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Effect of partial pressure on CO_2 solubility in ionic liquid mixtures of 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide

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ABSTRACT

The solubilities of CO_2 in ionic liquid mixtures composed of 1-butyl-3-methylimidazolium acetate, [BMIM][AcO] and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, [BMIM][Tf_2N] have been determined at different partial pressures of CO_2 balanced with N_2 at atmospheric pressure over the temperature range (284–334) K. The solubility of CO_2 was proportional to the concentration of [BMIM][AcO], which reacts stoichiometrically with CO_2 in [BMIM][Tf_2N]. The CO_2 absorption mechanism was discussed in terms of the densities, viscosities, and electrical conductivities for the IL mixtures before and after CO_2 saturation. It was concluded that 1-butyl-3-methylimidazolium-2-carboxylate zwitterion, [$BMIM^+$-CO_2^-], is produced with deprotonation of 2-hydrogen in $[BMIM]^+$. This leads to formation of acetic acid, resulting in the viscosity reduction. Moreover, the absorption and desorption experiments for extremely dilute gas mixture (4000 ppm CO_2 in N_2) in the [BMIM][AcO]-[BMIM][Tf_2N] mixtures were carried out. The ionic liquids mixtures can effectively remove CO_2 even at such dilute concentrations. The absorption and desorption rates increased with increasing temperature. At higher temperature, the absorption rate also increased with increasing the concentration of [BMIM][AcO]. The multicycle experiments using [BMIM][AcO] between 2 h absorption at 298 K and 2 h desorption under vacuum at 353 K demonstrated the practical efficiency for CO_2 separation under extremely dilute conditions. The air purification process using ionic liquids for a limited space such as aerospace has been proposed for one of the promising future applications.

1. Introduction

Ionic liquids (ILs) have attracted much attention as physical and/or chemical absorbents to separate acidic gases because they are less flammable, nearly involatile, chemically and thermally stable, and show excellent solubility for such gases. Solubilities of gases in typical ILs have extensively been studied [1–6]. We have investigated the physical solubilities of CO_2 in a series of ILs composed of different pairs of cations and anions with specific functional groups at high pressures [7–11] as well as the chemisorption behaviors in carboxylate ILs at atmospheric pressure [12,13]. However, most solubility data have been collected for single-component gases in ILs. According to the recent review [5], summarizing huge number of literature, solubilities of mixed gases in ILs have been scarcely reported compared to those of pure gases. The solubility data for gas mixtures are of great importance to develop practical gas separation processes because the gas solubility can be significantly affected by the presence of another gas as well as partial pressure.

Shiflett and coworkers [14–17] have determined CO_2 solubilities in a series of imidazolium-based carboxylates. CO_2 can be chemically absorbed in 1,3-dialkylimidazolium salts with acetate, trimethylacetate, propionate, isobutyrate, and acetylpropionate anions, but not with trifluoroacetate, which indicates that the higher acidity of trifluoroacetate salt prevents CO_2 chemisorption. As summarized in our recent paper [12], there have been debates on the mechanism of CO_2 chemisorption in 1,3-dialkylimidazolium carboxylates, i.e., which a cation or anion species can react with CO_2. It is concluded that formation of 1,3-dialkylimidazolium-2-carboxylate zwitterion, [$BMIM^+$-CO_2^-], is promoted in 1,3-

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Table 1
Chemicals used in the preset study.

Chemical	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
1-Butyl-3-methylimidazolium acetate ([BMIM][AcO])	Aldrich	0.95	Dried under vacuum	>0.96	NMR spectroscopy
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([BMIM][Tf_2N])	Synthesized	–	Wash with water and dried under vacuum	>0.99	NMR spectroscopy
CO_2	Showa Tansan Co., Ltd.	0.9999	none	–	–
N_2	Air Liquide Kogyo Gas Ltd.	0.9999995	none	–	–

dialkylimidazolium carboxylates with carboxylic acids being concurrently produced [18–23]. Note that the stability of carbene–CO_2 complex is comparable to that of carboxylate-CO_2. Actually, the direct anion–CO_2 complex formation was observed in some carboxylate salts with ammonium and phosphonium cations that have no reactive site with CO_2, leading to a carbene-CO_2 adduct [13,24,25].

