heat due to vapor loss is defined as the heat required to evaporate water in the regenerator. The saturated vapor pressure of solution (p_w) at the tower's top temperature t (°C) can be calculated based on the Tetens equation (eq 3).²¹

$$p_w = 6.1078 \times 10^{7.5 \times t / (t + 237.3)} \times \frac{1}{10} \quad (3)$$

The total pressure at the top of the regenerator is the sum of partial pressure of CO₂ (p_{CO_2}), water ($p_{\text{H}_2\text{O}}$), and amine (p_{amine}): $P_{\text{top}} = p_{\text{CO}_2} + p_{\text{H}_2\text{O}} + p_{\text{amine}}$, where p_{amine} is too small, which can be negligible. The partial pressure of water ($p_{\text{H}_2\text{O}}$, kPa) can be obtained by Raoult's law $p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^* \times x_{\text{H}_2\text{O}}$, where $x_{\text{H}_2\text{O}}$ is the mole fraction of water in the solution and $p_{\text{H}_2\text{O}}^*$ is the vapor pressure of pure water.

The vapor heat loss (Q_{vap} , kJ/mol-CO₂) is as below:

$$Q_{\text{vap}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{CO}_2}} \times \Delta H_{\text{vap}} \quad (4)$$

where p_{CO_2} [kPa] is the partial pressure of CO₂ and ΔH_{vap} is the enthalpy of water vaporization [kJ/mol].

Loading (α , mol-CO₂/mol-amine) is defined as the molar ratio between absorbed CO₂ and amine in solution. The sensible heat of absorbent (Q_{sen} , kJ/mol-CO₂) is the heat

Table 1. Materials

materials	CAS	abbr.	supplier	purity [%]
2-aminoethanol	141–43–5	MEA	Wako Pure Chemical Industries, Ltd.	99.0
<i>N</i> -methyl diethanolamine	105–59–9	MDEA	Tokyo Chemical Industry CO., Ltd.	99.0
2-(ethylamino)ethanol	110–73–6	EAE	Tokyo Chemical Industry CO., Ltd.	98.0
diethylene glycol diethyl ether	112–36–7	DEGDEE	Tokyo Chemical Industry CO., Ltd.	98.0
diethylene glycol monomethyl ether	111–77–3	DEGMME	Tokyo Chemical Industry CO., LTD	>99.0
ethylene glycol	107–21–1	EG	Tokyo Chemical Industry CO., Ltd.	99.5

necessary to raise the liquid's temperature to the temperature of regeneration. It can be calculated from the difference between CO₂-rich loading and CO₂-lean loading (i.e., cyclic capacity ($\Delta\alpha$), mol-CO₂/mol-amine), and the temperature difference between absorption and desorption (ΔT , K) (eq 5).

$$Q_{\text{sen}} = \Delta T c_p \frac{1}{\Delta\alpha} \times \frac{M_{\text{amine}}}{\text{weight fraction of amine insolution}} \times \frac{1}{1000} \quad (5)$$

where c_p represents the specific heat of the solution, and M_{amine} is the molecular weight of amine (g/mol).

Based on the above calculations, the CO₂ capture energy can be estimated. Therefore, the CO₂ solubility plays an important role in absorbent screening.

CO₂ solubility can be measured using various apparatuses such as a batch-type vapor–liquid equilibrium device,²² a flow-type method,²³ and headspace gas chromatography (HS-GC).²⁴ Both the batch type and the flow type require equilibration time, sample replacement, equipment cleaning, etc. As a result, time is required in the initial screening stage. Porcheron et al.²⁵ have introduced a high-throughput screening of the CO₂ solubility system, which can operate simultaneously six reactors from vacuum to 1×10^3 kPa. A vacuum condition before each experiment and a CO₂ injection program setting for various loadings are required under each isothermal condition. In this article, we introduced and evaluated a developed system to measure CO₂ solubility using the HS-GC method, which can save chemicals, time, and labor. In general, HS-GC is an analysis technique used to determine concentrations of the volatile compounds in the gaseous phase, which is in equilibrium with the liquid phase of the sample system to be analyzed. HS-GC analysis is generally classified as dynamic HS or static HS. In dynamic HS-GC, the sample is acquired by capturing the volatiles using a continuous gas streamed through a matrix onto a suitable trapping system, such as liquid stationary phases, cryotrap, and solid adsorbents. They are released when the trap is heated at some time and sent to the column to be analyzed.

In static HS-GC, the analyte is sampled from an encapsulated vial, which is shaken for a particular period to attain the vapor–liquid equilibrium at a predetermined temperature. The sample is then introduced directly into gas chromatography for analysis. During the state of equilibrium that is attained, the volatile compounds (analyte) in the sample begin to transfer into the gas phase. At equilibrium, the ratio of volatile chemical concentrations in the gas phase to those in the liquid or solid phase (if solids) is constant. The constant is defined as the partition coefficient:²⁶

$$K = \frac{C_L}{C_G} \quad (6)$$

where C_L (C_S is used if the sample is a solid) and C_G are the concentration of the analyte in the sample and that in the gas phase after equilibrium, respectively.

The partition coefficient decreases as the temperature increases (the C_G concentration increases) and varies with changes in the sample systems.

