

CO₂ absorption by binary mixture of ionic liquids-monoethanolamine at lower pressure



Guangren Yu^{a,*}, Sisi Fan^a, Xiaochun Chen^a, Ahmed A. Abdeltawab^b, Salem S. Al-Deyab^b

^a Beijing Key Laboratory of Membrane Science and Technology & College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

^b Petrochemicals Research Chair, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

ARTICLE INFO

Article history:

Received 14 July 2015

Received in revised form 16 October 2015

Accepted 8 November 2015

Available online 7 December 2015

Keywords:

Carbon dioxide

Absorption

Monoethanolamine

Ionic liquids

ABSTRACT

We studied the absorption capability for CO₂ of four binary mixtures of [BMIM][BF₄]-MEA, [EMIM][BF₄]-MEA, [BMIM][PF₆]-MEA and [EMIM][PF₆]-MEA at 298–318 K and 0.1–0.6 MPa, where BMIM is 1-butyl-3-methylimidazolium, EMIM is 1-ethyl-3-methylimidazolium, BF₄ is tetrafluoroborate, PF₆ is hexafluorophosphate, and MEA is monoethanolamine. Some factors such as ILs nature, MEA concentration, temperature, pressure, absorption rate and regeneration and recycling of absorbent were investigated. Compared with traditional aqueous amine, such water-free ILs-MEA does not suffer from water volatile loss and resulting corrosion that are typical problems in traditional aqueous amine process. With the addition of MEA, CO₂ absorption capacity in such ILs-MEA is much larger than that in the pure ILs and is comparable to that in some aqueous amines and tertiary mixture of ILs-amine-H₂O, typically, the CO₂ absorption capacity of [BMIM][BF₄]-MEA (50 v% MEA) is 0.519 mol CO₂/mol MEA at 298 K and 100 KPa. ILs nature has important effect, and the absorption capacity of BF₄ ILs-MEA for CO₂ is about 30% higher than that of PF₆ ILs-MEA where a precipitate is observed for the former while the absorption product of carbamate is soluble for the latter. Reasonable lower temperature and higher MEA concentration is favorable for CO₂ absorption. The absorbents can be regenerated and recycled with no remarkable change in CO₂ absorption.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The increasing concentration of greenhouse gases, mainly carbon dioxide (CO₂), is the primary cause to the global warming. Billions of tons of annual CO₂ emissions are the direct result of fossil fuel combustion to generate electricity (Gregg et al., 2008; White et al., 2003; Gray et al., 2008). Current technology for CO₂ removal from power plant emissions is aqueous amine process. In such aqueous amine processes, there are, however, a few problems such as the unaffordably high regeneration energy requirement, the uptake of water into the gas stream and the resulting corrosion, especially the high energy cost in the regeneration process (Song et al., 2013; Warudkar et al., 2013; Freeman et al., 2010; Soosaiprakasam and Amornvade, 2008). Alternative methods are desired.

Ionic liquids (ILs) present a highly versatile and tunable platform for the development of new processes and new materials

aimed at the capture of CO₂ from power plant flue gas. The desirable properties of ILs such as negligible vapor pressure, high thermal stability and wide liquidus range make them interesting candidates as new materials in CO₂ capture. Many researchers reported that CO₂ is highly soluble in some imidazolium ILs such as [BMIM][PF₆], [OMIM][BF₄], [EMIM][EtSO₄], [EMIM][Tf₂N], [EMIM][DCA] and [C₆mpy][Tf₂N] at high pressure (Pereira et al., 2013; Cesar et al., 2004; Anthony et al., 2005; Shiflett and Yokoziki, 2005; Anderson et al., 2007; Husson et al., 2003; Lei et al., 2010; Kroon et al., 2005; Kim et al., 2005; Almantariotis et al., 2012). CO₂ absorption in such common ILs is physical in nature and the solubility is small around ambient pressure. Grafting functional groups like amine onto ILs can enhance the CO₂ absorption. Amino-functionalized ILs such as [NH₂p-bim][BF₄], [aP₄₄₄₃][Gly] and [P₆₆₆₁₄][Met] present much higher absorption capacity for CO₂ (Bates et al., 2002; Zhang et al., 2006, 2009), where the absorption capacity can approach 0.5 mol CO₂/mol amine-group under ambient pressure, close to the absorption capacity of industrial aqueous amine. The viscosity of amino-functionalized ILs are high, especially after absorption of CO₂, and have to decrease in industrial application in future. Some mixtures composed of ILs and

* Corresponding author.

