Carbon Dioxide Absorption Heat in Liquid−Liquid and Solid−Liquid Phase-Change Solvents Using Continuous Calorimetry

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ABSTRACT: For three groups of systems—homogeneous, liquid−liquid, and solid−liquid—absorption heats of carbon dioxide capture by amine solutions were determined with continuous calorimetry. In the case of a phase-separation solvent, the heat of phase separation is added to conventional absorption heat, and the loading range of heat of phase separation is important in process design. With the merits of continuous measurement, the phase-change loading points were obtained in liquid−liquid and solid−liquid phase-separation systems as the heat release of carbon dioxide products to achieve a more stable state. The loading points where a leap in absorption heat appears coincide with those where the turbidity in solvents changes, which was confirmed by ocular inspection in both systems. In liquid−liquid systems, the presence of water in 2-(ethylamino)-ethanol:diethylene glycol diethyl ether:water contributes to the decrease in absorption heat. Even though the formation of bicarbonate is minor even in solvent with water, the increase in its formation contributes to this decrease in absorption heat because of its lower formation heat as compared to that of carbamate. In solid−liquid systems, a significant increase in absorption heat is attributed to the crystallization energy of carbonate salt emitted on the breakdown of the supersaturation.
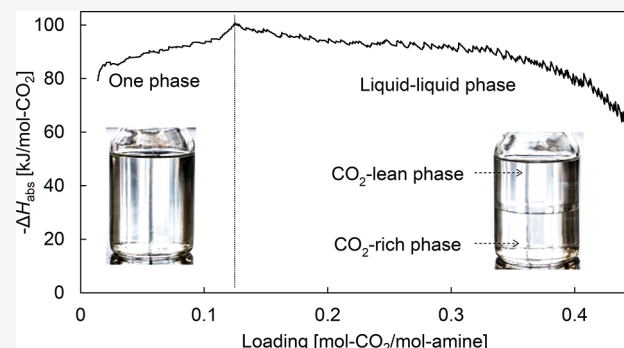
1. INTRODUCTION

Carbon dioxide from human activities contributes to a great part in global warming. Its level has been increasing from 280 to 400 ppm in the past 150 years, i.e., after the Industrial Revolution. As a consequence, Earth's temperature keeps increasing and has reached an alarming record, and a commitment was made at the Paris climate conference (COP21) to limit the temperature increase to 2 °C overall. Flue gas of industry is one of the main sources of carbon dioxide emission. Therefore, CO_2 capture and storage (CCS) or utilization (CCU) has been identified as a possible and sustainable solution to reduce CO_2 emission, for slowing down the global warming process further. Among carbon dioxide capture methods, the absorption method is currently most applied in industry using the popular monoethanolamine (MEA) aqueous solution. However, high energy consumption in the whole process is a problem needed to overcome.

The regeneration energy requirement in the CO_2 capture process is expressed as[1]

$$Q_{regeneration} \text{ [GJ/ton of } CO_2]$$
$$= Q_{sensible\ heat} + Q_{heat\ of\ vaporization} + Q_{absorption\ heat} \quad (1)$$

The sensible heat of solvent $Q_{sensible\ heat}$ is the heat to bring the solution to the desorption temperature. The heat of vaporization $Q_{heat\ of\ vaporization}$ is the energy for water to vaporize in

desorber. Lastly, absorption heat $Q_{absorption\ heat}$ is the heat when CO_2 dissolves and reacts with amines in solution. It is defined as absorption or desorption heat; both are equal in absolute quantity but opposite in sign. The last term—absorption heat—is an important parameter in solvent efficiency assessment and is related directly to the energy demand of the process.

Reaction heat ΔH [kJ/mol of CO_2] can be obtained via calorimetry or temperature-dependent solubility. The relation between Q [GJ/ton of CO_2] and ΔH [kJ/mol of CO_2] is expressed as follows.

$$Q = \Delta H / 44 \times 10^6 / 10^6 \quad (2)$$

From the solubility of CO_2 in solution, differentiation of partial pressure of CO_2 over amine solution with respect to temperature gives the absorption heat via the Gibbs−Helmholtz equation:[2,3]

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$$\left(\frac{\partial \ln p_{CO_2}}{\partial (1/T)}\right)_p = \frac{\Delta H}{R} \tag{3}$$

However, the differentiation in this method might magnify the error during solubility measurement. It does not allow examination of the effect of temperature, either. Besides solubility measurement, enthalpy can be obtained with direct calorimetry via the following two methods: (1) integral in loading but differential in temperature (flow calorimetry)[4−8] or (2) differential in both temperature and loading (reaction calorimetry).[9−15] These methods combine the heats of both physical dissolution of CO_2 into solution and chemical reactions between CO_2 and reactants. In both methods, result at only one loading is obtained from one experimental run. For the next loading, fresh amine is added into absorbed amines solution (flow calorimetry) or CO_2 is added in several steps (reaction calorimetry) for desired loading.

