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Non-dispersive absorption of CO_2 in [emim][$EtSO_4$] and [emim][Ac]: Temperature influence

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ABSTRACT

Post-combustion capture based on amines is conventionally used for carbon dioxide separation. Ionic liquids have emerged as new attractive alternative solvents because of their zero emission features compared to amines. The aim of the present work is to study the temperature influence on the efficiency in order to evaluate physical and chemical absorption using two ionic liquids, 1-Ethyl-3-methylimidazolium ethylsulfate [emim][$EtSO_4$], and 1-Ethyl-3-methylimidazolium acetate [emim][Ac]. The temperature ranges from room temperature to 333 K. A polypropylene hollow fiber module is the membrane device where the CO_2 absorption takes place. The CO_2 removal efficiency was obtained from experimental data, showing a temperature dependence only in the case of using [emim][Ac] which doubles from 291 K to 318 K (16–34% for one contactor and 27–53% when two contactors were operated in series). The behavior of [emim][Ac] was correlated with the mass transfer enhanced by the chemical reaction. When [emim][$EtSO_4$] is used, the efficiency is not influenced by the temperature and only the solubility controlled the mass transfer in the liquid phase.

1. Introduction

Carbon dioxide is one of the major contributors to climate change. The CO_2 capture and sequestration (CCS) is a major concern globally today to reduce the impact on the atmosphere and protect humans against the risks associated with CO_2 pollution. A wide range of technologies exist for CCS based on physical and chemical processes including absorption, adsorption, membranes and cryogenics [1].

Three main methods can be identified on the capture of CO_2: pre-combustion, post-combustion and oxy-combustion [2]. The present work is focused on post-combustion capture. This process route is ideally suitable for conventional power stations and energy conversion systems. CO_2 at low partial pressure is separated from the gas stream after the fuel has been burned completely [3]. The flue gas from a typical post-combustion process is composed by 10–15% CO_2, 70–75% N_2 and lower concentrations of other components. The temperature reached in this type of system is between 313 and 348 K [4].

Traditionally, amines have been used for capture due to their high reactivity to CO_2 forming complexes with weak chemical bonds and low cost achieving an outlet stream of very low CO_2 concentration [5]. The development of more beneficial solvents for the environment is a topic of great current interest.

The CO_2 capture processes on an industrial scale are usually carried out in packed or spray towers. In recent years, an intensification process has been proposed that replaces the equipment for a membrane device [6]. Hollow fiber membrane contactors have many advantages: controlled interfacial area, independent control of gas and liquid flow rates, reduction in solvent losses, much larger contact area per unit volume compared to tray and/or packed columns and no dispersion from one phase into another [7–9]. Different kinds of membrane materials are under research. The most common ones are polypropylene (PP) [5,10–13] and polyvinylidene fluoride (PVDF) [10,14,15]. Generally the membrane equipment operates with gas and liquid flowing on opposite sides of the membrane in parallel configuration [6] but sometimes the cross flow configuration is used [11].

The PP membranes have often been used in membrane contactors due to their low cost, hydrophobicity and commercial availability [16]. This type of asymmetric membranes provides also a great advantage because of their inability to dissolve in common solvents at low temperatures [17].

Ionic liquids (ILs) are compounds that have been considered in the last few years as solvents for CO_2 gas recovery [5]. ILs are salts that have an organic cation and an inorganic anion whose melting point is lower than 373 K and the vapor pressure is negligible

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Nomenclature

A	effective membrane area (m^2)
D	diffusivity ($m^2\ s^{-1}$)
d_{cont}	diameter of the contactor (m)
d_h	hydraulic diameter (m)
d_i	inside diameter of the fiber (m)
d_{lm}	log mean diameter of the fiber
d_o	outside diameter of the fiber (m)
E_a	enhancement factor
H_d	Henry's law constant
k_g	mass transfer coefficient in the gas phase (ms^{-1})
k_l	mass transfer coefficient in the liquid phase (ms^{-1})
k_{mg}	mass transfer coefficient of the membrane (ms^{-1})
$K_{overall}$	mass transfer coefficient (ms^{-1})
L	fiber length (m)
n	number of fibers
N_{CO2}	absorption flux of sulfur dioxide ($mol\ m^2\ s^{-1}$)
P_T	total pressure (bar)
Q	flow rate ($m^3\ s^{-1}$)
R	ideal gas constant ($bar\ L\ mol^{-1}\ K^{-1}$)
Re	Reynolds number
R_g	resistance in the gas side (sm^{-1})
R_l	resistance in the liquid side (sm^{-1})
R_{mg}	gas filled membrane resistance (sm^{-1})
R_{ml}	liquid filled membrane resistance (sm^{-1})
$R_{overall}$	overall resistance to mass transfer (experimentally obtained) (sm^{-1})
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
T	temperature (K)
v	velocity (ms^{-1})
x	liquid molar fraction
y	gas molar fraction

