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Effect of water activity on carbon dioxide transport in cholinium-based ionic liquids with carbonic anhydrase

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ABSTRACT

The present work reports a study of the affinity of carbon dioxide towards biocompatible cholinium-based ionic liquids, aiming the development of a sustainable process for carbon dioxide removal. Moreover, the enhancement on carbon dioxide transport by the addition of carbonic anhydrase, able to catalyze the reversible reaction of carbon dioxide with water, is also evaluated.

Cholinium acetate, cholinium propionate and cholinium hexanoate were the selected ionic liquids for this study. Carbon dioxide solubility and diffusion coefficients were determined in the three cholinium ionic liquids, at different water activities, in order to identify optimal conditions for the enzyme activity and stability. A carbon dioxide diffusion coefficient correlation for the cholinium-based ionic liquids with different water activities is proposed, allowing for estimation of carbon dioxide diffusion coefficients.

The results obtained show that the selected cholinium-based ionic liquids possess high affinity towards carbon dioxide, when compared with most used room temperature ionic liquids. Also, it was demonstrated that a small amount of the carbonic anhydrase (0.1 mgCA/gIL) promotes an enhancement of 63% on the carbon dioxide transport rate, for cholinium propionate with a water activity of 0.753.

1. Introduction

Conventional technologies for carbon dioxide capture from flue gas streams are based on absorption in amine solutions. Although amines are widely used due to their high affinity towards carbon dioxide, they present several limitations, such as high volatility, which is an extremely difficult issue to handle in high temperature processes, corrosive nature, high operational cost and environmental impact. In order to overcome these drawbacks, ionic liquids have been proposed as very promising substitutes of traditional organic absorbents [1]. Their unique properties, such as high thermal stability, non-volatility, solvation capability, no flammability and easy operation at liquid state, confer them the possibility to be used in a wide range of processes [2,3]. Furthermore, in the last decade, a new class of ionic liquids has emerged, the biocompatible and environmental-friendly ionic liquids. They are synthesized using naturally-derived materials, such as sugars and aminoacids, are economically attractive and environmental-friendly [4–6]. This new class of ionic liquids may provide an optimum media to stabilize proteins (e.g. enzymes), allowing replacement of traditional hazardous solvents used for stabilization and purification processes, possess potential to be used in biomedical devices [7]. As an example of biocompatible ionic liquids are those based on the cholinium cation. Studies on cholinium-based ionic liquids toxicity [8,9] have shown that the cholinium cation, which is a quaternary ammonium cation ([*N*,*N*,*N*-trimethylethanolammonium]$^+$), recognized as an essential nutrient totally derived from natural products [10], combined with a range of alkanoate anions or amino acids, may provide a media where living cells can actively grow. This demonstrates that, these ionic liquids are biocompatible, which is a feature required for biomedical applications [9,11].

The present work focuses on the study of carbon dioxide transport using cholinium-based ionic liquids combined with carboxylate anions derived from weak carboxylic acids which, according to the literature, can provide high carbon dioxide solubility [12–15]. It has been reported that carbon dioxide absorption is strongly dependent on the nature of the anion, while the nature of the cation has a decisive role in toxicity [9,16,17]. The present work reports a study about the affinity of cholinium-based ionic liquids towards carbon dioxide, using different anions, selected

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according to their chain length. It is also proposed the use of an enzyme, the carbonic anhydrase (CA), which is able to catalyze the reversible reaction of carbon dioxide with water to produce bicarbonate. The addition of this enzyme to the cholinium ionic liquids will enhance the carbon dioxide transport rate, due to the simultaneous absorption and reaction mechanisms. Furthermore, the hydrophilic character of these ionic liquids plays an important role in the catalytic reaction [18,19]. Biocatalysis in ionic liquids has attracted much attention in the last two decades. Up to the present, catalytic processes with lipases have benefited most from the use of ionic liquids as green solvents [20–22]. Nevertheless, there are several publications describing the use of CA with aqueous solutions of amines [23–29]. Despite of the carbon dioxide capture enhancement in the aqueous amine solutions due to the presence of the CA, this strategy does not overcome the drawbacks associated to the use of amine solutions.

As this work involves a completely biocompatible system, studies of pure gases absorption in the different cholinium-based ionic liquids in the absence of CA and with a low quantity of CA (0.1 mgCA/gIL), were also performed with xenon, oxygen and nitrogen, aiming the evaluation of this system for removal of carbon dioxide from anaesthetic circuits, when anaesthesia with assisted ventilation is involved.

