

Temperature Dependence of Absorption Heat of Phase-Change Solvent in Carbon Dioxide Capture Solvent

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Abstract

Capturing carbon dioxide using amine solvents has been a mature method. However, the energy penalty is the disadvantage of this chemical method. The homogeneous solvents that separate into liquid-liquid or solid-liquid phases after CO₂ absorption are named phase-change solvents (LLPS and SLPS solvents, respectively). Regenerating only the CO₂-rich phase or regeneration based on the properties of CO₂-rich and -lean phases is expected to overcome the energy consumption in the regeneration process [1, 2]. The absorption heat is an important property in evaluating the efficiency of solvent in CO₂ capture. In this study, LLPS solvents were investigated with 2-(ethylamino)ethanol (EAE) in organic solvent (Diethylene Glycol Diethyl Ether, DEGDEE) with/without water presence (named as EAE/DEGDEE 30/70 and EAE/DEGDEE/water 30/60/10 (weight base), respectively). In these solvents, the product of EAE and CO₂ – carbamate – has low affinity to the hydrophobic DEGDEE; therefore, it forms a new phase. Aqueous solution of 2-amino-2-methyl-1-propanol (AMP) at 50 wt% was used as SLPS solvent. The absorption heat of 100 g of each solvent was examined with absorption temperature range of 25 - 80°C with 1 L/min of N₂:CO₂ mixture (4:1 ratio). The amount of CO₂ absorbed was measured by the total organic carbon as well as the difference between the CO₂ concentrations of the inlet and the outlet gases. EasyMax102 (Mettler Toledo, Inc.) was used to continuously measure the generated heat and to maintain the isothermal condition during CO₂ absorption.

The obtained absorption heat curves exhibit the loading point – the ratio of the moles of CO₂ absorbed to that of amine in solvent – where the solvent changes its phase. The LLPS solvent with water presence separates at lower loading than that of LLPS solvent without water. The absorption heat of those phase change solvents and the loading point of phase change are independent to the absorption temperature.

Keywords

Absorption heat, Carbon dioxide capture, Phase-change solvent

1. Introduction

As one of the main components of greenhouse gases, CO₂ from industry flue gas is the main object to decrease its emission amount to the atmosphere. Scientists have been doing researches on capturing CO₂ via absorption, adsorption, or membrane. Among them, capturing CO₂ using chemicals is a mature method that has been applied in to industry with the benchmark aqueous monoethanolamine (MEA) solution. The largest disadvantage of this chemical method is in its energy consumption, especially in the regeneration of the amine solution.

The absorption heat (equivalent to the regeneration heat but different in sign) is directly related to the solution design and capturing efficiency evaluation. Moreover, it is a mandatory parameter in stimulating the absorption/regeneration processes. Therefore, investigation of absorption heat at various temperatures is necessary for carbon dioxide capture.

Amine reacts with CO₂ to form bicarbonate or carbamate salts of amine. While two amine molecules react with one CO₂ to form carbamate salt, carbonate salt requires only one amine to react with CO₂. The carbonate has lower reaction heat than that of carbamate. Formation of those products are influenced by amine classification: the primary and secondary amines prefer the carbamate products while the tertiary amines favor the carbonate product. Particularly the hindered amines react with CO₂ to form carbonate salt due to its structure. Although the amines preferring carbonate formation have higher capturing efficiency, it is reported that tertiary amine has a low reaction rate.

To overcome this energy penalty, the development of a new absorption solvent has been conducted. The phase-change solvents are solutions that change their phase from homogeneous before CO₂ absorption to the liquid-liquid or the solid-liquid phases after CO₂ is flown in (LLPS and SLPS solvents, respectively). The regeneration of only the CO₂-rich phase might require less energy [1]. The combination of amine and solvents also accelerates the regeneration process [2]. A LLPS solvent of 2-(Ethylamino) ethanol (EAE), Diethylene glycol diethyl ether (DEGDEE), water (at 30/60/10 weight base) showed the acceleration in regeneration [2]. Even though EAE is a secondary amine, the presence of organic solvent DEGDEE promotes the carbamate formation in this solvent. This carbamate product promotes separation, forming another liquid phase in the solution. As a result, the solution is divided into two: a CO₂-rich phase (with carbamate, amine, and water) and a CO₂-lean phase (with DEGDEE). In regeneration process, both phases are sent to the regeneration tower, in which the regenerated amine is dissolved into the ether phase. Consequently, the regeneration of amine is accelerated. As a result, this solution was reported to be able to be regenerated at a lower temperature (90°C) as compared to that of conventional amine (120°C). In case of SLPS solvent, the hindered amine