From eq 6, the compounds with a high partition coefficient lean to stay in the liquid or solid phase and the compounds with a low partition coefficient tend to transfer to the gas phase. Hence, the headspace detection range for analytes in a compatible sample system (high partition coefficient such as methanol in water) will be much higher than for analytes in an incompatible sample system (low partition coefficient such as toluene in water).

Another important parameter in these sample systems is the phase ratio β which is defined as the ratio of the volume of the gas phase to the volume of the liquid/solid phase in the headspace vial. HS-GC systems are highly sensitive to low-phase-ratio sample systems compared to high-phase-ratio sample systems. The amine in the solvent with a low boiling point will significantly increase the pressure in the headspace gas phase, i.e. amine has a high phase ratio. Therefore, β of amine in CO₂-loaded amine sample should be low to perform measurements with high accuracy. Static HS-GC can be applied to high-sensitivity analysis and was used in this study to determine the CO₂ solubility after the vapor–liquid equilibrium attained in the vials of CO₂-loaded amine solvent systems. This system has been used to obtain the CO₂ solubility as well as activity coefficients of mixtures.^{24,27} However, further applications of HS-GC in CO₂ capture have not been reported.

The experimental setup was described in other publications.²⁸ A short explanation of the methodology in our system is presented in Section 2.2. Our system can automatically measure the CO₂ solubility in a short time, which is superior in comparison with the batch-type vapor–liquid equilibrium and flow-type methods. In this article, the CO₂ solubilities of miscible absorbents and liquid–liquid phase separation absorbents were measured by an HS-GC system. From that, the absorption heats of the respective solvents were also estimated and compared with literature results. Tran et al. have reported the absorption heat of phase-separation solvent that was measured continuously.¹⁰ A leap in this absorption heat curve showed phase-change loading. Our obtained absorption heat was also compared with the literature data. To the best of our knowledge, it is the first report on the absorption heat of both miscible and liquid–liquid phase separation absorbents obtained from this CO₂ solubility data using the HS-GC system. We also reported the evaluation results of the new absorbent solution by this system in this article.

2. EXPERIMENTAL SECTION

2.1. Materials. Table 1 shows the amines and ethers that were used in this study. CO₂ (>99.50%) and N₂ (>99.99%) were purchased from Taiyo Nippon Sanso Corporation, and distilled water was prepared with a WG203 water purification system from Yamato Scientific Co., Ltd.

2.2. CO₂ Solubility Measurement with HS-GC. CO₂ solubility measurement was conducted using HS-GC. This system consists of a headspace autosampler (Turbomatrix HS16, PerkinElmer) and gas chromatography (GC-3200, GL Sciences) equipped with a thermal conductivity detector (TCD). The measurement procedure is briefly explained as follows. First, a blank solution of unloaded amine (i.e., CO₂-unloaded amine solution) was prepared at the desired concentration of components; then CO₂ was flown in it to make the stock solution (i.e., CO₂-loaded amine solution). The CO₂ concentration in the sample was determined by using TOC (total organic carbon analyzer, TOC-L, Shimadzu). The samples with desired CO₂ loadings were prepared by mixing the blank solution with the stock solution by weight (Figure 2).

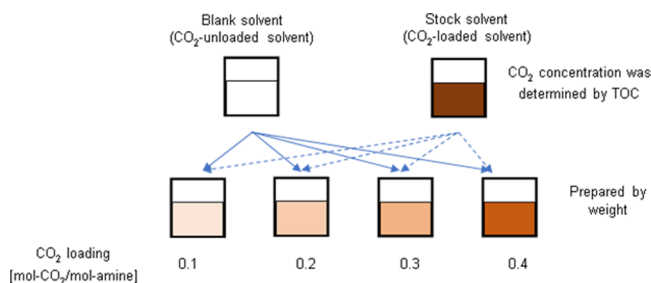


Figure 2. Image of sample preparation for CO₂ solubility measurement by HS-GC.

Five milliliters of each sample were filled in the vial (1/4th of the total volume of the vial). These samples were hermetically sealed in headspace vials and placed in the Turbomatrix HS16 headspace autosampler. In this work, an electronically controlled pressure balance methodology was used (Figure 3). There are two holes at the top and bottom of the vertical movement sample needle. First, each vial is heated to a predetermined temperature and shaken continuously for 30 min to attain the vapor–liquid equilibrium inside the vial at that thermostat condition. The needle at this step is on the top

of the vial, and the area around it is purged with carrier gas (equilibrium step). At the pressurization step, the needle moves lower and pierces the septum of the vial. Then, carrier gas pressurizes the headspace to a pressure higher than the pressure of the inlet gas to the column. At the sample transfer step, the solenoid valves are closed. As a result, the compressed gas in the headspace flows through a heated transfer line to the column of GC-3200 to record a chromatogram. The needle is sealed against the atmosphere by the O-rings, which means that there is no gas leakage during transfer. Moreover, the methodology we used can precisely regulate the carrier gas pressure, which helps to manage sample transfer.

The obtained CO₂ peak area from the GC-TCD measurement was converted to the partial pressure of CO₂ in the gas phase using the calibration curve. We used aqueous *N*-methyl diethanolamine (MDEA) solutions at different CO₂ loadings as reference (or calibration) standards. Each measurement sequence, a calibration sample MDEA with known CO₂ loading, was also measured to obtain its CO₂ peak area. This loading is collated to its partial pressure in the data reported by Ermatchkov et al.²⁴ Therefore, the detected CO₂ peak area of this MDEA calibration sample corresponds to the CO₂ partial pressure with the corresponding loading. This set of data of the CO₂ partial pressure and the CO₂ area of MDEA is used to calculate the partial pressures of other samples as in the following explanation.