Subscripts

g	gas
l	liquid
in	inlet of the contactor
out	outlet of the contactor

Greek letters

δ	membrane thickness (m)
ε	porosity of the membrane
μ	viscosity (cP)
τ	tortuosity
ρ	density ($kg\ m^{-3}$)
φ	packing factor

[18,19]. An important feature of ILs for potential use in industrial gas treating processes is the knowledge of the solubility and the diffusion coefficients of gases at various temperatures and pressures [20]. Commonly, the CO_2 absorption in the non-functionalized IL occurs through physisorption [21]. However, some ILs are able of forming chemical complexes with CO_2 [22]. The chemisorption of CO_2 in ionic liquids containing a carboxylic anion can be a promising alternative to common amine processes [23]. For this reason the 1-Ethyl-3-methylimidazolium acetate [emim][Ac] is an ideal candidate for CO_2 capture. An inexpensive and green solvent for petrochemical applications are important features to consider when choosing an ionic liquid for CO_2 absorption. The 1-Ethyl-3-methylimidazolium ethylsulfate [emim][$EtSO_4$] meets these features [24].

The mass transfer behavior for gas absorption into different absorbents liquids appears to be important for the process design. Some studies are reported for different hollow fiber membrane contactor [25], but there is a lack of data for the temperature influence, that is the aim of the present work in order to analyze the relevance of the temperature variable in the removal process efficiency.

The study of the temperature effect in the non-dispersive absorption of CO_2 was carried out in a polypropylene hollow fiber membrane contactor using two different ionic liquids [emim][Ac] and [emim][$EtSO_4$].

2. Experimental

2.1. Materials

A polypropylene hollow fiber membrane contactor in parallel configuration was supplied by Liquicel-Membrane Contactors (USA). The main characteristics of this system are shown in Table 1. Carbon dioxide 99.7 ± 0.01 vol.% and pure nitrogen 99.999 ± 0.001 vol.% were purchased from Air Liquide (Spain). The ionic liquids were supplied by Sigma Aldrich. The 1-Ethyl-3-methylimidazolium ethylsulfate [emim][$EtSO_4$] (⩾95%) was used as absorption liquid due to its low viscosity, low toxicity and low cost [26]. On the other hand, the 1-Ethyl-3-methylimidazolium acetate [emim][Ac] (⩾90%) was chosen because of its high CO_2 solubility. To ensure that the ionic liquid is suitable for our process despite its relatively low purity, solubility rates were measured and, compared with literature data, similar values were obtained [27,28].

2.2. Methods

The experimental setup is shown in Fig. 1. The feed gas mixture stream contains 15 vol.% CO_2 and N_2 (rest to balance) and it was adjusted by means of a mass flow controller (Brook instrument MFC 5850, Emerson Process Management Spain) that flows through the inside of the hollow fibers. The liquid absorbent flows counter-currently in a closed circuit through the shell side. The ILs were pumped from the storage tank. Control and measurement in the liquid line (50 mL min^{-1}) was carried out with a digital gear pump (Cole Parmer Instrument Company, Hucoa-Erloss SA, Spain). The liquid storage tank was kept under isothermal conditions

Table 1
Hollow fiber membrane contactor characteristics.

Membrane material	Polypropylene
Fiber o.d. d_o (m)	3×10^{-4}
Fiber i.d. d_i (m)	2.2×10^{-4}
Fiber length, L (m)	0.115
Number of fibers, n	2300
Effective inner membrane area, A (m^2)	0.18
Membrane thickness, δ (m)	0.4×10^{-4}
Membrane pore diameter, dp (μm)	0.04
Porosity (%)	40
Packing factor	0.39
Tortuosity[a]	2.50

[a] Assumed as $1/\varepsilon$.