As mentioned above, despite a lot of reports on CO_2 solubilities of pure gases in ILs, there have been a very limited number of papers on those of mixed gases. The physical solubilities of CO_2 for binary gas mixtures with N_2 [26], H_2 [27–30], O_2 [31,32], Ar [28], CH_4 [31,33], H_2S [34–37], and SO_2 [38,39] have been determined in typical 1,3-dialkylimidazolium salts. Although chemically reactive ILs, such as carboxylate salts, can effectively capture CO_2 even at lower partial pressures, there have been little attempt to determine chemisorption behavior of CO_2 for gas mixtures in such ILs. Moreover, it is noted that the carboxylate ILs unfortunately show higher viscosities, particularly at around room temperature. For example, the viscosities for CO_2-reactvive imidazolium acetates are five times or more as high as those for the analogous non-reactive imidazolium trifluoroacetates. This disadvantage seriously affects the CO_2 absorption kinetics, which can restrict practical use of such carboxylate ILs. One of the simple, but good solutions is to use the ionic liquid mixtures consisted of a chemically reactive IL and a non-reactive IL that physically absorbs CO_2. Such a combination of chemical and physical absorbents has several advantages for practical use. An admixture of non-reactive ILs can effectively reduce the relatively high viscosities of reactive ILs, and can prevent the solidification of the product resulting from the chemical reaction with CO_2. In this study, we have investigated the solubilities of CO_2 in the IL mixtures at different partial pressures of CO_2 balanced with N_2 at atmospheric pressure over the temperature range (283–333) K. The IL mixtures were composed of CO_2-reactive 1-butyl-3-methylimidazolium acetate ([BMIM][AcO], CAS No. 284049-75-8) and less viscous 1-butyl-3-methylimidazolium bis(-trifluoromethanesulfonyl)amide ([BMIM][Tf_2N], CAS No. 174899-83-3). The physical properties, densities, viscosities, and electrical conductivities, for the IL mixtures have recently been determined as a function of composition at different temperatures by our research group [12]. Moreover, our attempt was extended to CO_2 separation from extremely dilute gas mixture of CO_2, ~4000 ppm, in N_2, so as to maintain life environments in a close system such as aerospace. The time profiles of absorption and desorption of CO_2 in the [BMIM][AcO]-[BMIM][Tf_2N] mixtures were obtained at different temperatures. Finally, for a practical application, we performed multicycle experiments between absorption and desorption of CO_2 for the extremely dilute gas mixture.

2. Experimental

2.1. Materials

A pure CO_2 gas (purity: 99.99 mol%) and N_2 gas (purity:99.99995 mol%) were purchased from Showa Tansan Co., Ltd. and Air Liquide Kogyo Gas Ltd., respectively. Two standard gas mixtures of CO_2 balanced with N_2 were obtained from Toatsu Yamazaki Co., Ltd., by which the compositions of CO_2 were guaranteed as 24.08 mol% and 49.6 mol%. All the gases were used without further purification. [BMIM][Tf_2N] was synthesized as previously described [40–42]. [BMIM][AcO] was purchased from Aldrich (>95%). Both [BMIM][Tf_2N] and [BMIM][AcO] were dried under vacuum for >30 h at 343 and 313–323 K, respectively, to remove any excess water. The ILs dried were mixed at given mass fractions and transferred to closed cells or other instruments in a dry glove box under an atmosphere of argon, with a dew point less than 258 K. The water contents of [BMIM][Tf_2N] and [BMIM][AcO] were less than ~$20\cdot10^{-6}$ and ~$35\cdot10^{-4}$ mass fraction as determined by Karl Fischer coulometric titration (Kyoto Electronics Manufacturing Co., Ltd., MKC-510). The purities of [BMIM][Tf_2N] and [BMIM][AcO] were estimated to be better than 99 and 96 mol%, respectively, by NMR spectroscopy (Varian Inova 500 spectrometer, ^1H and ^{13}C resonances), as shown in Table 1.

2.2. Measurements

Solubilities of CO_2 in the IL mixtures for the standard gases 24.08 and 49.6 mol% were gravimetrically determined at atmospheric pressure with an electrical balance, Mettler Toledo AB204-S (±0.1 mg) or XP5003S (±1 mg), where the repeatability was given in parentheses. The sample temperature was kept within ±0.1 K. The IL samples were assumed to be completely non-volatile. This was confirmed in that the weight change at 313 K before and after each run of temperature cycle from 313 via 333, 283, and 298–313 K remained unchanged within ±2% except for the case, ±3.8%, for 24.08 mol% CO_2 in the IL mixture at the mass fraction of [BMIM][AcO], $W_1^* = 0.150$. This was attributed to a small weight change, i.e., low solubility of CO_2 in the IL mixture. In other experiments, the weight increase was larger than ~100 mg. This satisfied that the overall uncertainties of the CO_2 solubility are less than ±4% except for the lowest solubility, ±5.5%, in the mixture at $W_1^* = 0.150$ at high temperature. The partial pressures, p_{CO_2}, of CO_2 in the gas mixtures were calculated from the compositions of CO_2 and the atmospheric pressures measured with a digital pressure gage (Druck, DPI 145). The uncertainties of p_{CO_2} were less than ±2%. The experimental apparatuses and procedures were described in our recent paper [12]. For CO_2-saturated IL samples, viscosities and densities were measured at 313 K using an Anton Paar Stabinger SVM 3000 rotating-cylinder viscometer. Electrical conductivities were also determined at 313 K with an impedance analyzer, Bio