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From kinetics to equilibrium control in CO_2 capture columns using Encapsulated Ionic Liquids (ENILs)

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HIGHLIGHTS

- ILs with high viscosity values gets worse absorbent performance and CO_2 recovery.
- ENIL materials overcome the mass transfer constrains in CO_2 absorption by ILs.
- ENIL morphology increases the contact area of the neat IL.
- ENIL tests in fixed bed demonstrate the equilibrium control in CO_2 capture.

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ABSTRACT

A novel approach based on Encapsulated Ionic Liquids (ENILs) is proposed for overcoming the mass transfer constraints in CO_2 physical absorption by ILs. Absorption process simulation using COSMO-based/Aspen Plus methodology -an a priori approach- was carried to select four ILs with high and similar CO_2 absorption capacity but markedly different transport properties: EmimTCM, BmimTCM, BmimDCN, and $BmimOcSO_4$. Simulations using equilibrium- and rate-based column models for these ILs showed that CO_2 recovery and the absorbent performance are severely reduced when the viscosity of the IL increases. Experimental gravimetric analyses with the selected ILs confirmed the large differences in solubility and absorption rate, this last also dependent on viscosity. ENILs were prepared by encapsulation of ILs in hollow carbon sub-microcapsules with a porous shell. The experimental gravimetric analysis evidenced that the ILs maintain their CO_2 absorption capacity after encapsulation, whereas the absorption rate is ca. 50 times higher for ENILs than neat ILs. ENIL tests in fixed bed operation at different operating conditions yielded bed utilization values dependent on the CO_2 solubility in the ENIL, while equivalent mass transfer zone lengths were obtained for all the materials. The results demonstrate the fast CO_2 mass transfer rates in ENILs -related to the high contact area provided- allows overcoming the mass transfer limitations controlling the CO_2 rate of physical absorption by ILs.

1. Introduction

The greenhouse effect and global warming caused by CO_2 have become serious environmental concerns and have awakened the population attention [1]. One of the most promising methodologies for limiting the global warming effects caused by greenhouse gases consists on the direct physical or chemical absorption of CO_2 from post-combustion streams due to their efficiency and lower cost [2,3]. Regarding physical absorption, solvents such as Purisol [4], Rectisol [5] and Selexol [6], among others, are used to capture CO_2 working at high pressure. However, they present problems such as corrosive nature, toxicity and high volatility resulting in high solvent losses [3]. On the other hand, amines [7] are widely used in chemical absorption processes [8], but they present degradation and corrosivity, resulting in high solvent losses, environmental impact and substantial maintenance costs [9].

Therefore, there is a demand for innovative and cost-effective technologies capable of efficiently capturing CO_2, overcoming these problems of commercially available systems. In this sense, ILs are presented as promising novel solvents, which have attracted growing interests as shown by the number of studies on CO_2 capture [10]. The advantages of using ILs as absorbents are their high and tailorable absorption capacity, low vapor pressure and high thermal stability. However, they present some disadvantages such as: high price,

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environmental-concerns and limitations in their transport properties. The high viscosity of ILs is probably the main technical limitation for their practical application [11], which can even increase in some cases due to the dissolution of CO_2 [12]. In fact, recent process simulation analyses have demonstrated that the efficiency of CO_2 capture by physical absorption in packed columns is severely reduced by the strong kinetic control of the operation, obtaining CO_2 recoveries significantly lower than those expected from the high absorption capacities of ILs [13]. Therefore, modifications of neat ILs may be necessary before they can be widely accepted for CO_2 separation [14].

The Encapsulated Ionic Liquid (ENIL) concept has been proposed as a promising alternative to overcome the mass transfer rate limitations of separation process based on ILs [15]. ENILs consist of hollow carbonaceous sub-microcapsules (C_{cap}) filled with ILs [16]. The synthesis of ENILs is favored by the high affinity between ILs and porous carbons [17]. The ENILs can be prepared with a high proportion of IL (75–85% in weight) and small capsule size (500–700 nm). Therefore, the ENIL material involves a change from continuous to discrete IL phase with submicrometric drop size. Due to ENIL morphology, the specific contact area is drastically increased with respect to the neat IL, enhancing the rate of mass transfer phenomena but maintaining the properties of the ILs as solvents [15]. This novel approach, based on ENIL materials has been successfully applied to NH_3 separation [18] and CO_2 capture based on chemical absorbents as acetate-based ILs [19]. Recently, ENIL systems were also efficiently applied in CO_2 capture by physical absorption with ILs [20]. From an economical point of view, ENIL materials would not only improved the mass transport properties, but also enhance the regeneration step and take advantage from the amount of IL used, becoming a more effective material than neat ILs.

On the other hand, the evaluation of IL performance in practical applications at industrial scale is a key issue in the development of new separation processes based on ILs [21]. In the last years, our group has developed the COSMO-based/Aspen Plus multiscale methodology – based on integrating molecular and process simulation tools- of great utility in the preliminary: i) selection of ILs attending to thermodynamic, kinetic, technical or economical criteria; and ii) viability analysis of the proposed IL-based process and comparison to available technologies [22]. COSMO-based/Aspen methodology has been tested in the study of IL regeneration by distillation [23] and in toluene [24] and acetylene [25] absorption. In addition, it was applied to aromatic-aliphatic separation by liquid-liquid extraction [26] or by extractive distillation [27], CO_2 capture by physical absorption [13] and absorption refrigeration cycles based on ILs [28]. Since COSMO-based/Aspen methodology is an *a priori* approach, which does not require experimentation, process simulations can also be an alternative or a previous step to the experimentation, with the aim of reducing and focusing the number of ILs studied and, thereby, minimizing the consumption of resources in experimental work.

