

CO₂ absorption properties of imidazolium based ionic liquids using a magnetic suspension balance



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ABSTRACT

We have investigated the CO₂ absorption properties in 1-ethyl-3-methylimidazolium (Emim) ionic liquids with the anions (TFSA, bis(trifluoromethanesulfonyl)amide; BETA, bis(pentafluoroethanesulfonyl)amide; NFBS, nonafluorobutanesulfonate; BF₄, tetrafluoroborate) using a magnetic suspension balance at 313.15 K and pressures up to 6 MPa. To obtain accurate CO₂ solubility, the buoyancy correction was made by taking account of the volume expansion of ionic liquids caused by CO₂ dissolution. In the present work, Sanchez–Lacombe equation of state was used for such volume corrections at high pressures. As a result, the solubilities of carbon dioxide in [Emim][TFSA] are consistent with the literature data. The solubilities of carbon dioxide in the ionic liquids studied showed typical pressure dependence as physical absorption, and increased in the following order of the anion: BF₄ < NFBS < TFSA < BETA.

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1. Introduction

Ionic liquids (ILs) are salts with melting temperature being at or below ambient temperature. They generally have negligible vapor pressure, non-flammability, high thermal and chemical stability, low heat capacity, and favorable miscibility of acidic gases such as CO₂, NO_x and SO_x [1–3]. Because of these characteristics, ILs can overcome the issues of conventional absorbents, i.e. emission to the atmosphere, flammability, and high energy consumption. Therefore, ILs attract much attention as a potential absorbent for gas sweetening, in particular, CO₂ capture [4].

A number of studies have been performed to study the effect of chemical structure of IL on CO₂ physisorption [5], since the first report on the binary phase equilibria for the CO₂ + 1-butyl-3-methylimidazolium hexafluorophosphate [6]. According to the intensive study by the Brennecke and co-workers [1,7,8], anion influences on the CO₂ solubility more strongly than cation. Aki et al. [9] reported that the solubility of carbon dioxide in 1-butyl-3-

methylimidazolium (Bmim) based ILs increased in the following order of the anions: NO₃ < DCA (dicyanoamide) < BF₄ < PF₆ < TfO (trifluoromethanesulfonate) < TFSA < methide. Commonly, the fluorinated anions, like bis(trifluoromethanesulfonyl)amide (TFSA), improve the CO₂ solubility compared to other non-fluorinated anions. It is pointed out that the Lewis acid–base interaction between the oxygen atom on CO₂ and the fluorine atom on IL. Thus, it is expected that the intermolecular interaction between CO₂ and IL becomes stronger by increasing the number of the fluorine atom.

In the present study, we investigated the CO₂ absorption properties in 1-ethyl-3-methylimidazolium (Emim) ionic liquids with bis(pentafluoroethanesulfonyl)amide (BETA) and nonafluorobutanesulfonate (NFBS) at pressures up to 6 MPa and 313.15 K. There have been no CO₂ solubility data available for [Emim][BETA] and [Emim][NFBS]; therefore, we report them for the first time. These anions have larger number (10 for BETA and 9 for NFBS) of the fluorine atoms than TFSA. Furthermore, the CO₂ solubilities in [Emim][TFSA] and [Emim][BF₄] (1-ethyl-3-methylimidazolium tetrafluoroborate) were measured to compare those of [Emim][BETA] and [Emim][NFBS]. The chemical structures of the cation and anions studied are shown in Fig. 1.

The gravimetric microbalance method was applied to measure the CO₂ solubility in IL in the present study, because it requires a

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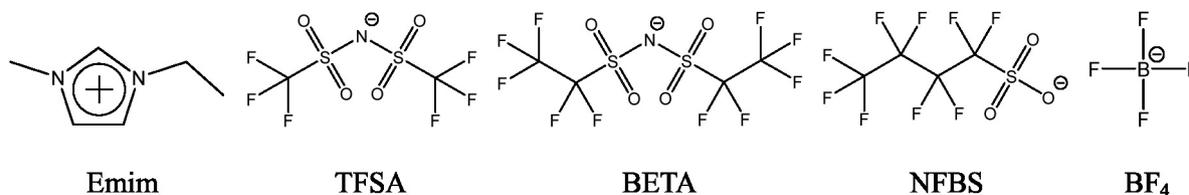


Fig. 1. Chemical structures of the cation and anions studied.

smaller amount of IL, ~1 g, than the conventional methods. The several groups have investigated the CO₂ + IL binary systems with this method [7,8,10,11]. This method requires the buoyancy correction to obtain accurate solubility data. For example, Shiflett et al. [10] made such correction, and they estimated the volume expansion from the arithmetic mean of molar volumes of CO₂ and neat IL. Soriano et al. [11] also corrected the sample volumes with the similar method, and they calculated the density of neat ionic liquid using the group contribution method. However, they do not take account of volume expansion of liquid phase. The IL phase expands several dozen of a percent under high CO₂-pressure conditions. Thus, it is important to correct the buoyancy with taking the volume expansion into account for more accurate solubility data. In this work, we tried to calculate the volume expansion of IL phase by using Sanchez–Lacombe equation of state and make the buoyancy correction more precisely. This was originally developed for the polymer-CO₂ solutions by Sato and coworkers [12].

