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A low-viscosity family of ionic liquids based on the tetracyanoborate anion for CO\textsubscript{2} capture

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ABSTRACT

The extraordinary properties of ionic liquids (ILs) such as their negligible vapor pressure have placed them in the spotlight of researchers as alternative solvents for separation processes. The large number of anion/cation combinations allows the possibility of “designing” ILs according to the specifications required for the process. ILs should be chemically and thermally stable. When used for gas purification and carbon dioxide (CO\textsubscript{2}) capture, ILs are required to have a high CO\textsubscript{2} absorption capacity and low viscosity.

The newly task-specific ILs achieve higher CO\textsubscript{2} loadings at moderate pressures, also at supercritical conditions. However, the relatively high high viscosities of some ILs is a drawback for their practical application, in spite of their high gas solubility.

The aim of this work is to study the feasibility of using tetracyanoborate-based ionic liquid for CO\textsubscript{2} capture. The main characteristic of this family of ILs is their low viscosity compared to “traditional” ionic liquids, such as tetrafluoroborate or hexafluoroborate. We will present some pure component properties such as viscosity, density and surface tension, as well as solubility measurements of the binary systems IL+ CO\textsubscript{2}.

The solubility of CO\textsubscript{2} in 1-ethyl-3-methylimidazolium tetracyanoborate [emim][TCB] and 1-hexyl-3-methylimidazolium tetracyanoborate [hmim][TCB] was measured using the Cailletet apparatus where the bubble point was visually determined. The encouraging results show that the tetracyanoborate ionic liquids have a large potential for CO\textsubscript{2} absorption applications.

INTRODUCTION

Understanding the phase behaviour of carbon dioxide (CO\textsubscript{2}) + IL systems is essential to determine the feasibility of applying ionic liquids for CO\textsubscript{2} absorption and to optimize the operational conditions (pressure and temperature). Therefore, the phase diagrams of binary systems of CO\textsubscript{2} with a large variety of ILs are available in literature.

Since the number of cation-anion combinations is enormous, we should establish criteria for short listing the candidates based on their CO\textsubscript{2} storage capacity, chemical/thermal stability and viscosity. The extremely high viscosity of “traditional” ILs such as 1-alkyl-3-methylimidazolium hexafluorophosphate ([C\textsubscript{n}mim][PF\textsubscript{6}]) and 1-alkyl-3-methylimidazolium tetrafluoroborate ([C\textsubscript{n}mim][BF\textsubscript{4}]) prohibits their use in many industrial applications. This motivated our study of new cation-anion combinations which may result in ILs with lower viscosities and enhanced other attractive specific-task properties at the same time.

The tetracyanoborate family of ionic liquid was reported to have low viscosities [1], and low toxicity [2]. For these reasons, [emim][TCB] and [hmim][TCB] were selected for our CO\textsubscript{2} solubility study.
MATERIAL AND METHODS

The [emim][TCB] and [hmim][TCB] ionic liquids were provided by Merck KgaA, Germany, and no further purification was done upon its use. The only precaution was to keep the ionic liquid in dry storage under vacuum conditions. NMR analysis showed no traces of fluorine in the ILs.

The CO$_2$ used for the measurements was supplied by Hoek Loos, The Netherlands, and had an ultrahigh purity of 99.995%.

The solubility of CO$_2$ in the ionic liquids was determined applying the synthetic method, i.e., the Cailletet apparatus. A well determined mass of the liquid is introduced in a thick-walled tube made of Pyrex glass. The tube is connected to a gas rack where it is degassed preceding the addition of a calibrated volume of CO$_2$ at a known temperature and pressure and sealed with mercury which is also acting as a pressure transmitter. More information on the experimental method can be found elsewhere. [3]

The experimental determination of the gas solubility in the liquid is based in the bubble point method. The temperature was regulated with a water bath and the pressure was adjusted until the liquid-gas to liquid phase transition is visually observed.

The viscosity of the ionic liquids was measured at room temperature using a calibrated BS/IP/RF U-Tube Reverse-Flow viscometer from Cannon Instruments Co.

RESULTS

The viscosity of [hmim][TCB] was measured at 298K, and was determined to be 45.1 mPa·s. In addition, the viscosity of [emim][TCB] was reported to be 21.8 mPa·s [4].

Figure 2: Isoplets of the binary system CO$_2$+[emim][TCB] (left) and CO$_2$+[hmim][TCB] (right) at different molar compositions of CO$_2$. In both cases, 20% , 40% , and 60% .

The solubility of CO$_2$ in [emim][TCB] and [hmim][TCB] is shown in Figure 2. It is highlighting the high solubility of CO$_2$ at moderate pressures. Both systems follow the typical trend of gas in liquids: the solubility
increases with the pressure, but decreases as the temperature is risen. As other imidazolium ionic liquids, the longer the alkyl chain, the higher the solubility. In other words, [hmim][TCB] is able to dissolve more moles of CO₂ per mole of ionic liquid than [emim][TCB].

It can be seen that the bubble point pressure curve for 60% of the CO₂+[emim][TCB] system is much more separated from the 40% curve than in the CO₂+[hmim][TCB] system. It has been found that the pressure changes slightly with the composition for low concentrations. However, at higher temperatures, a small change in composition leads to an abrupt change of the bubble pressure. [emim][TCB] presents that change at lower concentrations than [hmim][TCB] does. In other words, in the supercritical region, high solubility of CO₂ is achieved.

In Figure 3 the isotherms at 333K of four ionic liquids sharing the [hmim]+ are presented. The tetracyanoborate ionic liquid is able to dissolve more CO₂ than other “traditional” ionic liquids such as [hmim][BF₄] and [hmim][PF₆] and similar to [hmim][TF₂N] [5-7]. This last IL has a larger molecular weight. This means that when the composition is expressed in mass or volume units instead of mol fractions, [hmim][TCB] still shows a higher solubility of CO₂.

![Figure 3: Isotherms at 333K for several ionic liquids sharing the cation [hmim]⁺. [5-7].](image)

The solubility of CO₂ in ionic liquids has been found to be stronger dependent on the anion than the cation.

**CONCLUSIONS**

New generation ionic liquids achieve higher CO₂ absorption capacities.

The extremely high solubility of CO₂ in [emim][TCB] and [hmim][TCB] together with their low viscosity and low toxicity show that the tetracyanoborate-based ionic liquids are excellent candidates for CO₂ capture.