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Kinetics of CO_2 capture by ionic liquid—CO_2 binding organic liquid dual systems

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ABSTRACT

A dual system, which aims to combine the individual advantages of two different solvents, has been developed for CO_2 capture in order to intensify the process by reducing the reboiler duty. The dual system consisted of 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf2N]) and 1.8-diazabicyclo 5.4.0 undec-7-ene (DBU) in 1-hexanol medium and the relevant kinetics were determined by using a stopped flow equipment. Based on pseudo-first-order reaction kinetics of CO_2, the reaction was modeled by a modified termolecular reaction mechanism and rate constants and the activation energies of the [bmim][Tf2N]–DBU system were obtained. In addition, the absorption capacity and the initial absorption rate of the 10 wt% [bmim][Tf2N]-15 wt% DBU dual system were measured in a gas-liquid reactor at 303 K and 2 atm 0.815:1 mol ratio of CO_2:DBU was achieved with this dual system – which approximately doubles the capacity of commercial alkanolamine solutions – and the initial CO_2 absorption rate of the dual system was found to be 3.500×10^{-5} kmol/m^{2}s. Reversibility of dual system was also briefly investigated by using Fourier transform infrared spectrometry.

1. Introduction

Global warming is one of the major problems of the 21st century. The problem arises from the increasing emissions of CO_2 gas due to the increase in intense CO_2 producing industries, such as thermal power plants. There have been many attempts for post combustion capture of CO_2 from the flue gas streams of these industries [1]. Aqueous alkanolamine solutions being the earliest of these systems are still the most preferred method today [2]. However, this method has certain disadvantages such as corrosion, loss of solvent and high regeneration energy requirement [3,4]. Boiling of the solvent during the desorption process is the main reason of this high energy requirement [5]. Therefore any solvent which can be regenerated below its boiling temperature would lead to significant process intensification. To this end, innovative solvent regeneration techniques, such as electrochemically mediated amine regeneration [6] and ultrasonic desorption of CO_2 [7] are currently being developed. However, new nonaqueous solvents or their blends are likely to find applications soon. For instance, Heldebrant et al. have proposed a new class of solvents for CO_2 capture and named them carbon dioxide-binding organic liquids (CO_2BOLs) [8,9]. CO_2BOLs consist of an amidine or a guanidine base and a convenient alcohol (usually linear alcohols) [10]. When a CO_2BOL system reacts with CO_2 it produces alkyl carbonate salts as a product. This product has less hydrogen bond than the product of commercial alkanolamines which results in lower regeneration energy consumption [11,12]. Orhan et al. has confirmed that 10 wt% TMG/1-propanol solution can be regenerated at 70 °C which is far below its boiling temperature [13]. Another advantage of the CO_2BOLs systems is their CO_2 absorption capacity which is superior to alkanolamine solutions. Studies with TMG and DBU show that nearly 1:1 mol CO_2/reactant ratio can be achieved by using CO_2BOLs [14].

Ionic liquids (IL) have also been considered for capturing CO_2 [15]. They are molten salts at room temperatures and consist of organic cations and inorganic anions [16]. Ionic liquids are non-corrosive and most of them have good thermal stability at high temperature and low vapor pressure with tunable properties [17–19]. These properties would prevent the corrosion of the CO_2-capture equipment and reduce the solvent losses [20]. Further, solubility of CO_2 in imidazolium based ionic liquids was found to be very high [21]. However ionic liquids have lower absorption

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Abbreviations: CO_2, Carbon dioxide; CO_2BOLs, carbon dioxide-binding organic liquids; DBU, 1.8-diazabicyclo 5.4.0 undec-7-ene; FTIR, Fourier transform infrared spectroscopy; IL, Ionic liquid; MFC, mass flow controller; MFM, mass flow meter; N_2, Nitrogen; TMG, 1,1,3,3-Tetramethylguanidine; [bmim][Tf2N], 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

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Nomenclature

C^*(kmol/m^3)	Physical solubility of dissolved CO_2
D_C (m^2/s)	Molecular diffusivity of dissolved CO_2
k_0 (s^{-1})	Pseudo first order rate constant
k_1 (m^3/kmols)	Rate constant for termolecular mechanism according to Eq. (2.7)
k_2 (s^{-1})	Rate constant for termolecular mechanism according to Eq. (2.7)
k_3 (m^3/kmols)	Rate constant for termolecular mechanism according to Eq. (2.11)
k_4 (s^{-1})	Rate constant for termolecular mechanism according to Eq. (2.11)
k_{DBU} (m^6/kmol^{2}s)	Rate constant for DBU according to Eq. (2.7)
k_{IL} (m^6/kmol^{2}s)	Rate constant for IL according to Eq. (2.11)
r (kmol/m^3 s)	Specific reaction rate
μS	MicroSiemens

capacity when compare with the alkanolamine solutions [22]. Thus, instead of using an ionic liquid as a single solvent, a solution of an alkanolamine in an IL – rather than water – was suggested [23]. Camper et al. found that a solution of an amine in ionic liquids improved the solvent properties such as absorption capacity and reaction rate [24]. Subsequently, there have been several studies which showed the synergetic effect on CO_2 capture of ionic liquids –amine solutions [25–29].

