



Development of phase separation solvent for CO₂ capture by aqueous (amine + ether) solution



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ABSTRACT

Phase separation solvents for CO₂ absorption have been designed which transform into two liquid phases after CO₂ absorption. We studied seven types of amines and one type of ether-mixed solvents and observed that there are three types of phase phenomena, namely, no phase separation, phase separation with CO₂ scrubbing, and initially immiscible. We also observed that these types can be classified using the hydrophobicity of the amine. The solubility of CO₂ was measured in the phase separation solvent. In the lower-pressure region, the solvent formed a single liquid phase. When the amount of CO₂ in solution reached a separation point, the solvent separated into two liquid phases.

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1. Introduction

Carbon dioxide capture technology has been focused on applicable systems for mitigating the global warming problem. Amine scrubbing systems have been practically used in recent decades [1]. In these systems, most of the CO₂ separation energy comes from the energy used for amine regeneration. To develop an energy saving system, there have been many reports of the optimization of amine structures [2,3].

Recently, phase separation type solvents that show two liquid phases after CO₂ scrubbing, a CO₂ rich phase and a CO₂ lean phase, were reported. These systems are called “phase changing solvents,” “phase transition solvents,” “phase separation solvents,” or “biphasic solvents.” Raynal et al. reported the DMX™ process, a phase separation process that occurs after CO₂ absorption and thermal exchange [4,5], and this process has lower regeneration energy (2.3 GJ/ton-CO₂) compared to reference amine MEA (monoethanolamine) process (3.7 GJ per tonne-CO₂). The DMX is also summarized in the results of the ACACIA project [6]. Kim et al. reported the phase transitional CO₂ capture solvent of an alkanolamine-alcohol process and studied the absorption mechanism with NMR spectroscopy [7]. Ciftja et al. reported that the combination of 2-(dithylamino)-ethanol/3-(mMethylamino)propylamine (DEEA/ MAPA) shows phase separation after CO₂ scrubbing [8], and Wang et al. reported that the amino acid shows phase separation on CO₂

scrubbing [9]. Recently Zhuang et al. reported the review of the phase separation absorbents for carbon capture [10]. Physical absorbents like glycol or ionic liquid plus amine or base mixture were also recent new direction for CO₂ absorption [11–16]. Fu et al. reported small amount of ionic liquid enhanced the CO₂ solubility in K₂CO₃ solution [11].

In this work, to develop the phase separation solvent, we examined phase phenomena for seven types of amines and one type of ether-mixed solvents. Ether has been used as a physical absorbent for CO₂ capture [17,18]. The partition coefficient of solute between water and octanol phases (*K*_{OW}) was used for determining the types of phase separation solvents. The CO₂ solubility and compositions of both the CO₂-rich phase and the CO₂-lean phase were measured at temperatures from 313 K to 353 K and CO₂ pressures from 1 kPa to 100 kPa.

2. Experimental

2.1. Materials

Table 1 shows the amine and ether that were used. We selected seven types for amines; 2-(butylamino)ethanol (BAE), 2-amino-1-methoxybutane (AMB), 2-(ethylamino)ethanol (EAE), 1-amino-2-propanol (DAP), 2-(methylamino)ethanol (MAE), 2-(2-aminoethoxy)ethanol (AEE), and 2-aminoethanol (MEA) to check the hydrophobicity effect for phase phenomena and one ether solvent, Diethylene glycol diethyl ether (DEGDEE). The CO₂ (mole fraction purity >0.995) and N₂ (mole fraction purity

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Table 1

Purity and supplier of materials which we used.

| Materials | CAS | Abbreviation | Supplier | Mass fraction purity | Analysis method |
|---------------------------------|------------|--------------|-------------------|----------------------|-----------------|
| 2-(Butylamino)ethanol | 111-75-1 | BAE | TCI ^b | >0.980 | GC ^a |
| 2-Amino-1-methoxybutane | 63448-63-5 | AMB | TCI ^b | >0.900 | GC ^a |
| 2-(Ethylamino)ethanol | 110-73-6 | EAE | TCI ^b | >0.980 | GC ^a |
| DL-1-Amino-2-propanol | 78-96-6 | DAP | TCI ^b | >0.920 | GC ^a |
| 2-(Methylamino)ethanol | 109-83-1 | MAE | Wako ^c | >0.990 | GC ^a |
| 2-(2-Aminoethoxy)ethanol | 929-06-6 | AEE | TCI ^b | >0.980 | GC ^a |
| 2-Aminoethanol | 141-43-5 | MEA | Wako ^c | >0.990 | GC ^a |
| Diethylene Glycol Diethyl Ether | 112-36-7 | DEGDEE | TCI ^b | >0.980 | GC ^a |