At equilibrium, the comparison of partial pressures of CO₂ in two samples at the same temperature can be written as eq 7 (considering the same gas volume was examined at GC-TCD):

$$\frac{p_{\text{std}}}{p_{\text{sample}}} = \frac{n_{\text{std}}}{n_{\text{sample}}} \quad (7)$$

where p_{std} and p_{sample} are the CO₂ partial pressures in the MDEA calibration sample and unknown sample, respectively. n_{std} and n_{sample} are the moles of CO₂ gas in the MDEA calibration sample and the unknown sample, respectively. The moles of CO₂ gas are directly related to its area detected in GC-TCD. Equation 7, therefore, can be rewritten as:

$$\frac{p_{\text{std}}}{p_{\text{sample}}} = \frac{A_{\text{std}}}{A_{\text{sample}}} \quad (8)$$

where A_{std} and A_{sample} are the areas of CO₂ in the MDEA calibration sample and unknown sample, respectively. The CO₂ partial pressure of the MDEA calibration sample (p_{std})

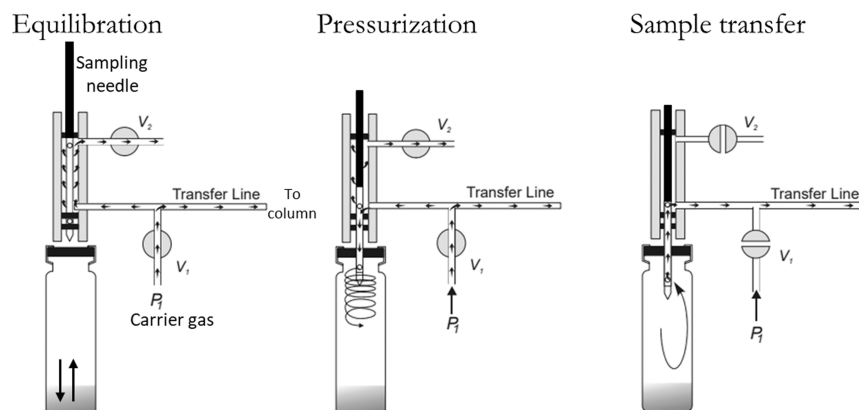


Figure 3. Schematic of the automated balanced pressure system. P_1 : Pressure of carrier gas, V_1 and V_2 : solenoid valves.²⁹

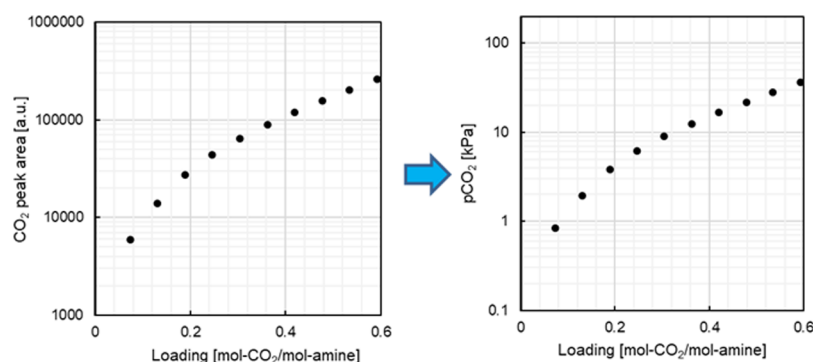


Figure 4. CO₂ peak area data and converted partial CO₂ pressure data.