Despite the fact that research on absorption capacities of the CO_2BOLs has gained much attention in recent years, there are limited studies on the kinetics of these systems in the literature [12–14]. On the other hand, in order to design and control of a CO_2 absorber rationally, availability of the kinetic parameters is essential. Therefore, this study aims to obtain the kinetic parameters of the dual system of [bmim][Tf2N]-DBU – namely rate constants and the activation energies- and also to examine the synergetic effect – if any- of using ionic liquids together with CO_2BOLs. Further, we investigated the absorption capacity, initial absorption rate, desorption temperature and the cyclic behavior of the 10 wt% [bmim][Tf2N]– 15 wt% DBU dual system. [bmim][Tf2N], which is an imidazolium based ionic liquid, was chosen due to its high CO_2 solubility [15].

2. Theoretical

Three applicable reaction mechanisms were proposed to explain the reaction between amines and carbon dioxide which are zwitterion mechanism, base-catalyzed hydration mechanism and termolecular reaction mechanism [30–32].

Crooks and Donnellan have proposed that an amine molecule reacts with both carbon dioxide and a base molecule simultaneously [31]. A carbamate and a protonated base molecule are formed as a result of this reaction. Eq. (2.1) shows a general expression of termolecular reaction mechanism for a secondary amine [33].

$$R_2R_2NH + CO_2 \ldots B \leftrightarrow R_1R_2NCOO^- \ldots BH^+ \tag{2.1}$$

At pseudo first order conditions, the observed rate equation with respect to CO_2 is given below:

$$r = k_o[CO_2] \tag{2.2}$$

In this equation k_o includes all the bases which affect the reaction. For an ionic liquid (IL) and a CO_2 binding organic liquid (CO_2BOL), which are the two components of the dual system in this study, termolecular reaction mechanism can be modified as:

$$k_o = k[IL] + k^*[DBU] + k_{IL}[IL]^2 + k_{DBU}[DBU]^2 + k_{IL-DBU}[IL][DBU] \tag{2.3}$$

For constant ionic liquid concentration, Eq. (2.3) leads to:

$$k_o = [IL](k + k_{IL}[IL]) + [DBU](k^* + k_{IL-DBU}[IL]) + k_{DBU}[DBU]^2 \tag{2.4}$$

$$k_2 = [IL](k + k_{IL}[IL]) \tag{2.5}$$

$$k_1 = k^* + k_{IL-DBU}[IL] \tag{2.6}$$

$$k_o = k_2 + k_1[DBU] + k_{DBU}[DBU]^2 \tag{2.7}$$

On the other hand, for constant DBU concentration, the followings apply:

$$k_o = [DBU](k^* + k_{DBU}[DBU]) + [IL](k + k_{IL-DBU}[DBU]) + k_{IL}[IL]^2 \tag{2.8}$$

$$k_4 = [DBU](k^* + k_{DBU}[DBU]) \tag{2.9}$$

$$k_3 = k + k_{IL-DBU}[DBU] \tag{2.10}$$

$$k_o = k_4 + k_3[IL] + k_{IL}[IL]^2 \tag{2.11}$$

Detailed derivations of these expressions could be found elsewhere [13].

3. Materials and methods

3.1. Materials

DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene (puriss-grade, CAS no. 6674-22-2) with 99% purity, [bmim][Tf2N] 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (CAS no. 174899-83-3) with 98% purity and 1-Hexanol (reagent-grade, CAS no. 111-27-3) with 98% purity were purchased from Sigma-Aldrich. Carbon dioxide gas was supplied by Linde (Germany) with 99.99% purity. No further purification was applied to these chemicals.

3.2. Stopped-flow experiments

The stopped-flow system (Model SF-61SX2, Hi-Tech Scientific, UK) was used for investigating the intrinsic kinetics of the reaction between CO_2 and the dual system. The system consists of a mixing unit and a conductivity detection unit (Model CAK-501, Hi-Tech Scientific, UK). All relevant parts of the equipment were thermostated. A typical output of the stopped-flow run is given in Fig. 1 and other pertinent details can be found elsewhere [13,14].

In order to satisfy the pseudo-first order condition, dual system concentrations were kept in excess of that of dissolved CO_2. Experiments with different concentrations of dual systems with respect to both IL and DBU in 1-hexanol were carried out. First, the effect of DBU concentration on the reaction rate was evaluated by keeping the IL concentration constant while increasing DBU concentration. Second, DBU concentration maintained constant and IL concentration was varied. In order to obtain consistent k_o values, experiments were repeated for 10 times. The observed