E-mail address: gryu@mail.buct.edu.cn (G. Yu).

aqueous amines were also investigated to absorb CO₂, which is from the concept of combining the performances of aqueous amine and ILs, e.g., [N₁₁₁₁][Gly]-MDEA-H₂O (Zhang et al., 2010, 2013), [gua][FAP]-MDEA-H₂O (Aziz et al., 2012), MDEA-[BMIM][BF₄]-H₂O (Ahmady et al., 2011a), (bheea)-MEA-H₂O (Taib and Murugesan, 2012), MEA-[BMIM][BF₄]-H₂O (Taib and Murugesan, 2012), MDEA-[BMIM][BF₄]-H₂O (Ahmady et al., 2011b). The absorption capability of such mixtures for CO₂ is comparable to that of aqueous amines. There is, however, still the risk of the corrosion from the volatilization of water.

Recently, Camper and his co-workers prepared the water-free mixture of [HMIM][Tf₂N] and MEA (50 mol% MEA) and experimentally determined the CO₂ absorption capability. It was interestingly observed that reversible absorption of CO₂ can be realized and CO₂ absorption capability of such a mixture is comparable to that of aqueous amine, approximately 0.5 mol CO₂/mol MEA at 313 K and 1 atm (Camper et al., 2008). Besides [HMIM][Tf₂N]-DEA (Camper et al., 2008; Rahman and Larachi, 2013), [EMIM][Tf₂N]-DEA and [BMIM][Tf₂N]-DEA (Hasib-ur-Rahman et al., 2012) were also been investigated to absorb CO₂, where similar CO₂ absorption capability were observed. In this work, we prepare four binary mixtures of [BMIM][BF₄]-MEA, [EMIM][BF₄]-MEA, [BMIM][PF₆]-MEA and [EMIM][PF₆]-MEA, where the ILs are easily prepared with cheaper starting raw materials. We experimentally determine the CO₂ absorption capability of such binary mixtures at 298–318 K and 0.1–0.6 MPa and investigate a variety of factors such as ILs nature, MEA concentration, temperature, pressure, absorption rate and regeneration and recycling of absorbent. This work will show the binary mixture composed of such ILs and MEA is very competitive absorbent for capturing CO₂, where the absorbents are water-free, the risk of the corrosion from water volatilization is eliminated, such ILs are easily prepared with cheap raw materials, and CO₂ absorption capability is comparable to that of other absorbents.

2. Experimental methods

2.1. Chemicals

Chemicals and suppliers are listed as follows: CO₂ (≥99.9%), Beijing Special Gas Co. Ltd.; N-methylimidazole (analytic grade), Shanghai Senhao Fine Chemicals Co. Ltd.; monoethanolamine (≥99.5%), chlorobutane (≥98%), ethyl bromide (≥98%), Beijing Yili Fine Chemicals Co. Ltd.; sodium tetrafluoroborate (≥98%) and potassium hexafluorophosphate (≥98%), Sinopharm Chemical Reagent Co. Ltd. [BMIM][BF₄], [BMIM][PF₆], [EMIM][BF₄] and [EMIM][PF₆] were synthesized according to the reported procedure (Alexia et al., 2008; Huddleston et al., 2001). The ILs were dried by heating at 353 K under high vacuum for 48 h prior to use. Their densities are determined and the values are provided in Table S1 in Supporting Information.