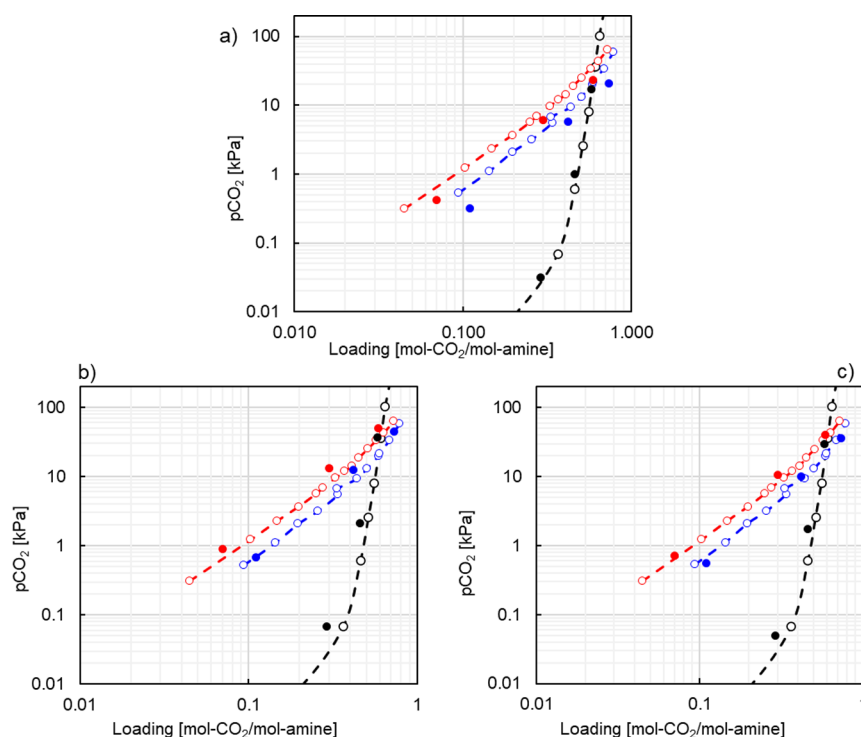


Figure 5. CO₂ solubility curve of aqueous solutions of MEA 30 wt %²² (black-filled circles), 2 mol/kg MDEA²⁴ (blue-filled circles), and 4 mol/kg MDEA²⁴ (red-filled circles) and their corresponding literature data (open circles with respective colors of circles) using different calibration samples to convert CO₂ peak areas. (a) calibration value: MEA 30 wt % base, (b) calibration value: 2 mol/kg MDEA, (c) calibration value: 4 mol/kg MDEA. Reproduced with permission from refs 22,24.

can be found in reference data of Ermatchkov et al. at its corresponding loading.²⁴

Figure 4 shows the conversion of the CO₂ peak area obtained at 40 °C from GC-3200 to the CO₂ partial pressure of MDEA 4 mol/kg solvent. This solvent was also used as our calibration sample in each batch of measurement (the explanation is in Section 3.1). The amine in the gas phase was not detected using gas chromatography with a column for amine, which means there was no amine in the gas phase.

3. RESULTS AND DISCUSSION

3.1. Calibration Sample Determination for HS-GC Measurement. The obtained CO₂ peak area of the highest loading of solvent was used to find the corresponding partial pressure of the CO₂ at that loading in the calibration sample. CO₂ partial pressure and loading have a linear relation in a small loading range. As a result, the partial pressures of other

loadings can be calculated based on this loading and the referred CO₂ partial pressure.

In this part, we will explain how the MDEA of 4 mol/kg was used as our calibration data. There are many reports on the CO₂ solubility of two major amines, MEA and MDEA. Among them, Jou et al.²² (MEA at 30 wt %) and Ermatchkov et al.²⁴ (MDEA at 2 and 4 mol/kg) reported data covering a very wide loading range.

We measured the three CO₂ solubility sets of aqueous solutions of 30% MEA, and MDEA at 2 and 4 mol/kg at 40 °C. The obtained CO₂ peak areas in our experiment were then converted into CO₂ partial pressure based on their data and presented in Figure 5. The highest loading of our MEA 30 wt % solvent (Figure 5a), 0.58 mol-CO₂/mol-amine, was collated to a CO₂ partial pressure of 17 kPa reported by Jou et al.²² Therefore, the peak area at this loading (i.e., 0.58 mol-CO₂/mol-amine) corresponds to 17 kPa, and this set of peak area and partial pressure was used to calculate the other partial

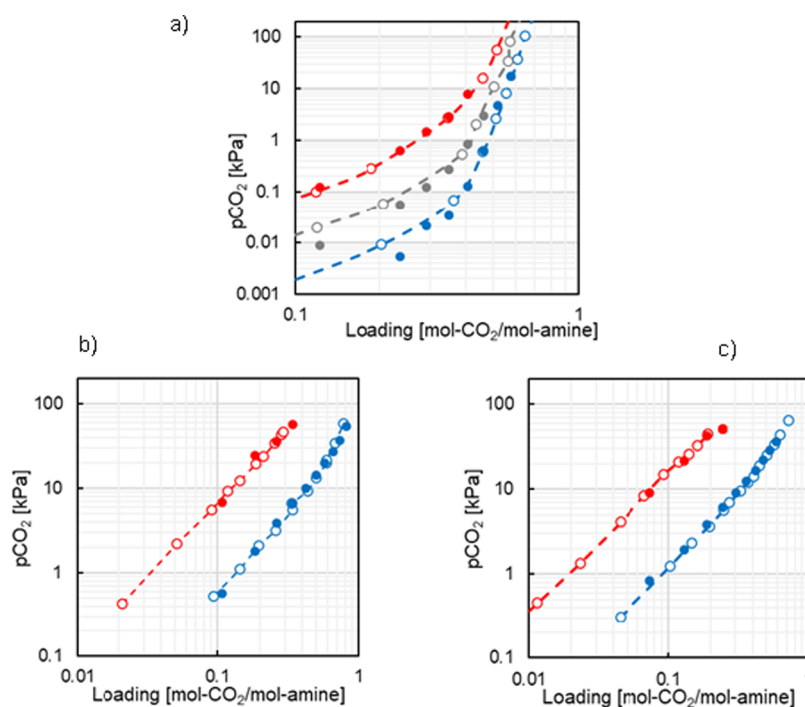


Figure 6. Comparison of CO₂ solubility data between our data obtained by HS-GC and literature values. (a) MEA (30 wt %),²² (b) MDEA (2 mol/kg),²⁴ and (c) MDEA (4 mol/kg)²⁴ at 40 °C (blue), 60 °C (gray), and 80 °C (red). Explanation: experimental data (filled circles) and literature data (blank circles). Reproduced with permission from refs 22,24.

