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A low-viscosity family of ionic liquids based on the tetracyanoborate anion for CO_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_2) capture, ILs are required to have a high CO_2 absorption capacity and low viscosity.

The newly task-specific ILs achieve higher CO_2 loadings at moderate pressures, also at supercritical conditions. However, the relatively high viscosity 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_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_2.

The solubility of CO_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_2 absorption applications.

INTRODUCTION

Understanding the phase behaviour of carbon dioxide (CO_2) + IL systems is essential to determine the feasibility of applying ionic liquids for CO_2 absorption and to optimize the operational conditions (pressure and temperature). Therefore, the phase diagrams of binary systems of CO_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_2 storage capacity, chemical/thermal stability and viscosity. The extremely high viscosity of “traditional” ILs such as 1-alkyl-3-methylimidazolium hexafluorophosphate ([$C_n$mim][PF_6]) and 1-alkyl-3-methylimidazolium tetrafluoroborate ([$C_n$mim][BF_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_2 solubility study

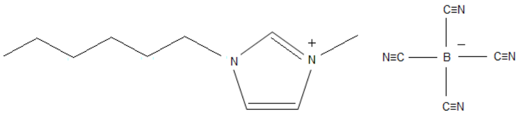

Figure 1. Chemical structure of 1-hexyl-3-methylimidazolium tetracyanoborate

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].

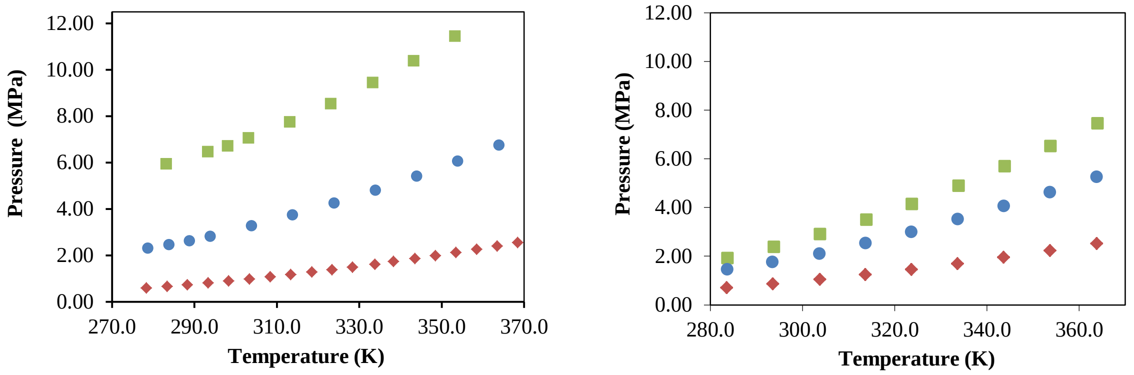

Figure 2: Isoplets of the binary system CO_2+[emim][TCB] (left) and CO_2+[hmim][TCB] (right) at different molar compositions of CO_2. In both cases, 20% ◆, 40 % ●, and 60% ■.

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 CO_2 per mole of ionic liquid than [emim][TCB].

It can be seen that the bubble point pressure curve for 60% of the CO_2+[emim][TCB] system is much more separated from the 40% curve than in the CO_2+[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 CO_2 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 CO_2 than other "traditional" ionic liquids such as [hmim][BF_4] and [hmim][PF_6] 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 CO_2.

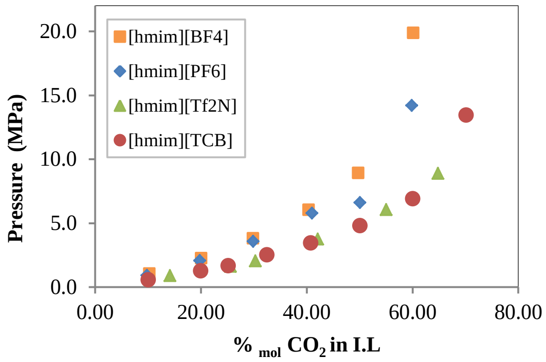

Figure 3: Isotherms at 333K for several ionic liquids sharing the cation [hmim]$^+$. [5-7].

The solubility of CO_2 in ionic liquids has been found to be stronger dependent on the anion than the cation.

CONCLUSIONS

New generation ionic liquids achieve higher CO_2 absorption capacities.

The extremely high solubility of CO_2 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 CO_2 capture.

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