



Kinetics of reaction *between* CO₂ and ionic liquid-carbon dioxide binding organic liquid hybrid systems: Analysis of gas-liquid absorption and stopped flow experiments



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HIGHLIGHTS

- For CO₂ capture, novel hybrid solvents – blends of [emim][Tf₂N] with DBU (or TMG) in 1-hexanol – were proposed.
- The absorption capacities and the initial absorption rates have been obtained in a gas-liquid contact reactor at 313 K.
- Reusability and performance were investigated by using FT-IR under sequential absorption-desorption cycles.
- The “intrinsic” reaction rate was measured in a “stopped flow” equipment for a temperature range of 283–303 K.
- k_o (s⁻¹) were compared with two different methods.

ARTICLE INFO

Article history:

Received 22 August 2016

Received in revised form 22 December 2016

Accepted 24 January 2017

Available online 7 February 2017

Keywords:

CO₂ absorption

Ionic liquid

Carbon dioxide binding organic liquid

Hybrid solvents

Stopped-flow

Gas-liquid contact reactor

ABSTRACT

It is generally accepted that CO₂ emissions from point sources – such as thermal power plants – can be controlled by gas-liquid absorption where the process is intensified significantly by introducing a reactant into solvent. In this work, blends of 1-ethyl-3-methyl imidazolium bis (trifluoromethylsulfonyl) imide ([emim][Tf₂N]) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (or 1,1,3,3-tetramethylguanidine (TMG)) in 1-hexanol were studied. Gas absorption experiments were carried out in a gas-liquid mini reactor for the hybrid systems containing different weight concentrations of organic bases while keeping the ionic-liquid weight percentage constant. Total amount of absorbed CO₂ was measured as function of time and the absorption (or loading) capacities and the initial absorption rates have been obtained at 313 K. It was found that increasing the amount of the organic base increased the loading capacity of CO₂. Also, reusability and performance loss of hybrid solutions were investigated by using Fourier transform infrared spectrometry under sequential absorption-desorption cycles. The intrinsic reaction rates were measured in a stopped flow equipment for a temperature range of 283–303 K. The empirical power law reaction orders with respect to DBU and TMG were found to be between 1.0 and 2.0 at different temperatures and the kinetic data could be interpreted satisfactorily by a modified termolecular reaction mechanism.

Finally, the observed reaction rate constants inferred from heterogeneous gas absorption rates – through estimated solubility and diffusivity – were compared with the homogeneous – intrinsic – reaction rate constants obtained by a rapid mixing technique, namely stopped-flow conductimetry. The observed pseudo first order rate constants at 313 K were found to be very similar and the deviations remained within 5–15%. Obtaining relevant data by these two very different techniques in the same laboratory provided pros and cons of each method and clarified – often – biased ambiguities.

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1. Introduction

It is a well-known fact that, as a major greenhouse gas, CO₂ emissions make a significant contribution to global warming and

climate change (McHugh et al., 2015). Therefore, carbon dioxide capture, utilisation and sequestration (CCUS) technologies have gained importance worldwide in recent years (Markewitz et al., 2012). Although various technologies are currently being developed for post combustion carbon dioxide capture (Cuellar-Franca and Azapagic, 2015) it is generally agreed that the most appropriate method is still the selective absorption of carbon dioxide from

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gas mixtures into aqueous amine solutions followed by regeneration of loaded solvent by desorption (Feron, 2016; Li et al., 2016; Liang et al., 2016; Rochelle, 2009). Currently, the benchmark solvent is 30 wt% aqueous monoethanolamine (MEA) even though this solvent has several shortcomings, such as low absorption capacity (maximum 0.5 mol CO₂/mol MEA) and high energy requirement which is around 4 GJ/ton CO₂ (Li et al., 2013). Therefore there is a quest for finding novel solvents – especially organic – which may have both high reaction rate and high loading capacity while exhibiting no or limited corrosion and degradation problems (Budzianowski, 2015; Mumford et al., 2015). Previously, we investigated carbon dioxide binding organic liquids (CO₂BOLs) which are the mixture of a strong amidine or guanidine bases and n-alcohols (Ozturk et al., 2014; Öztürk et al., 2012; Ume et al., 2012; Yuksel Orhan et al., 2015, 2016a, 2016b). The primary advantages of these CO₂BOLs systems are their high CO₂ loading capacities, low specific heat capacities and a less energy intensive solvent regeneration as compared to conventional aqueous alkanolamine solutions. The limited information available about the reaction kinetics of such systems indicates that they have potentials to be a suitable CO₂ capture solvent (Ozturk et al., 2014; Öztürk et al., 2012; Ume et al., 2012; Yuksel Orhan et al., 2015, 2016a, 2016b), especially with the addition of promoters (Orhan and Alper, 2015).