pressures of the three sets of experimental data using eq 8. Similarly, the highest loadings of 0.73 mol-CO₂/mol-amine (2 mol/kg MDEA solvent, Figure 5b), and 0.59 mol-CO₂/mol-amine (4 mol/kg MDEA solvent, Figure 5c) correspond to 45 and 36.5 kPa reported by Ermatchkov et al.²⁴ with respective concentration of MDEA solvents. In the CO₂ partial pressure calculation, data in Figure 5a used MEA 30 wt % as calibration data, while those in Figure 5b,c used the MDEA at 2 and 4 mol/kg as calibration data. No matter which calibration data were used, the solubility curves of our data reproduce well for the CO₂ solubility of other amines and concentrations. However, the data converted by 0.59 mol-CO₂/mol-amine of 4 mol/kg MDEA (Figure 5c) have the smallest deviation compared to the other two. MEA 30 wt % has a large CO₂ absorption capability; therefore, its steep slope of the CO₂ solubility curve is attributed to its largest deviation. Therefore, we used an aqueous solvent of MDEA 4 mol/kg as our calibration data in the CO₂ partial peak calculation.

3.2. CO₂ Solubility of Miscible Solvents. We employed the developed HS-GC system to obtain the CO₂ solubility data of phase separation solvents and miscible-type solvents. At first, to confirm the reliability of our system, the typical aqueous amine solvents of MEA 30 wt %²² and MDEA (2 and 4 mol/kg)²⁴ were measured. HS-GC conditions are summarized in the previous report.²⁸ Figure 6 shows the results of the equilibrium solubility measurement of MEA and MDEA and the comparison with literature values. The experimental data showed a good agreement with the literature data, thus confirming the accuracy of this HS-GC method.

In the conventional method, the flow-type CO₂ solubility measurement conducted in our laboratory requires 2 to 10 h depending on the partial pressure of CO₂ gas to measure one point of data. Particularly, to measure the absorbed CO₂ amount in the phase-change systems, the system must be set still for at least 30 min for complete phase separation after the

system has obtained the equilibrium. The components in each phase will be examined with TOC. However, with this HS-GC system, one point of data can be obtained within 35 min despite the homogeneity of the solution, in other words, the isothermal data with 10 points can be finished in 6 h. Compared to the conventional measurements, the data collection efficiency was improved remarkably with our developed HS-GC system. From this result, it can be said that our system is superior in evaluating the CO₂ solubility of amine solutions in the low-pressure range. As the amount of gas sample for GC-TCD is very small, the change in the amount of CO₂ in the vial can be negligible. Therefore, the system can be used to measure the solubility at other temperatures as well.

Besides the benchmark aqueous amine solvents, the HS-GC system was also employed to evaluate the CO₂ solubility and cyclic capacity of nonaqueous amine solvents like EAE 30 wt % and diethylene glycol monomethyl ether (DEGMME) 70 wt %. As reported in our previous article, this solution is suitable for the pressure swing process for CO₂ absorption–desorption which necessitates the requirement of CO₂ solubility, cyclic capacity, and the absorption heat evaluation.²⁸ After being transported to Japan in a liquid state, liquid natural gas is vaporized and used as the fuel. Until now, most of the cold energy in the vaporization process of liquid natural gas has been released into seawater or air. However, if this cold energy is applied in the regeneration tower, it helps to convert CO₂ into dry ice, from which CO₂ is regenerated voluntarily without any thermal energy.²⁸ As a result, this energy conservation reduces the total energy consumption compared with the conventional temperature-swing regeneration method. In this article, the CO₂ solubility of this solution was measured in the range of lean- to rich-CO₂ loading to predict its absorption heat and cyclic capacity for future applications (Figure 7). The cyclic capacity of this pressure swing process

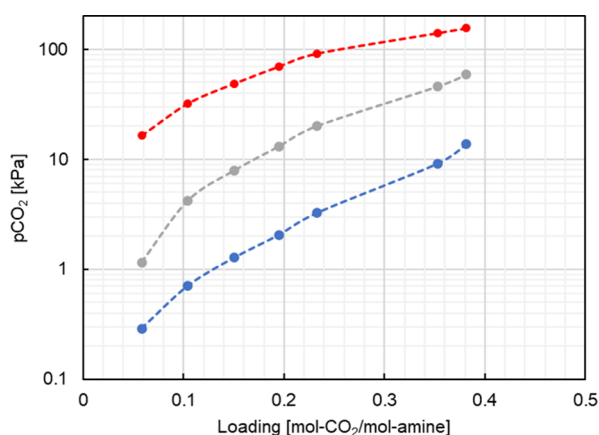


Figure 7. CO₂ solubility data of miscible solution of EAE 30 wt % and DEGMME 70 wt % at 40 °C (blue), 60 °C (gray), and 80 °C (red). Explanation: marks and lines: experimental data and its smooth data.

for the absorption conditions (40 °C, 10 kPa) and desorption conditions (40 °C, 1 kPa) for the solution of EAE 30 wt % and DEGMME 70 wt % is approximately 0.202 mol-CO₂/mol-amine, which is much higher than that of the MEA aqueous solvent 30 wt % at the same conditions (0.05 mol-CO₂/mol-amine). More details on absorption heat and the comparison with the calorimetry method are explained in further sections. Additionally, there is no water in this solution, which signifies that less energy is required, especially in the energy of vapor loss systems. The selection of this solution will be reported in another article.