2.2. Absorption experiment

The equipment for CO₂ absorption is illustrated in Fig. 1, and is manufactured by Machine Workshop, Beijing University of Chemical Technology. It mainly consists of a stainless steel gas buffer reservoir (196.7 ml) and a stainless steel absorption chamber (112.3 ml) with magnetic stirring. There is an inner layer of polytetrafluoroethylene in the reservoir and chamber. These two tanks are put into a thermostatic water bath. The temperature is monitored with K-type thermocouple (TS404 with an accuracy of 0.1 K, Tiantai Tech. Co. Ltd. in Beijing). The pressure is measured by pressure transducer (TS200-T1 with an accuracy of 0.001 bar, Tiantai Tech. Co. Ltd. in Beijing). The temperature and pressure are

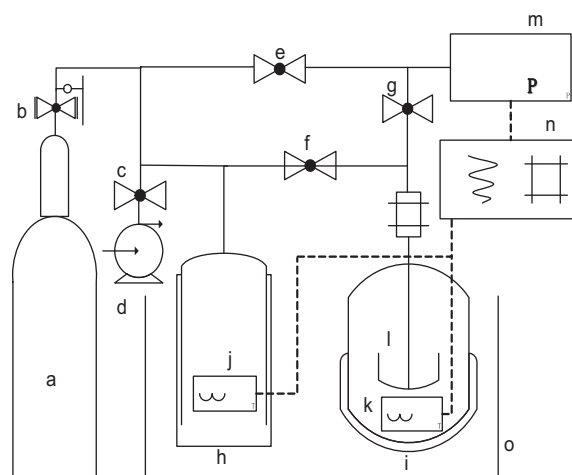


Fig. 1. Experimental apparatus for determining CO₂ absorption by ILs or ILs-MEA mixture: a, CO₂ cylinder; b, reducing valve; c, e, f, g, ball valve; d, vacuum pump; h, buffer reservoir; i, absorption chamber; j, k, temperature sensor; l, stirrer; m, pressure sensor; n, paperless recorder; o, water bath.

recorded by a paperless recorder (TS606, Tiantai Tech. Co. Ltd. in Beijing).

Before the absorption experiment, the gas tightness of system is confirmed through filling 8 bar nitrogen gas with a constant pressure for 2 h. In a typical experiment, absorbent is put into the absorption chamber; air is evacuated (<0.001 MPa) from gas reservoir and absorption chamber by a vacuum pump to ensure that absorbent is free of dissolved gas. Gas is injected into reservoir to a desired pressure. The valve connecting reservoir and chamber is turned on and the gas flows into absorption chamber. Absorption equilibrium is reached after the pressure is constant for 20 min. The final temperature and pressure are recorded.

The determination of absorption uses the constant volume method. The amount of absorbed CO₂ can be calculated by the following equation:

$$n_{\text{absorbed}} = n_{\text{initial}} - n_{\text{final}} = \frac{V}{R} \left(\frac{p_{\text{initial}}}{T_{\text{initial}}} - \frac{p_{\text{final}}}{T_{\text{final}}} \right)$$

with the assumptions that absorbent is non-volatile during the absorption, its volume is consistent after gas absorption, and the gas is regarded as ideal gas.

3. Results and discussion

3.1. Absorption of pure ILs

The results of equilibrium isothermal of CO₂ in [BMIM][PF₆], [BMIM][BF₄], [EMIM][BF₄] and [EMIM][PF₆] at 298 K and 0.1–0.6 MPa are given in Fig. 2, where the results from literature are also shown for comparison. Fig. 2 indicates that the absorption results obtained by us are in good agreement with that by others, typically the absolute value of relative deviation of mole fraction of CO₂ in ILs is less than 10% at lower than 0.6 MPa. The absorption of CO₂ increases along with pressure almost linearly at less than 0.6 MPa, which implies a physical absorption, consistent with Henry's law. The absorption capacity for CO₂ follows this order [BMIM][PF₆] > [BMIM][BF₄] > [EMIM][BF₄] > [EMIM][PF₆]. The absorption of CO₂ in [BMIM] ILs is much higher than that in [EMIM] ILs, which can be ascribed to the longer alkyl side chain and the resulting stronger van der Waals interaction with CO₂ (Cesar et al., 2004). The anion has also a remarkable effect. PF₆ ILs has higher capacity for CO₂ than BF₄ ILs if we do not include [EMIM][PF₆] (solid at 298 K), which has been understood from

Download English Version:

<https://daneshyari.com/en/article/1742947>

Download Persian Version:

<https://daneshyari.com/article/1742947>

[Daneshyari.com](https://daneshyari.com)