Amine reacts with CO_2 as in eqs 4 and 5:

$$2RR'NH + CO_2 \rightleftarrows RR'NH_2^+ + RR'NCOO^- \tag{4}$$

$$RR'NH + CO_2 + H_2O \rightleftarrows RR'NH_2^+ + HCO_3^- \tag{5}$$
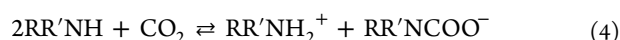
where R and R′ are alkyl group or hydrogen atom. Primary and secondary amines prefer reaction 4, while only reaction 5 occurs for tertiary amine. For a hindered amine, reaction 5 is favored due to the steric hindrance of its bulky group near the nitrogen atom of the amine. To absorb a CO_2 molecule, reaction 4 requires two amine molecules while only one amine molecule is required in reaction 5. In addition, the absorption heat in reaction 4 is 81 kJ/mol while that of reaction 5 is 67 kJ/mol in MEA 30 wt % aqueous solution.[5,16] Consequently, tertiary amine and hindered amine absorb more CO_2 than primary and secondary ones and have a lower absorption heat, which suggests higher efficiency in carbon dioxide capture. However, tertiary amine shows a slower absorption rate than primary and secondary amines. In the case of hindered amine, it has blend characteristics of the fast reaction rate of primary/secondary amines and the high loading of tertiary amines. Its main product with carbon dioxide is bicarbonate as in reaction 5; hence a higher absorption capacity as compared to that of unhindered primary/secondary amines is obtained. Consequently, it requires less energy to regenerate.

For postcombustion amine scrubbing processes, piperazine (PZ) has been identified as a second-generation solvent because it is resistant to oxidative degradation, less volatile than MEA, and not corrosive to stainless steel.[17] PZ with the advanced flash stripper (AFS) has been demonstrated with more than 2000 h of operation on 0.6 MWe of coal-fired flue gas at the National Carbon Capture Center.[18] For practical use of the PZ process, physical properties[19] or aerosol analysis[20] were also reported.

There has been research on combination of amines and various solvents in carbon dioxide capture in order to reduce energy consumption. Normally, a tertiary amine with high loading capacity and a primary/secondary amine with high reaction rate are combined. The product of tertiary amine is bicarbonate—a low absorption heat product. Therefore, low energy cost is also achieved with tertiary amine. The examples are piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP),[21] 2-(diethylamino)ethanol (DEEA) and 3-(methylamino)propylamine (MAPA),[9] and methyldiethanolamine (MDEA) and piperazine (PZ).[22] Water-lean solvents

are proposed as alternatives for typical aqueous amine solvents. They consist of blends of amine and organic diluents and possess low or no water content, such as an array of amines (monoethanolamine, 2-methylpiperazine, and N-methyl diethanolamine) and diluents (sulfolane, ethylene glycol, 1-methylimidazole, dimethyl sulfoxide, and N-methyl-2-pyrrolidinone),[23] or piperazine/H_2O/sulfolane or imidazole.[24] Wanderley et al. evaluated the equilibrium shift caused by organic diluents in terms of destabilization of the CO_2-derived species in the solvent.[23]

Two-phase-separation solutions after CO_2 absorption are also considered due to the possibility in reducing the liquid amount entering the desorber and lowering the regeneration temperature.[25] Those two-phase-separation solutions are mainly blends of amines such as triethylenetetramine (TETA)/DEEA, N,N-dimethylbutylamine (DMBA)/triethylamine (TEA), dimethylcyclohexylamine (DMCA)/dipropylamine (DPA), etc.

Machida et al. suggested a solvent that separates into two phases after CO_2 absorption, which is composed of 2-(ethylamino)ethanol (EAE), diethylene glycol diethyl ether (DEGDEE), and water in 30:60:10 weight ratio.[26−28] Its constituents are commercially available chemical absorbent (amine) and physical absorbent (polyether), so that an increase in the cost of the solvent is expected to be prevented. Since DEGDEE is a hydrophobic solvent, DEGDEE low-affinity carbamate will form another phase after CO_2 is absorbed into solution. Solvent is divided into two phases: a CO_2-lean phase, which is mainly composed of ether; a CO_2-rich phase, which includes CO_2, amine, and water. Both phases are stirred, mixed well, and then sent to a regeneration tower where freed amine is again dissolved into the ether phase, which means that ether boosts the regeneration stage. In fact, this solvent can be regenerated at 363 K, as compared to 393 K for conventional MEA solvent. The CO_2 solubility difference between absorber and desorber (defined as cyclic capacity) of this phase-separation solvent is 0.315 mol of CO_2/mol of amine, while that of conventional solvent (MEA solvent) is 0.041 mol of CO_2/mol of amine under the same conditions of absorber and desorber (P_{CO_2} = 10 kPa, 313 K, and P_{CO_2} = 100 kPa, 363 K, respectively).[28] In a conventional MEA process at the desorber condition of 393 K, the steam stripping effect makes the partial CO_2 pressure decrease and the CO_2 solubility difference shows around 0.26. Overall energy duty is the combination of other parameters and the design of the process. Hence, to assess a solvent efficiency, regeneration temperature and cyclic capacity should be taken into account as well. Absorption heat recovery using a heat pump was applied to develop an energy-saving absorption process. Since the coefficient of performance improves when the temperature difference between the absorber and desorber decreases, high efficiency is achieved by our phase-separation solvent. Energy consumption of CO_2 capture by the phase-separation solvent with a heat pump system showed about 1.6 GJ/ton of CO_2.