3.3. CO₂ Solubility of the Phase Separation Solvent.

In this part, the CO₂ solubility in the phase separation type solvent and that of the miscible type of solvent were measured by the HS-GC method and compared with each other. Phase separation solvent (EAE 30 wt %, DEGDEE, 60 wt %, water 10 wt % in weight base) shows a single liquid phase before loading of 0.121 mol-CO₂/mol-amine, though it shows a liquid–liquid phase at higher loading.^{10,11} Miscible solvent composed of EAE 30 wt % and ethylene glycol (EG) 70 wt % shows a single liquid phase in the overall loading range. Figure 8 presents the CO₂ solubility of those solvents at 40 °C. The miscible solvent (black triangle marks) shows a linear CO₂ solubility curve at

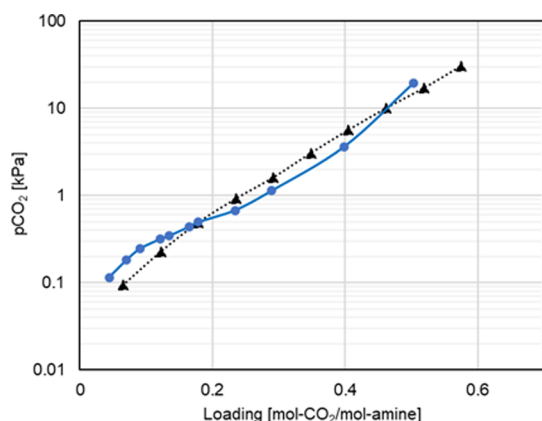


Figure 8. Comparison of CO₂ solubility data at 40 °C. Explanation: blue marks and line: phase separation solvent (EAE 30 wt %, DEGDEE, 60 wt %, water 10 wt %), and gray marks and line: miscible-type solvent (EAE 30 wt %, EG 70 wt %).

this temperature. However, the data of phase separation solvent (blue circle marks) shows a tendency for the slope to decrease in the loading range of 0.119–0.121 mol-CO₂/mol-amine, which is consistent with the phase separation point 0.121 mol-CO₂/mol-amine in calorimetry method. In the phase separation solvent, amine, water, and carbamate are the main components in the CO₂-rich phase, while ether is the main component in the CO₂-lean phase. As a result, the amine-rich phase (i.e., CO₂-rich phase) formed after phase separation has improved carbamate stability during CO₂ absorption compared to the ether environment before separation.¹⁰ Similar phenomena (solubility shift) were also observed at other temperatures when the loadings exceeded 0.121 mol-CO₂/mol-amine. Since a small slope indicates that the change in CO₂ loading per unit pressure is large, utilizing this range leads to efficient CO₂ recovery. To the best of our knowledge, there has been no report on the CO₂ solubility of phase separation solvents with phase-transition loading. Moreover, compared to the conventional measurement methods mentioned in Section 3.1, the sampling time decreases significantly in the HS-GC method, especially in phase separation solutions. Therefore, the HS-GC system can give not only the accurate CO₂ solubility but also the change in the CO₂ solubility tendency at phase-transition loading in a short time measurement.

Figure 9 presents the CO₂ solubility of the phase separation solvent of EAE 30 wt %, DEGDEE 60 wt %, and water 10 wt %

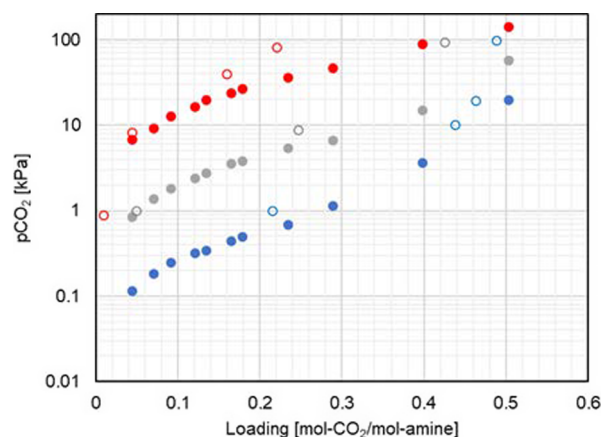


Figure 9. CO₂ solubility data of phase-separation solvent (EAE 30 wt %, DEGDEE, 60 wt %, water 10 wt %) at 40 °C (blue), 60 °C (gray), and 80 °C (red). Open marks: Machida et al.,⁴ and filled marks: this work. Reproduced with permission from ref 4.

determined by HS-GC and that by calorimetry.⁴ This CO₂ solubility measured by the HS-GC method is lower than that obtained by the calorimetry method. In HS-GC, the partial CO₂ pressure is reported to be pure CO₂. In calorimetry measurement, the CO₂ partial pressure includes the vapor pressure, especially at high temperatures such as 60 or 80 °C. Therefore, water vapor pressure is attributed to the deviation between the calorimetry method and the HS-GC method.