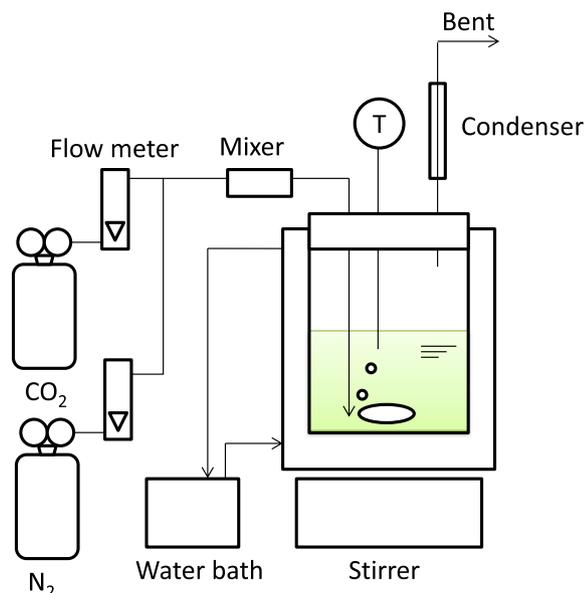
All components were used without further treatment.

^a Gas chromatography.^b Tokyo Chemical Industry CO., Ltd.^c Wako Pure Chemical Industries, Ltd.

>0.9999) 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. Phase separation tests and CO₂ solubility for phase separation solvent

Fig. 1 shows the schematic diagram of the equipment used to check the phase phenomena. The solvent was loaded in a temperature-controlled glass cell and CO₂ and N₂ mixture gas flowed into the cell at ambient pressure via the KOFLOK1250 flow controller. After equilibrium was reached, the CO₂ concentration in the gas phase was determined by gas chromatography (GC) (Shimadzu GC-8A), and uncertainty in CO₂ partial pressure was 0.2 kPa. The concentration of each substance (amine, ether, water, and CO₂) in the liquid phase was determined by GC (Shimadzu GC-14B, flame ionization detector, column temperature 200 °C, Inert-Cap for amines) and total organic carbon analysis (Shimadzu TOC-V CPH). First, organic carbon (amine and ether) and inorganic carbon (CO₂) contents were determined by TOC, and the amine/ether ratio was determined by GC. The water content was determined from other component fractions; some points were also checked with a Karl Fischer titration method, which showed good agreement. When two liquid phases were observed, the composition of each phase was determined. After CO₂ dissolved in the solvent, CO₂ formed either carbamate or bicarbonate. In our analysis,

**Fig. 1.** Experimental apparatus.

CO₂ in carbamate and bicarbonate counted as CO₂ molecules, and amine in carbamate counted as neutral amine. Uncertainty in the composition was 0.005 mol fraction.

3. Results and discussion

3.1. LLE phase separation with CO₂ scrubbing

Table 2 shows the results of the phase separation tests that showed three types, and Fig. 2 shows the results obtained for phase separation on combining EAE and DEGDEE. Weight base initial ratio of solvent was amine:DEGDEE:water = 30:60:10. We also examined solvents with no water content; however, the viscosity of the solvent was too high to mix the solvent with a stirrer.

First, we checked the relation between phase separation and alkyl chain length of the amine MEA, EAE and BAE. These three amines have the same structure with the exception of alkyl chain length; thus, the hydrophobicity is considered to increase as MEA < EAE < BAE. MEA initially showed two liquid phases before CO₂ scrubbing, EAE showed phase separation occurred with CO₂ scrubbing, and BAE showed phase separation did not occur with CO₂ scrubbing.

Fig. 3 shows the mechanism of phase separation. The amine transforms into protonated amine and carbamate after reaction with CO₂. These ion species lead to phase separation after CO₂ absorption. MEA has high polarity and is initially immiscible with DEGDEE. EAE has lower polarity than MEA and is miscible with DEGDEE before CO₂ scrubbing. After CO₂ is absorbed, ionized EAE is immiscible with DEGDEE. Since BAE has very high hydrophobicity, it is miscible with DEGDEE before and after CO₂ absorption (Fig. 4).

3.2. Classification of amine–ether combination

We consider that hydrophobicity of ion species, which is formed by the CO₂-amine reaction, is greater than neutral amine and the hydrophobic order of ion species follows that of neutral amine, so that hydrophobicity of neutral amine is considered to classify the phase separation type; thus, we selected the K_{OW} as a hydrophobicity parameter. The K_{OW} is the solute partition coefficient between the water phase and the octanol phase. It was calculated by the group contribution activity model UNIFAC with PRO/II software [19] since it needs only the chemical structural formula.

$$K_{OW} = \frac{\text{solute concentration in octanol phase}}{\text{solute concentration in water phase}} \quad (1)$$

Table 2 shows the phase separation test results for the seven amine and DEGDEE combinations. The amine and ether combinations are arranged by the estimated K_{OW} . The high values of the

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