Besides the development of liquid−liquid phase-separation solvent, solid−liquid phase-changing systems also have attracted researchers for improvement in energy consumption.[29−32] AMP, a hindered amine that has high loading capacity and thermal stability, has been studied as an alternative to conventional amines due to its contribution to equipment corrosion prevention and regeneration heat decrease. Its carbamate precipitates in organic solvents such

Table 1. Chemicals Explanation

system	amine (weight/g)	ether (weight/g)	water (weight/g)	classification of amine	phase
MEA	MEA (30)		70	primary	homogeneous
EAE30	EAE (30)		70	secondary	homogeneous
EAE80	EAE (80)		20	secondary	homogeneous
AMP25	AMP (25)		75	primary (hindered)	homogeneous
EAE/DEGDEE(30/70)	EAE (30)	DEGDEE (70)		secondary	liquid−liquid
EAE/DEGDEE/water(30/60/10)	EAE (30)	DEGDEE (60)	10	secondary	liquid−liquid
AMP50	AMP (50)		50	primary (hindered)	solid−liquid

as ethylene glycol (EG), 1-propanol, N-methyl-2-pyrrolidone (NMP), triethylene glycol dimethyl ether (TEGDME), etc. The amount of liquid sent to the regeneration tower therefore decreases, which leads to an improvement in energy consumption. Combination of alkanolamine and ionic liquid (IL) emulsions shows the carbamate precipitation due to the hydrophobicity of ILs and the density differences between solid and liquid phases. This is reported in experiments with diethanolamine (DEA) and 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([EMIM][Tf_2N]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]), or 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([HMIM][Tf_2N]).[33] Because the precipitate is separated from the solution, the reaction has priority in creating more carbamate, which means more CO_2 is captured. Potassium taurate aqueous solution shows vapor−liquid−solid equilibrium and simulations have been carried out in ASPEN Plus.[34−36] With the formation of precipitate, less solvent is regenerated. The energy for desorption is therefore reduced. Furthermore, low desorption temperature can be used for regeneration of solid AMP carbamate (between 323 and 338 K).[29] On the other hand, the formation of solid leads to undesirable operational problems. Solids formation causes blockage in the absorber as well as retardation of the stirrer speed.[32]

In these solvent systems, the change in absorption heat on phase transition is important and needed to be studied in detail. In solvent that exhibits phase separation or solid precipitation, a leap of the absorption heat curve indicates the onset of phase separation which depends on the solvent compositions. This is an important property in solvent design. Within single continuous calorimetry measurement, the absorption heat and phase-transition loading point can be obtained simultaneously, which makes it a convenient and less time-consuming method.

Measurement of absorption heat is important in the process design of a phase-separation solvent. In particular, the phase-separation solvent generates heat during phase separation in addition to the conventional absorption heat. For the measurement of phase-separation heat, the conventional integral method or semidifferential method is not suitable because the heat change at the moment of phase separation cannot be determined. In this study, we use a continuous absorption heat measurement. The accuracy of the apparatus was confirmed by measuring the absorption heat of the homogeneous solvent, and then the absorption heats of liquid−liquid type and solid−liquid type phase-separation solvents were measured.

2. EXPERIMENTS

2-(Ethylamino)ethanol (>98.0%, EAE, $C_4H_{11}NO$, M_w = 89.14), 2-amino-2-methyl-1-propanol (>90.0%, AMP,

$C_4H_{11}NO$, M_w = 89.14), and diethylene glycol diethyl ether (>98.0%, DEGDEE, $C_8H_{18}O_3$, M_w = 162.23) were purchased from TCI. 2-Aminoethanol (>99.0%, MEA, C_2H_7NO, M_w = 61.08) was purchased from Wako. All were used as supplied without purification. To eliminate the influence of CO_2 from other sources, all experiments were carried out with ultrafine water supplied by Simplicity UV (Merck Millipore).

Three groups of systems were investigated in this study: four homogeneous systems (MEA 30 wt %, EAE 30 wt %, EAE 80 wt %, and AMP 25 wt % aqueous solutions), two liquid−liquid systems (EAE:DEGDEE:water = 30:60:10 and EAE:DEGDEE = 30:70 (weight base)), and a solid−liquid system (AMP 50 wt % aqueous solution) (Table 1). They are abbreviated as MEA, EAE30, EAE80, AMP25, EAE/DEGDEE/water(30/60/10), EAE/DEGDEE(30/70), and AMP50, respectively. MEA and AMP25 solvents were employed to validate the method and analysis of this research. The influence of concentration in homogeneous EAE aqueous solvents on absorption heat was investigated in EAE30 and EAE80 solvents as well. Moreover, EAE30 was chosen with a concentration similar to that of the benchmark MEA solvent. The 80 wt % EAE aqueous solvent has a composition similar to that of the rich phase in EAE/DEGDEE/water.[27] For liquid−liquid systems, EAE/DEGDEE systems with and without water, the solvents suggested by Machida et al. were chosen.[26−28] AMP, a hindered amine that has recently attracted attention, is used the for solid−liquid system.[29−32]

Generated heat was measured by a reaction calorimeter (EasyMax102, Mettler Toledo) under isothermal condition of 313.2 K. One hundred grams of solution was prepared by weight with a scale with an accuracy of 0.1 g. Before each experiment, the heat transfer coefficient of the reactor wall was calibrated with an electrical calibration heater. The flow rates of carbon dioxide and nitrogen inlet gases (supplied by Nagoya Nissan Ltd.) were controlled at 1 L/min with a ratio of N_2:CO_2 simulating typical flue gas components (80:20 (v/v)) by two digital gas flow meters (Azbil, Japan). The solution was mixed at 200 rpm during the heat of reaction measurements. To avoid heat loss due to the sensible heat of the inlet gas, the gas was preheated to 313.2 K before it was introduced into solution by passing through a bath heater. N_2 was purged into solution before CO_2 absorption to estimate the heat associated with vaporization of water. The carbon dioxide concentration in outlet gas was monitored with an infrared gas analyzer (EXAIR, Yokogawa) after flowing through a condenser (Figure 1). The intervals of the experimental data acquisition of generated heat and CO_2 concentration were 1 s, which ensured all the changes in solution were captured and reflected in the absorption heat curve. Absorbed CO_2 was calculated as the deduction of CO_2 concentration between the inlet and outlet gases.
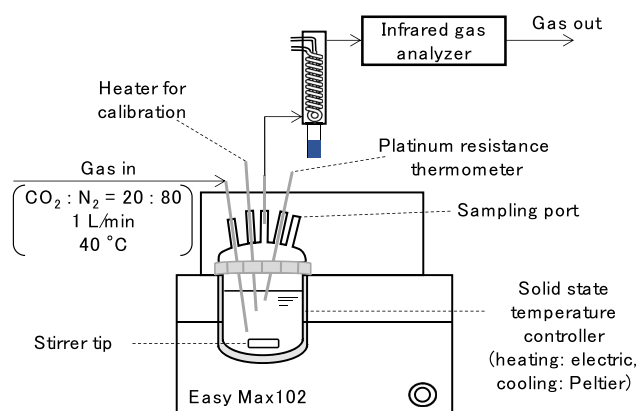
Figure 1. Experimental outline.

