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Review

Comparative study of CO_2 absorption in packed column using imidazolium based ionic liquids and MEA solution

R. Krupiczka, A. Rotkegel *, Z. Ziobrowski

Instytut Inżynierii Chemicznej Polskiej Akademii Nauk, Gliwice, Poland

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ABSTRACT

The comparative study of CO_2 absorption in ionic liquids: [Emim][Ac], [Bmim][Ac] and 15% MEA solution in packed bed column is presented. Investigations were performed for low pressures, what is important in the case of post combustion flue gases. Absorption column (0.3 m length, inner diameter 0.05 m) was filled with Raschig rings $\phi 5 \times 5 \times 1$ mm. The influence of initial CO_2 concentration, absorption temperature, gas and liquid flow direction on removal efficiency was investigated. Experiments were compared with calculation based upon resistance in series model of the absorption process in packed column taking into account enhancement factor of reaction between CO_2 and investigated liquids. The results show that in the same experimental conditions ILs have comparable CO_2 absorption capacities with MEA solution. However ILs need much longer times to absorb the same amount of carbon dioxide from gas mixture. The research for new ILs with lower viscosity and price is needed to take advantages of ionic liquids for the process of CO_2 stripping in packed column.

Contents

1. Introduction

The growth in worldwide carbon dioxide emission from utilization of fossil fuels is predicted to 40.2 GT by the year 2030 [1]. Therefore, developing technologies for efficient capture and sequestration of large quantities of CO_2 becomes an important issue [2,3].

A number of CO_2 capture technologies being used on laboratory scale or industrially are processes based on physisorption or chemisorption [4,5], membrane separation [6], molecular sieves [7], carbamation [8], amine physical adsorption [9], amine dry scrubbing [10], mineral carbonation [11,12] and absorption in ILs [13–16].

Using aqueous amine solutions – MEA (monoethanolamine), DEA (diethanolamine), MDEA (methyldiethanolamine) – in scrubbing processes as the chemisorptions medium for CO_2 capture is one of the most widespread techniques in industry [17,18]. Drawbacks being reproached are: insufficient CO_2 capture capacity, high solvent losses caused by evaporation, degradation and poor thermal stability, as well as the equipment corrosion [3,16,19–22]. The regeneration step may increase the total operating costs of the capture plant up to 70% [23], especially for primary and tertiary amines where the heat of reaction is quite high [24,25].

To overcome these problems, ionic liquids (ILs) can be an alternative option [2]. They are defined as fluids, which contain only anions and cations and have a melting point below 100 °C [26,27].

The special properties of ionic liquids: broad liquid range, thermal stability, negligible vapor pressure, tunable physicochemical character and high CO_2 solubility, more environmentally friendly

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* Corresponding author.
E-mail address: arot@iich.gliwice.pl (A. Rotkegel).

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Nomenclature

A	column fixed bed area (m^2)
a	specific packing area ($m^2\ m^{-3}$)
C	concentration of CO_2 in gas phase
D	diffusivity ($m^2\ s^{-1}$)
E	enhancement factor
F	cross-section column area (m^2)
G_L	total mass of the liquid (kmol)
H	Henry's law constant
h	column length (m)
Ha	Hatta number
k	mass transfer coefficient (kmol $m^{-2}\ s^{-1}$)
k_{CF}	reaction rate constant ($kmol^{-1}\ s^{-1}$)
K_{ov}	overall mass transfer coefficient (kmol $m^{-2}\ s^{-1}$)
N_{CO_2}	absorption flux of CO_2 (kmol $m^{-2}\ s^{-1}$)
r	reaction rate (kmol s^{-1})
Re	Reynolds number
s	absorption capacity
Sc	Schmidt number
Sh	Sherwood number
T	temperature (°C)
V	flow rate (kmol s^{-1})
x	liquid molar fraction
y	gas molar fraction

Greek letters

α	loading ratio
δ	film thickness (m)
ε	bed porosity
$\Delta\pi$	mass transfer driving force
η	viscosity (Pa s)
τ	time (s)
ϑ_z	equivalent linear dimension (m)

Subscripts

CO_2	carbon dioxide
G	gas
i	inert
in	column inlet
L	liquid
out	column outlet

Superscripts

$*$	equilibrium

character [16,28–33] make them attractive for an application as reversible CO_2 capture absorbents. Thus far, some ILs (especially imidazolium based) have diminished corrosion of the equipment, and the heat capacity of IL is almost one-third of that of aqueous systems, which may have profound effect in reducing the high investment and operation cost [13,15]. An important drawback in the case of ILs is their high viscosity. However, by choosing an appropriate combination of cation and anion, the viscosities can be adjusted.