2-Amino-2-methyl-1-propanol (AMP) was reported to form solid carbamate salt in an organic solvent or at high concentration of aqueous solutions [1]. As mentioned above, the regeneration of only the solid product can reduce energy consumption. In this study, temperature dependence of the absorption heat of LLPS solvents of EAE/DEGDEE/water (at 30/60/10 and 30/70/0 weight basis) and that of SLPS aqueous solution AMP 50 wt% at various temperatures was investigated. A continuous measurement of absorption heat used in this study also showed the change of this parameter during absorption.

2. Experimental

2.1. Materials

A secondary amine EAE (>98.0%, $C_4H_{11}NO$), a hindered amine AMP (>90.0%, $C_4H_{11}NO$), and an organic solvent DEGDEE (>98.0%, $C_8H_{18}O_3$) from TCI were used without further purification. Basically, there were three systems studied in this work, two LLPS solutions of EAE/DEGDEE/water at 30/60/10 and 30/70/0 weight bases and a SLPS aqueous solution of AMP at 50wt%.

2.2. Apparatus and procedure

A reaction calorimeter (EasyMax102, Mettler Toledo) was used to continuously measure the generated heat under isothermal condition. The reaction temperature range was varied from 25 - 60°C. 100 g of solution was flown with a 1 L/min mixture of $N_2:CO_2$ (4:1 in volume ratio, Nagoya Nissan Ltd.) until equilibrium. The CO_2 concentration in the outlet gas was measured by an infrared gas analyzer (EXAIR, Yokogawa). The amount of CO_2 absorbed was determined by the difference of CO_2 between the inlet and the outlet gases. For cross-check, the amount of CO_2 absorbed in the solution was evaluated by using TOC (Total Organic Carbon analyzer). An outline of the experiment was described in our previous paper (Fig. 1) [3].

Absorption heat was calculated as

$$\Delta H_{abs} [kJ/mol-CO_2] = \text{generated heat [W]} / \text{absorbed } CO_2 [mmol/s]$$

3. Results and discussion

Loading point is defined as the ratio of the moles of CO_2 absorbed to that of amine in solvent. The change of absorption heat of LLPS solvent of EAE/DEGDEE/water 30/60/10 versus loading at various temperature is presented in Fig. 2. In this LLPS solvent, the solvent

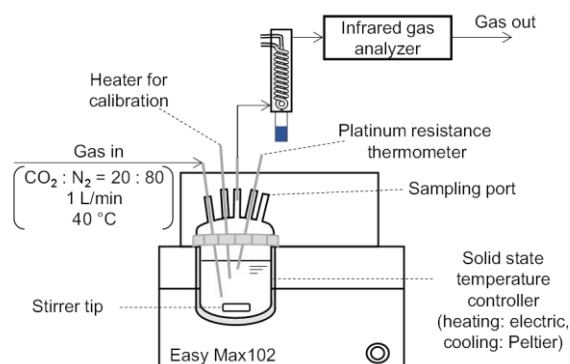


Fig. 1. Sketch of experimental setup (Adopted from Ref. 3).

separates into two liquid phases after CO₂ absorption at 25°C, 40°C, and 60°C. The loading points where phase separation occurs are 0.117, 0.122 and 0.139 mol-CO₂/mol-amine at 25°C, 40°C and 60°C absorption temperature, respectively. However, this loading point is not influenced by absorption heat when the whole loading range is considered. The absorption heat at 25°C is lower than those at 40°C and 60°C. It can be said that absorption heat as well as the loading point where phase separation occurs are affected by temperature.

References

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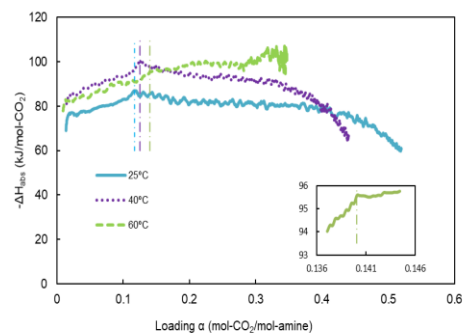


Fig. 2. Absorption heat of EAE/DEGDEE/water 30/60/10 solvent at 25°C (green line), 40°C (purple line), and 60°C (green line). Dash-dot lines: the loading where the solvents change their phases. Inset: the leap in absorption heat curve at 60°C).