Example data (MEA30) of generated heat and the absorbed CO_2 in every second are shown in Figure 2. Absorption heat is obtained by the quotient of the generated heat and the absorbed CO_2 in every second.

$$\Delta H \text{ [kJ/mol of } CO_2]$$

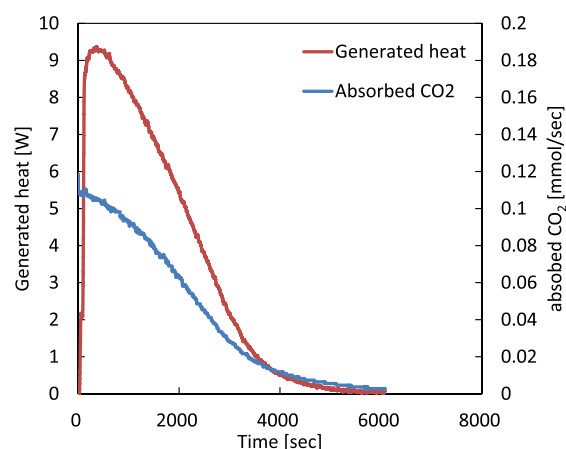$$= \text{generated heat [W]/absorbed } CO_2 \text{ [mmol/s]} \quad (6)$$

Figure 2. Example of obtained data for generated heat and absorbed CO_2 (MEA30 case).

The overall absorption heat is the sum of this quotient with loading range consideration.

We determined that the solution no longer absorbed CO_2 when no changes were observed in both generated heat and CO_2 concentration in the outlet gas.

Absorbed CO_2 amounts after equilibrium condition were measured by sampling in order to check the accuracy of the CO_2 concentration determined by gas concentration. On sampling, a micropipet was inserted through the sampling port to get a portion of sample in cases of homogeneous solvents (Figure 1). A total organic carbon (TOC) analyzer was used for determining the absorbed CO_2 amount; the method is described in detail elsewhere.[27] The TOC analyzer was not applied to the solid−liquid solvent, because TOC is designed for liquid analysis. The absorbed CO_2 amount from the sampling method and that from the gas concentration method matched within 8.9 (MEA), 2.3 (EAE30), 0.7 (EAE80), 5.8 (AMP25), and 6.4% (EAE/DEGDEE(30/70)), respectively.

The measurements were performed at least three times on each solvent, and the result closest to their average was presented in this study.

3. RESULTS AND DISCUSSION

In section 3.1, we demonstrate that the methodology in this study is reliable and comparable to other methodologies in homogeneous systems. Thereafter, the superiority of this method in other systems is described in sections 3.2 and 3.3. The advantages of this method mainly come from the ability to observe the whole change in absorption heat and the leap in absorption heat on phase change in solution.

For MEA30 and EAE/DEGDEE/water(30/60/10), measurements were performed three times on each system, and we confirmed the reproducibility within 4% in both cases.

3.1. Homogeneous Systems. Aqueous solutions of MEA 30 wt % and AMP 25 wt % were first measured to verify the reliability of the experimental apparatus, procedure, and data analysis. The results on these two solutions are shown in Figures 3 and 4, respectively, as a function of loading, defined
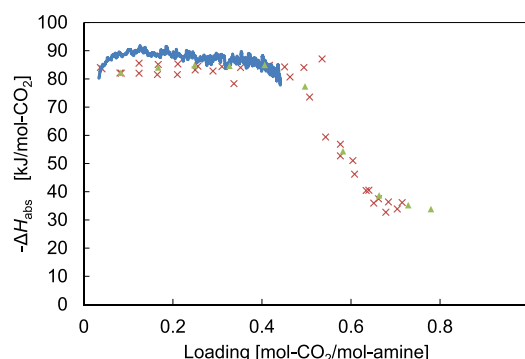

Figure 3. Absorption heat of MEA 30 wt % at 313.2 K. Line, this research; ×, Kim et al.;[12] ▲, Arshad et al.[9] The latter two literature data are reproduced from Figure 2 of ref 12 and Figure 3 of ref 9, respectively.