In 2002 Bates et al. proposed the use of an amine functionalized task specific ionic liquid (TSIL) for CO_2 separation [34]. The loading capacity was similar to a MEA solution, while the main drawback was the increased viscosity compared to other ILs. These investigations were supported by Bara et al. in 2009 [35]. The solubility of CO_2 in a series of imidazolium based ILs at low pressure has been determined by Baltus et al. [36]. It was found to increase with the length of the alkyl side chain on the imidazolium ring. The CO_2 solubility is greater in ionic liquids with Tf_2N^- anions than that in ILs with PF_6^- anions. Anderson et al. [37] measured the solubility of CO_2, C_2H_4, C_2H_6, CH_4, O_2 and N_2 in [C_6mpy][Tf_2N], they found this IL as a potential CO_2 absorbent with high selectivity. Camper et al. decided to use additives to improve CO_2 absorption ability. They mix MEA with [Bmim][Tf_2N] in a 1:1 mol ratio and observed increased loading capacities, while an insoluble carbamate salt was formed [38]. Wang et al. [39] found the formation of carboxylate at the imidazolium ring. The carboxylate formation was also found by Maginn et al. Instead of adding a superbase to the IL, they just used an ionic liquid containing an acetate anion [40]. Shiflett et al. showed that the absorption abilities depend strongly on the anion. They compared the CO_2-loading capacities of imidazolium based ionic liquids with an $[Emim]^+$ cation combined with an acetate anion respectively trifluoroacetate anion [41].

In order to develop new technologies using ionic liquids for carbon dioxide capture a significant research work has been carried involving room temperature (RTIL), task-specific (TSIL), supported membranes (SILM), polymerized (PIL) [42–45] ionic liquids. The thermophysical properties of ILs (density, viscosity and surface tension) as well as the effects of cation and anion of ILs on CO_2 solubility and their properties have been extensively studied. With respect to energy consumption and process simulation for a CO_2 separation process using ILs as liquid absorbent, Shiflett et al. [15,46] evaluated the performance of [Bmim][Ac] and compared with the MEA technology. Basha et al. [47,48] developed a conceptual process for CO_2 capture from the fuel gas streams produced in a 400 MWe IGCC power plant, in which [Bmim][Tf_2N] and two TEGO ILs (compound mixtures supplied by Evonik-Degussa GmbH Co., Hopewell, VA, USA) were used as liquid absorbents. Their results showed that the studied ILs can be used as a physical solvent for CO_2 capture. Huang et al. [49] compared the IL-MEA and MEA processes and found that the IL-MEA process saves 15% regeneration heat duty compared to the MEA process. In order to analyze the energy consumption for a CO_2 separation process, enthalpy is one of the most important properties [28,50–52]. Research continues to develop the most economical and efficient technologies in this regard.

Using ionic liquids with a dominant physical absorption mechanism leads to low loading capacities compared to MEA solutions [53] but also to easier desorption process [54–58]. The chemical absorption of CO_2 in ionic liquids containing a carboxylic anion can be a alternative to common amine scrubbing processes to overcome their disadvantages [2,59–61].

At present, the lack of availability of inexpensive ionic liquids is the major obstacle in employing ionic liquid systems for CO_2 capture on large scales [6]. Mass production of ionic liquids, and also increased stability, low corrosion of equipment may decrease the ionic liquids based CO_2 capture system price.

Up to now, some research in CO_2 solubility in [$C_n$mim][Ac] was performed at laboratory scale [13,15,62–64]. [Emim][Ac] is a promising ionic liquid for CO_2 absorption. Furthermore, its CO_2 absorption ability can be improved by adding 20 wt.% of DBU (1,8-diazabicycloundec-7-ene) [2]. Simulation results of carbon dioxide capture from post-combustion flue gas using [Emim][Ac] show lower energy requirements and higher investments cost of IL-based process compared to MEA-based process [64]. Focusing on a high pressure application, as it is the case for natural gas treatment Shiflett et al. calculated that a process based on [Bmim][Ac] can replace a MEA-based scrubbing system in a coal