The objective of this work is to evaluate the potential application of ENIL materials in the capture of CO_2 by physical absorption with ILs. For this purpose, unfavorable conditions from the kinetic point of view were selected, i.e. postcombustion processes (10–13% CO_2 concentrations). Firstly, process simulations using COSMO-based/Aspen Plus methodology are carried out to evaluate the behavior of a large set of ILs in the physical absorption of CO_2 in commercial packed columns. From this theoretical analysis, a selection of 4 ILs with similar absorption capacities (provided by equilibrium-based column model) and markedly different kinetic behavior (provided by the Rated-Based column model) is made. The reason to select ILs providing different absorption rates is to analyze if the encapsulation in ENILs maintain the CO_2 absorption capacity of ILs and also improves the kinetics of the CO_2 uptake. The ILs selected were characterized using a high-pressure microbalance to obtain CO_2 absorption capacities and CO_2 diffusion values at three temperatures and pressures (301–333 K and 1–6 bar). The next step is the synthesis and characterization of ENIL materials using the previously selected ILs. The ENIL were tested in gravimetric essays to analyze their CO_2 sorption capacity and rate. Finally, fixed-bed sorption experiments were carried out at temperatures from 303 to 333 K and 0.1 bar CO_2, in order to evaluate if the application of the proposed approach based on ENIL systems allows overcoming the mass transfer rate limitations of the CO_2 physical absorption by the free ILs.

2. Experimental section

2.1. Materials

The ILs 1-butyl-3-methylimidazolium dicyanamide (95%) BmimDCN, 1-butyl-3-methylimidazolium tricyanomethanide (95%) BmimTCM and 1-ethyl-3-methylimidazolium tricyanomethanide (95%) EmimTCM were purchased from Iolitec and 1-butyl-3-methylimidazolium octylsulfate (95%) $BmimOcSO_4$ from Sigma-Aldrich. The synthesis of the hollow sub-microcapsules was carried out using phenol (99%), paraformaldehyde (95–100%), aluminum trichloride (95–100%), ammonia (34%) and absolute ethanol supplied by Panreac. Tetraethylorthosilicate (98%) (TEOS), hexadecyltrimethoxysilane (90%) (C16TMS) and hydrofluoric acid (48%) were supplied by Sigma-Aldrich. Carbon dioxide, nitrogen, and helium were supplied by Praxair, Inc., with a minimum purity of 99.999%. Furthermore, a mixture containing 10,000 ppmv of carbon dioxide in nitrogen was supplied by Praxair, Inc and used in fixed bed capture experiments.

Before the absorption experiments, all the ILs and ENIL materials used were dried and degassed at 333 K under vacuum (10^{-3} mbar) during 24 h to ensure a water content lower than 200 ppm.

2.2. ENIL preparation and characterization

The hollow sub-microcapsules (C_{Cap}) synthesized for their use as ENIL support were prepared following the methodology reported by our group in previous works [16,18,19] and based on the procedure described by Büchel et al. [29]. In summary, C_{Cap} were prepared by a templating method using an aluminosilicate template formed by a solid core and a mesoporous shell. A phenolic resin was infiltrated into the template to serve as a carbon precursor. Then, the infiltrated template was subjected to pyrolysis at 700 °C during 5 h and the template was removed using HF.

The ENIL materials were prepared by incipient wetness impregnation of 100 mg of C_{Cap} with 1 mL of an IL-acetone solution. The solution was added dropwise onto the support. After impregnation acetone was removed by evaporation at 333 K during 24 h. In the current work, the four ENIL tested were prepared with an IL nominal load of 80%w/w. The amount of IL incorporated was checked by elemental analysis. This methodology was successfully applied in our previous publications allowing a homogeneous distribution of the IL inside the C_{Cap} [18,19].

The CHN content of the hollow sub-microcapsules and ENIL materials were characterized by elemental analysis in a LECO CHNS-932 apparatus. The IL amount loaded into the spheres could be calculated by this characterization essay. Then, the porous texture of the carbon material was characterized by 77 K N_2 adsorption/desorption in a TriStar II 3020 (Micromeritics) system after 12 h of degassing at 0.1 mbar and 393 K. The surface area was calculated by using the BET equation. The microstructure and morphology of C_{Cap} and ENILs were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM analyses were performed with a Hitachi S-3000N apparatus and TEM images were obtained in Philips 420, JEM-2000 FX and JEM-4000 EX microscopes.

2.3. Gravimetric CO_2 absorption measurements

The measurements of CO_2 solubility (mg CO_2/g IL) in ILs and ENILs were performed in a gravimetric high-pressure sorption analyzer (ISOSORP GAS LP-flow, Rubotherm) equipped with a magnetic suspension balance (MSB). The balance covers a weight range up to 10 g,