as the moles of CO_2 absorbed divided by the moles of amine in solution. Then the influence of concentration on absorption heat was investigated with EAE 30 and 80 wt % aqueous solvents, whose results are shown in Figures 5 and 6, respectively.
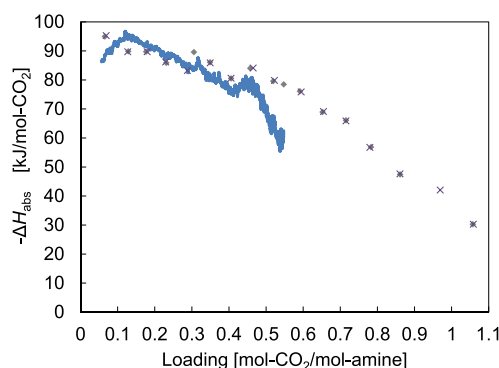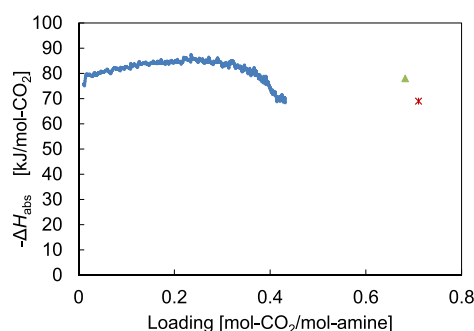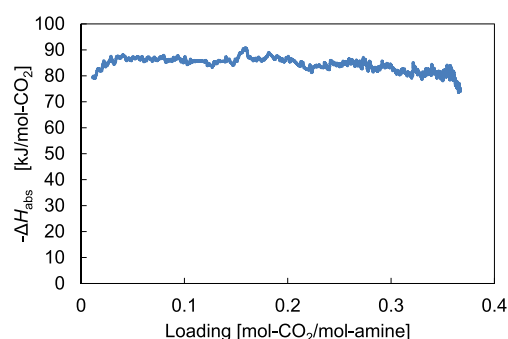

Figure 4. Absorption heat of AMP 25% at 313.2 K. Line, this research; ◆, Kim et al.;[12] ×, Mehdizadeh et al.[11] The latter two literature data are reproduced from Figure 6 of ref 11 and Figure 2 of ref 12, respectively.

Figure 5. Absorption heat of EAE 30 wt %. Line, this research; ∗, Al Hinai et al.;[4] ▲, Goto et al.[13] at 313.2 K.

Figure 6. Absorption heat of EAE 80 wt % at 313.2 K.

MEA 30 wt % Aqueous Solution. As a primary amine, carbamate is the dominant product over the bicarbonate in aqueous MEA solution.[37] The maximum loading that can be attained in aqueous primary amine (nonhindered) is 0.5 mol of CO_2/mol of amine as in eq 4. After this theoretical maximum loading has been reached, bicarbonate is formed from the hydrolysis of carbamate at loading higher than 0.5, which decreases the absorption heat. However, the absorption heat of MEA 30 wt % was measured continuously only up to a loading of 0.448 in this study due to the limitation of apparatus accuracy; the higher region of loading was not examined to validate this conclusion of the decrease in absorption heat (Figure 3). With a loading below 0.2 mol of CO_2/mol of amine, the result of this study is higher than those in the literature with an error under 8%, which we consider an acceptable deviation.[9,10] At higher loading, our result is in good agreement with those of Arshad et al. and Kim and Svendsen.[9,12]
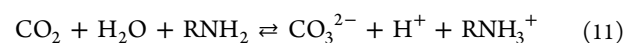
AMP 25 wt % Aqueous Solution. AMP is a primary amine; however, due to its steric hindrance of the bulky group near the amino group, it absorbs CO_2 in a different mechanism from MEA. Although the formation of carbamate is not impossible, it is unstable and easily degraded into bicarbonate. Richner and Puxty[38] studied the CO_2 absorption by AMP 30 wt % solution with Fourier transform infrared (FTIR) spectroscopy, and they confirmed that the formation of carbamate is negligible. Therefore, carbamate was excluded from their species-concentration calculation from FTIR spectra. Zanone et al.[39] observed AMP carbamate at low loading. However, as absorption continued, carbamate was dissociated into bicarbonate. Carbamate formation in AMP aqueous solution was also reported by Ciftja et al.[40] They showed that, despite the fact that the carbamate concentration was very low in comparison with those of carbonate products and protonated

AMP in AMP aqueous solution of 30 wt %, it could be observed quantitatively. Anyway, it can be concluded that, in AMP aqueous solution, carbonate forms (carbonate and bicarbonate products) are dominant over the carbamate one.

Reaction of CO_2 and AMP can be described in detail as follows:[38,41]

$$CO_2 + H_2O = H_2CO_3 \tag{7}$$

$$H_2CO_3 = H^+ + HCO_3^- \tag{8}$$

$$HCO_3^- = CO_3^{2-} + H^+ \tag{9}$$

$$RNH_2 + H^+ = RNH_3^+ \tag{10}$$

net:

$$CO_2 + H_2O + RNH_2 \rightleftarrows CO_3^{2-} + H^+ + RNH_3^+ \tag{11}$$

In the case of reactions 7−9, pK was quoted from Saruhashi:[42]

$$pK_1 = 3405/T + 0.0328T - 14.84 \tag{12}$$

$$-pK_2 = -2902.39/T - 0.02379T + 6.4980 \tag{13}$$

Dissociation heats of carbonic acid and bicarbonate at 313.15 K obtained from eqs 12 and 13 are 6.306 and −10.90 kJ/mol, respectively. The temperature dependence of the protonation heat of AMP$^+$ was determined by Simond et al.[43] The value at 313.15 K is $\Delta H° = -42.65$ kJ/mol. Therefore, the absorption heat of eq 11 is −47.24 kJ/mol. Reaction 11 is exothermic to the right and vice versa. Since carbonate is degraded into bicarbonate at loading higher than 0.5 in AMP 25 wt % aqueous solution, the overall absorption heat decreases. Arcis et al. have reported that the absorption heat of aqueous AMP solution under 0.6 mol of CO_2/mol of amine is stable and is not influenced by loading.[8] In a study by Richner,[38] CO_3^{2-} was formed at low loading; its concentration reached a maximum at 0.5 loading and then decreased. In consequence, absorption heat decreases due to the hydrolysis of carbonate into bicarbonate at loading higher than 0.5. Unfortunately, our study could not validate the higher loading results due to apparatus accuracy. However, literature data of Kim et al. and Mehdizadeh et al. showed good agreement with the above discussion.[11,12] The line in Figure 4 well regenerated those literature data with the same AMP 25 wt % aqueous solution at 313.2 K.