Another potential method is the absorption of CO₂ by certain ionic liquids (ILs) which are composed of big heterocyclic organic cations and various small anions (Zhao et al., 2012). ILs have negligible vapour pressures, high thermal stabilities, and favourable CO₂ solubilities and can remain liquid over a large temperature range with several other tunable physicochemical properties (Earle et al., 2006; Wang et al., 2009). Compared with the conventional amine-based methods, CO₂ capture by ILs have several advantages. For instance, Wang et al. reported that a quarter of the energy of the amine-based method is sufficient for the regeneration of ILs (Wang et al., 2013). Moreover, the specific heat capacity of ILs is only about a third of that of water and it is therefore possible to reduce partially the energy costs. As a major disadvantage, most of the known ILs have high viscosities to the extent that they may not be processed with conventional equipment. For instance, the viscosity of [bmim][BF₄] at 33 °C is 79.5 cP which is 40 times higher than that of an aqueous solution of 30% MEA (2 cP) (Iliuta et al., 2014; Sanchez et al., 2007). The viscosity of ILs is thought to be determined by van der Waal forces and hydrogen bonding. However, by selecting an appropriate anion-cation combination the viscosity can be brought to a range of 30–50 cP (Hasib-ur-Rahman et al., 2010). In this respect, it was reported that the viscosity of imidazolium based cations depends on both the length of alkyl chain and the nature of anion. This is due to increased van der Waal interactions upon increasing alkyl chain length as shown in Table 1. In order to overcome viscosity related

problems ILs are often mixed with water or other ordinary solvents such as alcohols (Carvalho et al., 2009).

Theoretical simulations and the experimental works showed that CO₂ is more soluble in certain imidazolium based ILs (see Table 2) (Cadena et al., 2004). It is seen that ILs containing fluor in their anions have increased CO₂ binding. Unfortunately, their viscosities also increase significantly (Baltus et al., 2004; Hou and Baltus, 2007; Palgunadi et al., 2009; Shiflett and Yokozeki, 2005; Shin and Lee, 2008).

As seen from Table 2, CO₂ solubilities in certain ILs are high, however low CO₂ absorption rate of ordinary ionic liquids restricts their usage as a single solvent (Ozkutlu et al., 2016b).

In order to increase both the capacity and the reaction rate, ionic liquids have been functionalised by certain amine groups but such solvents had viscosity problems upon CO₂ loading (Gurkan et al., 2010). Another approach is to use ionic liquids together with common alkanolamines (Camper et al., 2008; Ozkutlu et al., 2016b). For instance, Ahmady et al. have studied the kinetics of CO₂ absorption into aqueous MDEA/[bmim][BF₄] solutions and found that the addition of an IL significantly decreased the activation energy (Ahmady et al., 2012). Lu et al. have studied the CO₂ absorption performance of aqueous MEA/[bmim][BF₄] solutions where they observed that the hybrid system shows higher absorption capacity than the pure MEA solution. Also they investigated the cyclic regeneration behaviour of the hybrid system and found that the addition of IL resulted with high thermal stability (Lu et al., 2012). Recently, Ozkutlu et al. studied an organic solvent consisting DEA/[bmim][Tf₂N] in n-hexanol to provide a dual solvent with high absorption capacity and low regeneration energy in addition to decreased corrosion (Ozkutlu et al., 2016b).

The hybrid solvent system consisting of an IL and a CO₂BOL – which is amidine or guanidine based – has not yet been investigated even though their molecular structures are opportune to design by attachment of functional groups (Yuksel Orhan et al., 2016a, 2016b). In this study, because of the most appropriate properties, such as low viscosity and the high CO₂ solubility (see Tables 1 and 2) – as well as availability – an imidazolium based ionic liquid (1-ethyl-3-methyl imidazolium bis (trifluoromethylsulfonyl) imide ([emim][Tf₂N]) was selected and blended with an amidine (DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or a guanidine (TMG (1,1,3,3-tetramethylguanidine) in 1-hexanol.

The guideline about effectively screening solvents needs basically three data, namely, CO₂ absorption capacity (or equilibrium solubility), reaction kinetics and heat of CO₂ absorption. The primary aim of this work is to investigate the potentials of IL-CO₂BOL hybrid solvent systems for CO₂ capture by obtaining absorption capacities and kinetics data. The latter will be obtained by both gas absorption and rapid mixing experiments. Reaction kinetics data obtained by these two very different techniques in

Table 1
Viscosity and density data for various ionic liquids.

Abbreviation	Temperature (°C)	Viscosity (cP)	Ref.	Density (g/cm ³)	Ref.
[emim][BF ₄]	25	43	McEwen et al. (1999)	1.29	Arshad (2009)
[emim][PF ₆]	70	23.4	Seddon et al. (2000)	–	–
[emim][Tf ₂ N]	25	32.6	McEwen et al. (1999)	1.51	Bonhote et al. (1996)
[emim][OTf]	20	50	Seddon et al. (2000)	1.39	Bonhote et al. (1996)
[bmim][PF ₆]	25	450	Huddleston et al. (2001)	1.36	Huddleston et al. (2001)
[bmim]Cl	50	1534	Seddon et al. (2000)	1.08	Huddleston et al. (2001)
[bmim][BF ₄]	25	219	Huddleston et al. (2001)	1.17	Suarez et al. (1998)
[bmim][I]	25	1110	Huddleston et al. (2001)	1.44	Huddleston et al. (2001)
[bmim][Tf ₂ N]	25	69	Huddleston et al. (2001)	1.43	Huddleston et al. (2001)
[hmim][PF ₆]	25	585	Huddleston et al. (2001)	1.29	Huddleston et al. (2001)
[hmim]Cl	25	716	Huddleston et al. (2001)	1.03	Huddleston et al. (2001)
[hmim][BF ₄]	20	314	Seddon et al. (2000)	1.15	Seddon et al. (2000)
[omim]Cl	25	337	Huddleston et al. (2001)	1.00	Huddleston et al. (2001)
[omim][PF ₆]	25	682	Huddleston et al. (2001)	1.22	Huddleston et al. (2001)

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