Experiment and simulation study of CO_2 solubility in dimethyl carbonate, 1-octyl-3-methylimidazolium tetrafluoroborate and their mixtures

Zhijun Zhao [a, *], Xiao Xing [a], Zhigang Tang [a, **], Yong Zheng [b], Weiyang Fei [a], Xiangfeng Liang [c], E. Ataeivarjovi [a], Dong Guo [a]

[a] State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, 100084, China
[b] College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang, 455000, Henan, China
[c] Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China

ARTICLE INFO

ABSTRACT

CO_2 capture with solvent-based process is known as a promising technology for controlling the global warming. In this work, the constant-volume method was used to investigate CO_2 solubility in DMC, ionic liquid of [Omim][BF_4], and their mixtures from 298.15 to 328.15 K under pressures up to about 3 MPa. The COSMO-RS model was used to predict the Henry's constants and the vapor pressures of DMC in the mixtures. The experimental results showed the CO_2 solubility in [Omim][BF_4] is higher than DMC at 318.15–328.15 K and adding [Omim][BF_4] into DMC can decrease the viscosity compared to the pure [Omim][BF_4]. Besides, the COSMO-RS simulation results showed the Henry's constants in the mixtures increases with the decreasing mass ratio of [Omim][BF_4] which are consistent with experimental values and the vapor pressures of DMC in the mixtures decreases with the increasing mass ratio of [Omim][BF_4]. Moreover, the activation energy (*Ea*) predicted from viscosity showed the higher viscosity mean the larger *Ea* and the larger *Ea* indicate the higher CO_2 solubility in these solvents. Finally, the mixtures of DMC and [Omim][BF_4] may be used as promising physical solvents to capture CO_2 with high partial pressures, which combine the advantages of organic solvents and ionic liquids.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The greenhouse effect and global warming caused by CO_2 have become serious environmental issues and attracted worldwide public attention [1–4]. Moreover, the industrial gas resources, such as natural gas, shale gas, biogas, syngas and so on, contains a certain amount of CO_2 as impurity, which decreases the heating values and the qualities of the gases, demands high energy consumption for conversion and transport, and corrodes some pipelines and equipments [5–7]. So, CO_2 capture is an important way to improve the greenhouse gas control and upgrade or purify gas purification. By far, there are many technologies for CO_2 capture such as membrane separation, pressure swing adsorption (PSA), and physical or chemical solvent scrubbing [8–11]. Membrane processes are promising technology but the selectivity and productivity will be lost in the presence of CO_2 [12] and these processes are not likely to treat mixtures with low CO_2 partial pressure because additional energy is needed to compress the feed gas [13]. As for the PSA, it is promising technology because of the low energy requirement and fast regeneration [14], but the cost of the absorbent materials such as metal-organic frameworks (MOF) is not acceptable and the pressurizing the large feed stream is cost prohibitive [15]. Compared with other two technologies, the solvent-based process is still the most economically feasible and commonly used one [16–18] which includes chemisorption and physisorption process. The chemical absorption solvents such as amine [19], mixed amine [20,21], aqueous ammonia [22,23], potassium carbonate (K_2CO_3) [24,25] and so on, among of which the mainly used for commercial CO_2 separation are aqueous monoethanolamine (MEA) solution because of its maturity and low price [26]. However, this kind of solution is highly energy intensive and prone to degradation, which causes corrosion problems and also results in high solvent losses

and reclaiming costs [19,27–29]. While the physical absorption solvents such as poly (ethylene glycol) dimethyl ether (DEPG) (Selexol) [30], methanol (Rectisol) [31], propylene carbonate (PC) (Fluor) [32], N-methyl-2-pyrrolidone (NMP) (Purisol) [33], glycol [34] and so on can be used for capturing CO_2 in pre-combustion process from synthesis gas (or syngas) at high pressure and then CO_2 can be easily regenerated by pressure decreasing and/or temperature increasing [35,36]. However, the main problem with physical solvents is that the industrial gas resources should better be cooled before capture because this kind of solvents possess the best capacity at low temperatures, which will decrease the thermal efficiency and thus increases the overall cost [32]. Otherwise, the physical solvents also suffer from other problems such as high viscosity at low temperature (DEPG), corrosion and low absorption capacity (PC), toxity and complexity (methanol), high cost (NMP) and so on [37–39].

Some studies showed that the CO_2 solubility in dimethyl carbonate (DMC) whose chemical structure is illustrated in Fig. 1 is about 30% higher than that of PC under the same experimental conditions [36,40]. Moreover, DMC can be solvent to capture CO_2 with the advantage of low viscosity, low corrosive behavior, and friendly impact to the environment [35,41].