Those stand-alone amine (single-component amine) aqueous solvents in validation experiments are homogeneous solvents. Two solvents replicated the literature data well, which confirms the reliability of method and analysis of this research.

EAE 30 wt % Aqueous Solution. In the case of secondary amine, carbon dioxide is absorbed into solution in two pathways to form carbamate and bicarbonate as in eqs 4 and 5, respectively. The carbamate of the secondary amine has weaker stability than that of primary amine. Yamada et al. have studied aqueous solution of EAE 30 wt % by ^{13}C NMR after 30 min of CO_2 absorption.[44] Secondary amine favors bicarbonate rather than carbamate, and the formation of the former has a lower absorption heat than that of the latter. However, HCO_3^- keeps increasing, while carbamate is abundant at loading under 0.5 but then decreases due to carbamate hydrolysis. Because the absorption heat of HCO_3^- is smaller than that of carbamate, a decrease is observed in the absorption heat with loading higher

than 0.5.[45] The accuracy of this measurement with EAE 30 wt % is limited up to 0.432 loading; therefore, the decrease in absorption heat at loading higher than 0.5 could not be validated in this study (Figure 5). In comparison with literature data, the integrated absorption heat values of EAE 30 wt % solution at 313.2 K by Goto et al. and Al Hinai et al. are presented as symbols in Figure 5 (78 kJ/mol of CO_2 and 69 kJ/mol of CO_2 at loadings of 0.682 and 0.710, respectively).[4,13] However, both have loadings higher than 0.5, a loading region where carbamate is hydrolyzed, and the absorption heat decreases as a consequence. Therefore, the symbols in Figure 5 show lower values than the line values; i.e., the literature data are lower than those in this study.

EAE 80 wt % Aqueous Solvent. Another homogeneous solvent, which has not been reported in the literature to the best of our knowledge, is EAE 80 wt %. At this high concentration, an amine is solvated in this solvent mainly by other amine molecules rather than by water. As mentioned above, EAE aqueous solution creates more bicarbonate than MEA aqueous solution. However, at high concentration amine aqueous solution, carbamate is more favored due to a deficiency in water for reaction 5. The solution after CO_2 absorption was investigated with ^{13}C NMR, which showed that bicarbonate is at negligible concentration (unpublished data). Therefore, the absorption heat curve is similar to that of MEA 30 wt % even though EAE is a secondary amine (Figure 6).

3.2. Liquid−Liquid Phase-Separation Systems. Experiments on liquid−liquid phase-separation solvents were carried out with mixture solvents of ether and amine with and without water, EAE/DEGDEE/water(30/60/10) (Figure 7) and EAE/DEGDEE(30/70) (Figure 8), respectively. In the EAE/DEGDEE/water(30/60/10) case, composition data for each phase were summarized in previous work.[27]
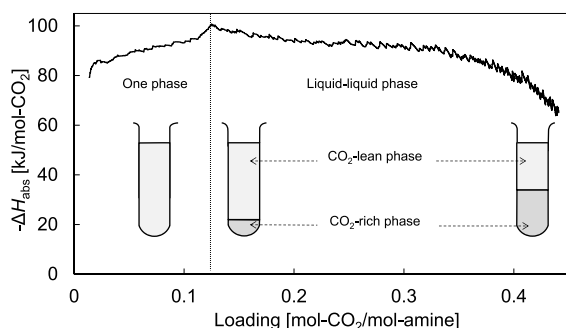

Figure 7. Absorption heat of EAE/DEGDEE/water(30/60/10) at 313.2 K.
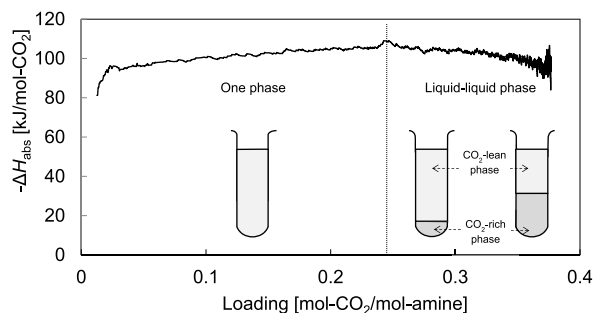
Figure 8. Absorption heat of EAE/DEGDEE(30/70) at 313.2 K.