2. Experimental

2.1. Materials

CO₂ (purity, 99.999vol%) was obtained from Showa Denko Gas Products Co., Ltd. [Emim][TFSA], [Emim][BETA], and [Emim][NFBS] were prepared in our laboratory. Lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]; Kanto Chemical Co., Ltd.), lithium bis(pentafluoroethanesulfonyl)amide (Li[BETA]; Kishida Chemical Co., Ltd.), lithium nonafluorobutanesulfonate (Li[NFBS]; Wako Pure Chemical Industries, Ltd.), 1-methylimidazole (Tokyo Chemical Industry Co., Ltd.) and bromoethane (Tokyo Chemical Industry Co., Ltd.) were purchased and used without further purification. [Emim][BF₄] (purity, ≥98%) was purchased from Kanto Chemical Co., Inc.

2.2. Synthesis

[Emim][TFSA] was synthesized according to the previous report [13]. First, 1-ethyl-3-methylimidazolium bromide ([Emim]Br) was synthesized by mixing equimolar amounts of 1-methylimidazole and bromoethane in acetonitrile at room temperature for more than 1 week. Then, the mixture was evacuated to remove acetonitrile at 313 K and the residual solid was dissolved in water. To exchange Br for TFSA, an aqueous solution of Li[TFSA] was slowly added to the aqueous solution of [Emim]Br with stirring. The biphasic mixture was stirred for more than 6 h, IL phase was washed with distilled water more than five times. Finally, the residual water was removed by evacuation. [Emim][BETA] and [Emim][NFBS] were also synthesized by the similar procedure. For the case of [Emim][NFBS], IL was extracted with dichloromethane after the anion exchange because the solution was monophasic. The dichloromethane solution was washed with distilled water more than five times to remove Li and Br ions. The present ILs were characterized by using a JEOL JNM-ECX400 NMR spectrometer with DMSO-*d*₆ as the standard at ~293 K. Chemical shifts of ¹H are

described in the Supporting information. The purities of ILs are estimated as follows: 99% for [Emim][TFSA], 99% for [Emim][BETA], and 98% for [Emim][NFBS]. The halogen constants of aqueous solutions in contact with the samples were less than the detection limit of AgNO₃ testing. Just before the measurements, IL was dried under vacuum at 343 K for more than 40 h to remove any excess water. The water contents in the ionic liquids were less than 50 ppm as determined by Karl-Fischer titration (Kyoto Electronics Manufacturing Co., Ltd., MKC-520).

2.3. Apparatus and procedure

2.3.1. Density measurement

ILs were transferred to an air-tight syringe under dry nitrogen atmosphere, and injected into densimeters without contacting moisture. The density at atmospheric pressure was determined using an Anton Paar DMA 5000 M vibrating tube density meter (uncertainty ±0.05 kg m⁻³). The instrumental constants were calibrated with dry air and Milli-Q water (Millipore Direct-Q 3 UV). The density at high pressures was measured by using Anton Paar DMA HP vibrating tube density meter (uncertainty ±0.1 kg m⁻³). The instrumental constants were calibrated with dry air and dodecane (Tokyo Chemical Industry Co., Ltd.). Pressure was measured using Druck DPI145 pressure indicator and PDCR911 pressure transducer (uncertainty ±0.004 MPa).

2.3.2. CO₂ solubility measurement

Fig. 2 shows a schematic diagram of a magnetic suspension balance [14] (Rubotherm GmbH, Germany), which was used to measure the CO₂ solubility in ILs. The magnetic suspension balance can be operated at pressures up to 13.8 MPa and temperatures up to 373 K. The resolution and repeatability of a microbalance are 10 μg and ±30 μg, respectively. Pressure was measured with a Paroscientific pressure transducer (Model 735, accuracy ±0.0005 MPa). Temperature of the high-pressure cell was measured with a Pt 100 Ω probe (Netsushin Co., Ltd.) and temperature indicator (Fluke, 1502A, accuracy ±0.01 K).

Before the measurement, a weight and volume of blank sample basket were measured at 313.15 K and pressures up to 6 MPa. The volume of blank sample basket was determined by the buoyancy method. CO₂ solubility measurement was conducted as the following procedure. A 1 g of ionic liquid was loaded in the sample basket, and then the high-pressure cell was vacuumed about 24 h at 313.15 K. After the evacuation, a weight of the neat IL at vacuum was recorded. A desired amount of CO₂ was loaded into the high-pressure cell, and the temperature kept within ±0.01 K. When the changes of weight, temperature and pressure were less than ±0.1 mg h⁻¹, ±0.01 K h⁻¹ and 0.001 MPa h⁻¹, respectively, we assumed the IL was saturated with CO₂ and recorded a weight of the saturated IL. Subsequent measurements were repeated to obtain isothermal solubility data at pressures up to 6 MPa.

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