In a previous work [19] the removal of carbon dioxide from flue gas streams was achieved, using the ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIMTf$_2$-N]) combined with CA for the enhancement of the selective transport of carbon dioxide. The results showed that it was possible to increase the carbon dioxide solubility coefficient up to 30%, even when using a low enzyme concentration (0.1 mgCA/gIL). The present work follows the concept described in the previous work, using biocompatible ionic liquids.

Aiming the optimal conditions for the enzyme activity and stability in these biocompatible ionic liquids, water activity studies were performed. The impact of water activity on the viscosity of cholinium-based ionic liquids is evaluated as well as its impact on the transport of carbon dioxide. Several works report diffusion coefficient correlations for gas compounds in room temperature ionic liquids based on imidazolium, phosphonium and ammonium cations [30–37]. Correlations to predict gas diffusion are required, in order to minimize time and resources usually spent on measuring the solubility and diffusion for every new system. Consequently, predictive models are an extremely powerful tool when attempting to develop new processes and applications. The present work proposes a carbon dioxide diffusion coefficient correlation for cholinium-based ionic liquids at different water activities.

To validate the concept proposed in the present work, the following aspects were investigated: 1 – determination of the carbon dioxide solubility and diffusion coefficient in cholinium-based ionic liquids; 2 – evaluation of xenon, oxygen and nitrogen transport through cholinium-based ionic liquids; 3 – evaluation of the effect of the enzyme in the absorption of carbon dioxide, xenon, oxygen and nitrogen; 4 – the effect of water activity on the enzyme activity/stability and on the carbon dioxide solubility and diffusion coefficient; and 5 – determination of a predictive correlation of gas diffusion in the cholinium-based ionic liquids.

2. Materials and methods

2.1. Materials

2.1.1. Cholinium-based ionic liquids

Cholinium-based ionic liquids possess a quaternary ammonium cation (*N*,*N*,*N*-trimethylethanolammonium), which is a substituted tetra-alkylammonium containing one primary hydroxyl group. These ionic liquids (ILs) were selected according to the cation and anion properties. Ammonium cations possess good affinity towards carbon dioxide, as reported in the literature [31]. The anions used in this study possess high affinity towards carbon dioxide (CO_2), because they derived from week carboxylic acids [12]. In Table 1 are represented the ionic liquids studied.

Cholinium hexanoate ([Cho][Hexanoate]), cholinium propionate ([Cho][Propionate]) and cholinium acetate ([Cho][Acetate]) ionic liquids were prepared by neutralization of the respective carboxylic acids dissolved in methanol with choline hydroxide ([Cho][OH]), as reported elsewhere [9], with the following modifications: to a solution of acid (1 equiv.) in methanol was slowly added to [Cho][OH] (1 equiv.). The solution was stirred overnight at room temperature, followed by solvent evaporation on a rotary evaporator. The salt obtained was stirred under vacuum (<1 mmHg) at 60°C overnight. The structure and purity of the prepared ILs were confirmed by ^{1}H NMR and ^{13}C NMR, where no impurities peaks were observed. Choline hydroxide, hexanoic acid, propionic acid and acetic acid were purchased from Sigma-Aldrich (USA) and were used without further purification or drying.

The cholinium-based ionic liquids were equilibrated with four different salts in order to provide the water activities presented in Table 2. Potassium acetate (Merck®, Germany), sodium bromide (Applichem, Panreac®, Germany), sodium chloride (Applichem, Panreac®, Germany) and potassium chloride (Panreac®, Germany) were used for that purpose.

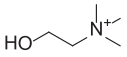
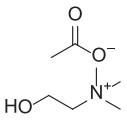
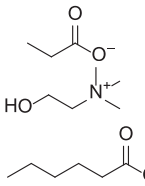
2.1.2. Carbonic anhydrase enzyme

Carbonic anhydrase lyophilized from bovine erythrocytes from Sigma-Aldrich (USA) (reference C3934) was used in this work, without any additional purification.

2.1.3. Gases

The gases used in the experiments were carbon dioxide, CO_2 (high-purity grade 99.998%, Praxair, USA), xenon, Xe (purity grade 99.999%, Praxair, USA), oxygen, O_2 (purity grade 99.999%, Praxair, USA) and nitrogen, N_2 (purity grade 99.998%, Praxair, USA).

Table 1
Cholinium-based ionic liquids molecular structure, chemical formula and molecular weight.

Ionic liquid	Molecular structure	Chemical formula	Molecular weight (g·mol^{-1})
[Cho][Acetate]		$C_7H_{17}NO_3$	163.21
[Cho][Propionate]		$C_8H_{19}NO_3$	177.24
[Cho][Hexanoate]		$C_{11}H_{25}NO_3$	219.32