In the recent years, ionic liquids (ILs) with a low volatility, high thermal stability, wide liquid range, have been emerging as nonvolatile and reversible absorbents for acid gases capture [9,42,43]. Compared with traditional organic solvents, the nonvolatile and environmentally friendly character gives ILs some advantage to be used to capture CO_2 [44–47]. For example, Brennecke's group [48] studied the behavior of CO_2 in ten imidazolium-based ionic liquids and showed the changing of anion and cation of ILs can affect the CO_2 solubility. Zhang's group [49] studied the CO_2 solubility of in imidazolium-based tetrafluoroborate ILs and showed the CO_2 solubility increases with increasing chain length of alkyl substituents on the imidazolium ring. As expected, the CO_2 solubility in these ILs decreases with increasing temperature and increases with increasing pressure. In addition, the CO_2 solubility can be increased by increasing the alkyl chain length on the cation, as for the solubility in $[BF_4]^-$ anion based ILs increasing in the order: $[Bmim]^+ < [Hmim]^+ < [Omim]^+$. Moreover, the cost of the imidazolium-based ILs is relatively economical by comparison with other kinds of ILs. For these reasons, the ionic liquid $[Omim][BF_4]$ was chosen for CO_2 capture, whose chemical structure is shown in Fig. 2.

Though the DMC has some advantages to capture CO_2 while its high volatility will cause the solvent loss in CO_2 regeneration process (the boiling point of DMC is only about 363.45 K at 1 atm) [50]. As for the ILs, the drawbacks of high cost have limited their large-scale industrial applications [51–53]. Therefore, in order to combine the advantages of organic solvent and the ionic liquids, $[Omim][BF_4]$ was added into DMC to make mixtures as CO_2 absorption solvent. The mixtures can achieve the economical cost, minimize the solvent loss, and get high CO_2 capacity because DMC possesses low price, decreasing the cost of these mixtures, and the ionic liquid provides non-volatility and high CO_2 capacity, decreasing the amount and loss of DMC and increasing the CO_2 solubility in the mixtures. For this purpose, the CO_2 solubility in
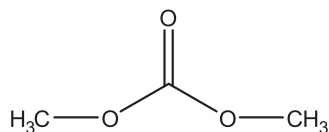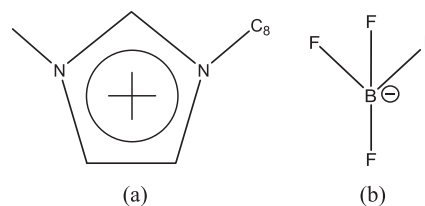

Fig. 2. The chemical structure of ionic liquid $[Omim]^+[BF_4]^-$

these solvents was investigated under isothermal conditions at T = (298.15, 308.15, 318.15 and 328.15) K with the pressures up to about 3.0 MPa because the thermodynamic data are important in predicting the future applications in industry. In addition, COSMO-RS (conductor-like screening for real solvents) have been performed to investigate the Henry's constants and the vapor pressure of DMC in the mixtures.

2. Experimental section

2.1. Materials

CO_2 with a volume fraction of 0.9999 was supplied by BeiWen Gas in Beijing. Diethyl carbonate (DMC) ($C_3H_6O_3$, with a mass fraction of 0.999, made in China) was obtained from Aladdin-Reagent Company in Shanghai. The ionic liquid of 1-octyl-3-methylimidazolium tetrafluoroborate $[Omim][BF_4]$ was obtained from Lanzhou Institute of Chemical Physics (Lanzhou Greenchem ILs, LICP, CAS, China), with a mass fraction purity higher than 99%. Before experiments, $[Omim][BF_4]$ was dried for 24 h under high vacuum at 333.15–338.15 K to remove volatile impurities and traces of water. The water content in $[Omim][BF_4]$ after drying (before solubility experiments) was less than 400 ppm as determined by Karl Fischer titration (SC-6).

2.2. Apparatus and experimental procedures

The constant-volume method was taken to measure the CO_2 solubility in absorption solvents with the experimental apparatus in Fig. 3. The viscosities of the solvents were measured by an automated micro viscometer (Anton Paar AMVn). The details of experimental apparatus and procedure are similar to our previous work [35,36]. In this work, the experiments were finished respectively at 298.15, 308.15, 318.15, and 328.15 K in the equilibrium cell. The equilibrium was considered to be reached when the pressure and temperature kept stable over 20 min in the equilibrium cell. Then, the vapor–liquid phase equilibrium data were calculated from pressure balance. Finally, the amount of CO_2 absorbed in the solvent was calculated using the equation of state by virtue of the difference between the initial and final equilibrium pressure of the two cells.

2.3. Reliability and accuracy of apparatus

In order to verify the reliability of the apparatus used, the CO_2 solubility in DMC in this work was compared to the previous study at same pressures with similar temperatures as shown in Fig. 4, where the x_{exp} represents the experimental solubility in this work, x_{ref} represents the solubility data in reference, and the relative deviation (RD) can be estimated by equation (1).

$$RD = \left(x_{exp} - x_{ref}\right)\Big/x_{exp} \tag{1}$$

The results in Fig. 4 shows the measured data are in good

Fig. 1. The chemical structure of dimethyl carbonate (DMC).