Similarly, we also obtained the CO₂ solubility of EAE 30 wt % and DEGDEE 70 wt % which showed the phase separation at 0.243 mol-CO₂/mol-amine (Figures 10, and S2). As shown in Figure S2, the samples at loading lower than 0.239 mol-CO₂/mol-amine are homogeneous, while those at higher loadings show the liquid–liquid phase separation. However, the tendency of decreasing the CO₂ solubility curve is 0.214

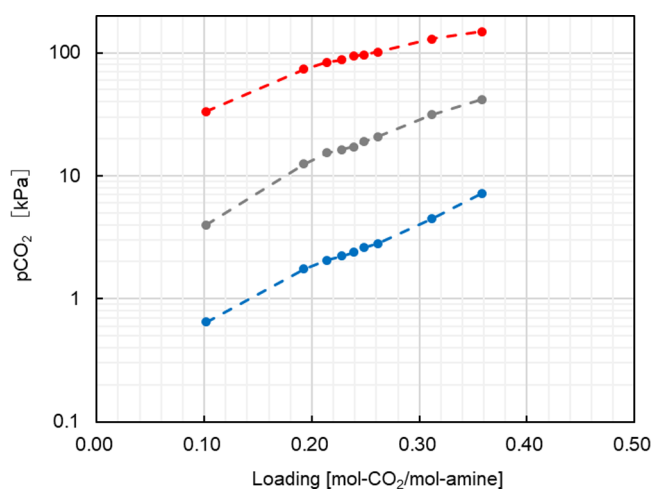


Figure 10. CO₂ solubility data of phase-separation solvent (EAE 30 wt %, and DEGDEE 70 wt %) at 40 °C (blue), 60 °C (gray), and 80 °C (red). Explanation: marks and lines: experimental data and its smooth data.

mol-CO₂/mol-amine, which is lower than the value reported by calorimetry.

3.4. Absorption Heat Estimation. CO₂ solubility measurements taken by HS-GC are distinguished from conventional solubility methods using the same loading sample for various temperatures. Thus, it allows us to estimate the absorption heat of amine solutions directly from these CO₂ solubility curves according to the Gibbs–Helmholtz equation (eq 2). The absorption heat of MEA was calculated from Figure 6 and compared with literature data (Figure 11).

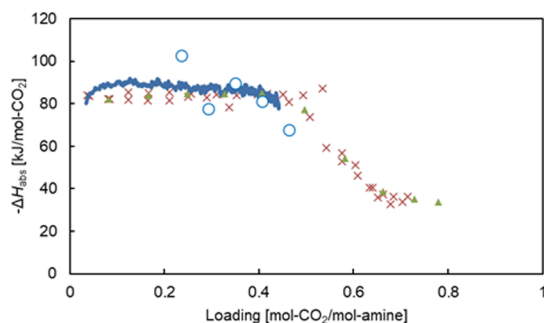


Figure 11. Comparison of CO₂ absorption heat of MEA 30 wt % solvent at 40 °C between the calorimetry method and that estimated from CO₂ solubility by HS-GC. Explanation: blue line: continuous absorption heat (Tran et al.¹⁰), red cross marks (X): Kim et al.,²⁰ triangle green marks (▲): Arshad et al.,¹⁸ and blue circles (O): this work. Reproduced with permission from refs 10,18,20.

Although the data taken by HS-GC were not enough to reproduce the whole continuous absorption heat curve of MEA 30 wt %, it replicates well the absorption heat. The error varied from 4 to 14% with the continuous absorption heat.

Absorption heat of another miscible solution of EAE 30 wt % and DEGMME 70 wt % was also measured by calorimetry (Figure 12) and compared with the estimated one obtained from the CO₂ solubility curve in Figure 7. The absorption heat experiment was described in our previous article.¹⁰ The data from the two methods show good agreement in the 0.100–0.350 loading range. When CO₂ reacts with amine, there are two products: carbamate (without water as a reactant) and

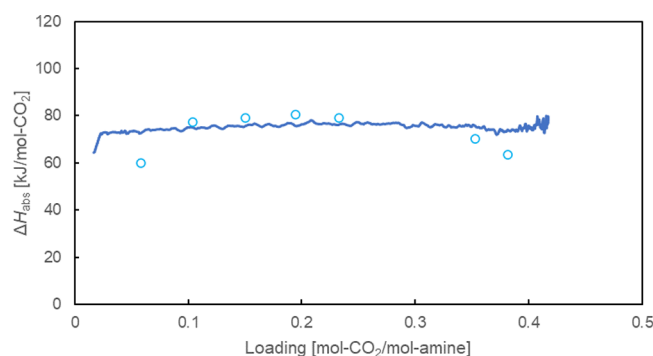


Figure 12. Absorption heat of miscible solvent of EAE 30 wt % and DEGMME 70 wt % at 40 °C by calorimetry method (blue line) and by estimation from CO₂ solubility (blue circles).

bicarbonate (with water as a reactant). The reaction heat of carbamate is higher than that of bicarbonate. Due to the lack of water in this solution, the main product in EAE 30 wt % and DEGMME 70 wt % is carbamate. In the benchmark aqueous solution of MEA 30 wt %, bicarbonate which has lower reaction heat is also formed beside carbamate. In general, our EAE/DEGMME solvent has lower absorption heat compared to the benchmark MEA 30 wt %, which makes it a less energy-consuming solvent.