Trends in two solvents are similar to each other, although there is a difference in magnitude. Both solvents show a slight increase in absorption heat at loadings of 0.121 and 0.243 for EAE/DEGDEE/water(30/60/10) and EAE/DEGDEE(30/70) solvents, respectively. We observed the phase separation at the corresponding points with our naked eyes, and the increase in absorption heat is ascribed to phase-separation energy (Figure 9). For EAE/DEGDEE/water(30/60/10), the
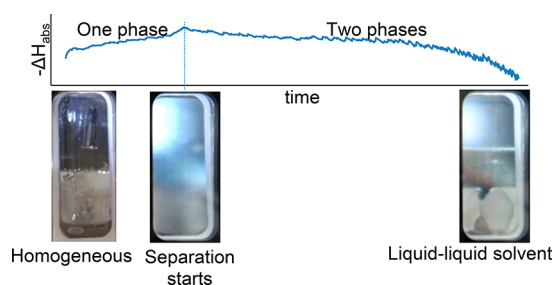
Figure 9. Liquid−liquid phase separation for EAE/DEGDEE/water(30/60/10).

measurements were performed three times. The obtained phase-separation points were 0.119, 0.122, and 0.123, whose variation among experimental runs was thus rather small. Without water, phase separation occurs with difficulty; therefore, phase separation of EAE/DEGDEE(30/70) solvent occurred at higher loading. Moreover, this solvent has a higher absorption heat compared to that of solvent containing water. Bicarbonate formation is minor in EAE/DEGDEE/water(30/60/10); however, its existence is still confirmable by ^{13}C NMR.[46] Absorption heat therefore decreases as compared to that of non-water solvent (EAE/DEGDEE(30/70)).

The energy requirement for the process includes the absorption heat at the absorption process, sensible heat for bringing the solution to the regeneration temperature, and the evaporation heat of water (latent heat) in solution at the regeneration process. Regeneration is carried out at 393 K with conventional solvent (i.e., MEA 30 wt % solvent), which means that the sensible heat is large. Furthermore, since water occupies 70% of solvent components, latent heat is also noticeable. Water in the phase-separation solvent occupies only 10% of solvent weight, which means that the evaporation heat amount is remarkably decreased. However, the main product of EAE/DEGDEE/water(30/60/10) solvent is carbamate, which explains the higher absorption heat of this solvent as compared to that of EAE 30 wt % aqueous solvent.

DEEA and MAPA mixture shows a single aqueous phase, but it turns into two liquid phases upon CO_2 absorption. Arshad et al. has measured mixtures of 5 M DEEA and MAPA at 2 or 1 M to observe the liquid−liquid phase separation.[9] Those amine blends exhibit phase separation upon CO_2 absorption. The important point is that their phase-separation observation was carried out with full-loaded samples at 298 K, not during CO_2 absorption experiments. Moreover, the absorption heat curve was not discussed in terms of phase behavior. Arshad et al. also built a thermodynamic model for 5 M DEEA + 2 M MAPA aqueous mixture. However, it was not mentioned at what loading the phase separation occurred.[47] If the loading interval was smaller, phase separation might be observed in those studies.

Knuutila et al. observed the formation of two phases after CO_2 absorption at room temperature in 3 M DEEA + 3 M

MAPA solution (CO_2 absorption was carried out at 313, 353, and 393 K) and 3 M DEEA + 3.5 M MAPA solution (CO_2 absorption was carried out at 353 and 393 K).[48] However, those phase-separation phenomena are all observed at room temperature, not during absorption, and the formation of two phases does not seem to have any influence on the absorption heats of solutions. Moreover, at what loading the two liquid phases are formed is not known.

It can be said that our study reports for the first time a slight increase in absorption heat at the loading point where solution separates into two phases. This is important information in solvent and process design. The heat of phase separation is added to the conventional absorption heat, and the loading range of the heat of phase separation is important in process design.

3.3. Solid−Liquid Phase-Separation System.
Figure 10 shows the change of absorption heat of AMP 50 wt % aqueous
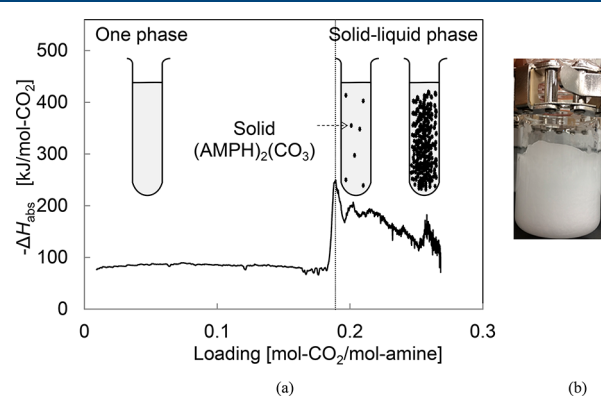
Figure 10. AMP 50 wt % solution. (a) Absorption heat; (b) solution at equilibrium. The black dots represent the solid formation in solution.

solution with increasing loading. At a loading of 0.18, the absorption heat increases noticeably up to −250 kJ/mol of CO_2. At that time, a white precipitation was formed in the reactor. In other words, crystallization is reflected in the abrupt increase in absorption heat. An investigation on solid formation in pure CO_2 absorption of AMP in EG/1-propanol mixture with and without $ZnCl_2$ by X-ray diffraction analysis revealed the structure of AMP carbamate, (AMPH)-($AMPCO_2$), or carbonate of protonated AMP, $(AMPH)_2(CO_3)$.[49] As carbamate formation in AMP aqueous solution is negligible, the crystal in our experiment is considered to be carbonate salt of protonated AMP.

As mentioned in the section AMP 25 wt % Aqueous Solution, since reaction 11 is exothermic, large energy is emitted when more CO_3^{2-} is formed. Therefore, the solid formation of CO_3^{2-} in AMP 50 wt % releases a large amount of heat. However, as in Figure 10 at a loading of 0.18, the increase in apparent absorption heat from liquid to solid state in this aqueous solution is much larger than the formation heat of carbonate (−47.24 kJ/mol). Svensson et al. reported the increase of absorption heat to −200 kJ/mol of CO_2 obtained at the onset of precipitation of AMP carbamate in AMP−NMP solvent at 323 K,[31] and they attributed the increase to the supersaturation and crystallization energies. We consider the same explanation applies to our system. The crystallization in single amine solution of AMP at high concentration caused difficulty in regeneration. Therefore, this solution was not

examined in the study on the reboiler heat duty of blended alkanolamines by Sakwattanapong et al.[50]

The precipitation onset in our experiment varied from loading of 0.151 to loading of 0.175 in different experimental runs. Svensson et al. also reported the variation in loadings when precipitation of AMP carbamate started in AMP/NMP at 298 K, which amounted to 15 wt % among experimental runs.[32] The solution might be supersaturated with AMP carbonate before crystallization. Therefore, the presence of any impurities might cause the early precipitation of AMP carbonate in solution, i.e., at lower loadings. Therefore, the ability of solvent to stabilize the precipitation contributes to the difference in the onset of solid formation.[51]

The solid−liquid system shows oversaturation, and the experimental condition should thus affect the phase-separation point. On the other hand, the phase-separation point was reproducible for the liquid−liquid system. We consider that it is due to the small activation energy of nucleation for the liquid−liquid phase.

As water occupies half of AMP 50 wt % aqueous solution, reaction 5 shifts to the right as more CO_2 is supplied into the solution after crystallization. Consequently, carbonate keeps precipitated at higher loading. This trend differs from the precipitation of AMP carbamate in organic solvents. In organic solvent, the highest loading that can be attained is 0.5. Therefore, Svensson et al. reported the domination of physical absorption of CO_2 in solution loading over 0.5, which leads to the decrease in absorption heat.[31]

Carbamate formation of AMP in organic solvent or amine mixture has been reported in much research. Svensson et al. reported the formation of unstable carbamate of AMP in NMP or TEGDME solvent.[51] Barzagli reported the solid AMP carbamate formation in AMP/diethanolamine (DEA)/1-propanol/CO_2 system, and it was identified as (AMPH)-($AMPCO_2$) by ^{13}C NMR.[29] Jo et al. also reported the crystal structure of this compound by density functional theory calculations and natural bond orbital analyses.[52] White precipitation of carbamate was observed when the loading and concentration of AMP were high in nonaqueous solvent AMP/1-propanol.[53] AMP/PZ mixture forms precipitation at high concentrations of amine and CO_2.[30] However, the actual loading of the solid formation in their experiments was not reported. With continuous absorption heat change observed in this study, the loading where solid is formed is clearly observed. Relationships of absorption heat with temperature, mixture components, amine concentration, and phase transition should be studied in detail in further experiments. Moreover, it is useful in case the onset of the precipitation is needed to be under control, for example, the addition of additives to accelerate the crystallization formation.

As mentioned in the Introduction, absorption heat includes the dissolution heat of CO_2 into solution and the absorption heat of CO_2 with amines in solution. For phase-separation systems, the formation of liquid−liquid phase separation or solid precipitation also causes the exothermic process in the reactor. It can be named as the heat of phase separation. Although the heat generated by the phase change does not change between liquid−liquid and solid−liquid, the amount of heat is overwhelmingly larger in solid−liquid. The reason is probably that solid−liquid forms strong ionic crystals. Since the enthalpy change of the phase change rides on the heat consumption during regeneration, the energy increases

correspondingly in the case of solid—liquid, but the increase in energy in the case of liquid—liquid is not significant.

3.4. Overall Absorption Heats of All Systems. Table S1 in the Supporting Information summarizes the values of the overall integral of absorption heat per loading in our experiments and literature data. As the loading interval of our experiment is large compared with other data, we show the average value of absorption heat.

In comparison with MEA 30 wt % aqueous solution, the absorption heat of EAE is smaller due to less formation of carbamate.[3] Therefore, the overall absorption heat of EAE is smaller than that of MEA aqueous solution in our study. The overall absorption heat of single aqueous amines decreases in the order primary > secondary. However, the concentration of AMP is only 25 wt %, so the results of AMP cannot be compared with those of MEA and EAE in this study.

It can be seen that phase-separation solvents have higher absorption heats compared to those of single amine solvents. In this paper, our main focus is on introducing a continuous calorimetric method that can provide information on the phase-separation loading point; a more specific study on the overall assessment of solvent should be carried out in detail. The values in Table S1 for comparison of the absorption heat do not reflect the phase-separation loading point, if any. With our continuous calorimetry, this phase-separation loading is easily detected.

4. CONCLUSIONS

Carbon dioxide absorption heats of three classes of systems were investigated by means of continuous calorimetry. The results showed good agreement with literature values. The high absorption heat of EAE 80 wt % is attributed to the carbamate formation in high concentration solution. For EAE 30 wt %, the solution heat is lower due to bicarbonate and carbamate formation in solution. For AMP 25 wt %, carbamate is formed at low loading; however, as loading increases, this unstable carbamate is hydrolyzed into bicarbonate. The decrease in absorption heat is explained by the formation of bicarbonate by the hydrolysis of unstable carbamate and carbonate. For the first time, to the best of our knowledge, the change in enthalpy of solution is continuously observed when the solution is separated into two phases or solid is formed in solution. A slight increase in liquid—liquid systems is ascribed to phase-separation energy. In solid—liquid systems, the significant increase in absorption heat is attributed to supersaturation and the crystallization energy of AMP carbonate salt. The relationship between load range and heat absorption is important because it is directly related to the energy calculations required in the process design.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.9b04672.

Absorption heat of amine solvents in this research compared to those of literature data (PDF)

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

H = heat [kJ/mol of CO_2]
P = pressure [kPa]
Q = heat [GJ/ton of CO_2]
R = gas constant [J/K mol]
T = temperature [K]

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