The absorption heat was also estimated for the phase-separation solvents. Figure 13 shows the comparison of CO₂

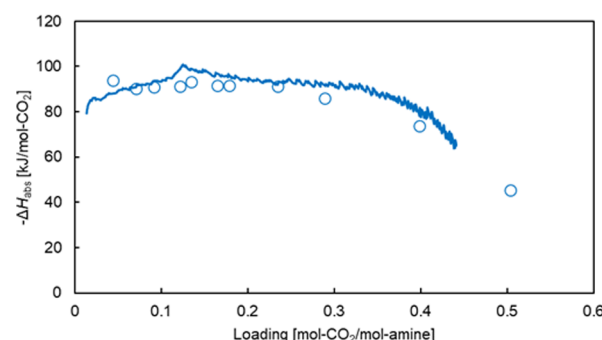


Figure 13. Comparison of CO₂ absorption heat of phase separation solvent (EAE 30 wt %, DEGDEE 60 wt %, water 10 wt %) at 40 °C between calorimetry method (blue line: Tran et al.¹⁰) and estimation from CO₂ solubility (blue circle: this work). Reproduced with permission from ref 10.

absorption heat at 40 °C between the literature value measured with a reaction calorimeter¹⁰ and the estimated values from CO₂ solubility. In the literature, the absorption heat curve was measured continuously, and its leap corresponds to the loading of 0.121 mol-CO₂/mol-amine, where phase separation occurs. A decrease in absorption heat at a high loading range is due to the formation of bicarbonate. Although the number of samples was increased to replicate the leap in the absorption heat curve of the continuous calorimeter method, it was not observed in the absorption heat obtained by HS-GC. However, our estimated data replicate well the literature data, including the decrease of absorption heat at high loading.

Absorption heat of another phase separation solvent of EAE 30 wt % and DEGDEE 70 wt % was also estimated and presented in Figure 14. The absorption heat estimated by solubility data also demonstrates the approximate matching

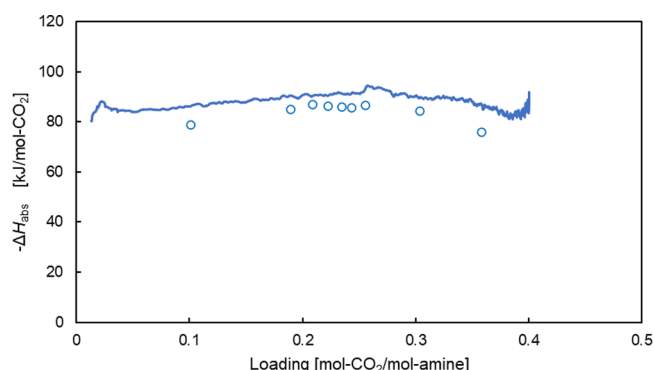


Figure 14. Comparison of CO₂ absorption heat of phase separation solvent (EAE 30 wt % and DEGDEE 70 wt %) at 40 °C between the calorimetry method (blue line: Tran et al.¹⁰) and estimation from CO₂ solubility (blue circle: this work). Reproduced with permission from ref 10.

with that of the literature, which proves the reliability of the absorption heat estimated from HS-GC.

Our work mainly focused on obtaining CO₂ solubility data by HS-GC and the estimation of absorption heat from the CO₂ solubility data. From the absorption heat estimated from HS-GC for both miscible and phase separation solvents, it can be inferred that this HS-GC system can provide a good “continuous” absorption heat curve for an amine solvent. This is a significant improvement in the CO₂ capture solvent development, saving time and labor while providing acceptable data. Absorption heat obtained from the differentiation of CO₂ solubility might not give it an accurate value.^{10,30} However, with fair agreement between the calorimetry method and the CO₂ solubility estimation method, it can be said that our developed system gives fast and accurate results in absorbent screening. In future work, we would like to improve the measurement at the lower range of the CO₂ partial pressure in direct air capture.

4. CONCLUSIONS

An HS-GC system was introduced to measure the CO₂ solubility of the CO₂ capture solvent from the miscible type to the liquid–liquid phase separation type. This system is possible to measure at a remarkably shorter measurement time compared with conventional batch-type and flow-type measurements. The accuracy and reliability of CO₂ solubility obtained by this HS-GC system have been verified. In addition to demonstrating good agreement with literature data of benchmark amine solvents, the system can successfully evaluate the CO₂ solubility of phase separation solvents upon CO₂ absorption (for example, EAE 30 wt %, DEGDEE 60 wt %, water 10 wt %, EAE 30 wt %, and DEGDEE 70 wt %). Through continuous data acquisition, we were able to observe the specific inflections exhibited by phase separation, which is approximate to that of experimental data. Moreover, as one sample at a certain loading was used to measure the CO₂ solubility at various temperatures, the absorption heat of the solvent can be estimated from the obtained CO₂ solubility, which matches the absorption heat measured by the calorimetry method.

In the present system, the lowest partial pressure of CO₂ is only 0.1 kPa. In future work, we are also building a new system with a detector suitable for measuring ppm level of CO₂ which is suitable for DAC.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c03314>.

Information on the effect of equilibration time, sample pictures of the phase-separation solvent of EAE 30 wt % and DEGDEE 70 wt %, and setting conditions of HS-GC (PDF)

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All the authors have equivalent contributions to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Japan Science and Technology Agency through its Advanced Low-carbon Technology Research and Development Program (JST-ALCA), Grant JPMJAL1511.

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