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Low viscosity protic ionic liquid for CO_2/CH_4 separation: Thermophysical and high-pressure phase equilibria for diethylammonium butanoate

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ABSTRACT

This is a study of a potential low viscous protic IL to be used in CO_2 capture processes. High-pressure phase equilibria data were measured for diethylammonium butanoate [DEA][Bu] + CO_2, CH_4 or N_2 from 303 to 333 K and up to 20 MPa. The experimental data of density, viscosity and sound speed were measured from mixtures of [DEA][Bu] + water with different water amounts and at several temperatures. This protic ionic liquid was characterized by water content, FT-IR, ^1H and ^{13}C NMR, which were used to determine the IL molecular structure and estimate its purity, before and after phase equilibria experiments. A comparison among 38 ionic liquids indicates that [DEA][Bu] has a significantly low viscosity. Phase equilibria data were adjusted by Peng-Robinson and sPC-SAFT EoSs with high accuracy, mainly for CO_2 data. sPC-SAFT also well fitted the density and sound speed of pure [DEA][Bu] (dev. < 0.2%). [DEA][Bu] Henry's law constants and ideal CO_2/CH_4 selectivity values were compared with those of other ILs at different temperatures, molecular weights and pressures. The comparisons indicate that [DEA][Bu] presents moderate to low CO_2 solubilities and CO_2/CH_4 selectivities but a low pressure sensibility. Thus, at high pressures, this PIL would present higher selectivities than most ILs studied.

1. Introduction

Carbon dioxide capture has been the focus of several recent studies. Its removal from gaseous streams can promote financial gain since this gas promotes the reduction of natural gas value and promotes pipeline corrosion. Carbon dioxide might also be produced during some industrial processes, such as biomass pyrolysis. To reuse an inert gas, such as nitrogen, it would be necessary to purify the stream by removing contaminant gases, such as CO_2.

Therefore, there is great economic interest in removing this greenhouse gas from several streams. Several CO_2 capture processes use aqueous ethanolamine solutions. This mixture is used as a medium to selectively remove CO_2 through carbamate/carbonate formation [1]. Some of its main drawbacks are solvent evaporation, low thermal stability, and equipment corrosion, as well as the fact that solvent regeneration requires the consumption of a high amount of energy and promotes partial solvent degradation [2].

The use of ionic liquids (ILs) has great potential on overcoming these drawbacks because of their unique characteristics, such as negligible vapour pressure, CO_2 selectivity and high thermal stability [3–15]. Other authors studied ILs with part of these ethanolamines incorporated within the protic ionic liquid (PIL) structure [4,5,7–10]. These task-specific ILs might promote high CO_2 selectivity and an absorption capacity associated with high thermal stability, low solvent loss through evaporation, low equipment corrosion and possible brand routes for solvent regeneration.

However, despite their promising results with respect to CO_2

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capture, all of these PILs still present one of the main drawbacks of IL's application in separation processes: high viscosity [3]. This high viscosity is a result of strong interactions between the ions through, mainly, the hydrogen bonds of hydroxyl groups and protic ion-ion interactions.

It was expected that removing the hydroxyl groups from these PILs would disperse the IL charge density and reduce the hydrogen bounds strength. Therefore, reducing the ion-ion interactions strength and reducing its viscosity. However, a previous study [7] reported that the CO_2/CH_4 selectivity, at low pressures and gas solubilities, is related to the IL polarity. Therefore, by removing the hydroxyl group, the observation of a reduction of IL selectivity would also be expected. However, how much would this reduction of viscosity and CO_2/CH_4 selectivity be?

Therefore, in the present paper the IL chosen to be studied was diethylammonium butanoate ([DEA][Bu]), a protic IL with a similar structure to those of ethanolamine ILs but without the hydroxyl groups. The IL's structures were confirmed by $^1H/^{13}C$ NMR (Nuclear magnetic resonance) and FTIR (Fourier transform infrared spectroscopy). The IL's charge density distribution was analysed through its sigma profile, and the IL's viscosity was compared with those of other ILs.

High-pressure phase equilibria of this PIL + CO_2, CH_4 or N_2 were investigated to study the solubility of these gases in [DEA][Bu] at different pressures. CH_4 and N_2 were chosen to be studied due to their frequent use in several fields, such as natural gas and biomass pyrolysis. Being important to some applications, several models of phase equilibria and other thermophysical properties, such as density and sound speed, were also measured. Since [DEA][Bu] presented high hygroscopic properties, these properties were measured at different water contents.

The high-pressure phase equilibria of [DEA][Bu] with CO_2, CH_4 and N_2 were modelled through the Peng-Robinson equation of state (EoS), a simple and widely known and applied model, and sPC-SAFT EoS, a complex and robust model that shows an incredibly high accuracy on the estimation of density, sound speed and phase equilibria of both protic and aprotic ILs [9].

2. Material and methods

2.1. IL synthesizing method

[DEA][Bu] (Fig. 1) was obtained by a reaction of butanoic acid with diethylamine. The 3D structures were estimated by geometrical and energetic optimization using Material Studios software (Supp. Mat.), and their charge profiles were also calculated. The precursors were used with no further purification, and further material characteristics are given in Table 1.

Briefly, the synthesis procedure consisted of the use of a three-necked glass flask, as the reactor, connected to a reflux condenser, a PT-100 temperature probe and a dropping funnel, all mounted inside a thermal bath at 283.1 K. Nitrogen gas was flooded inside the reactor to assure an inert environment. Then, the organic acid was added dropwise to the flask containing the amine precursor to avoid unwanted reactions. Stirring at 450 rpm was used to promote good heat dispersion. To decrease the reagents' content and moisture, the mixture was exposed to a moderate vacuum (20 kPa) at 333.15 K for 48 h under continuous stirring. During the steps of purification and storage of ionic liquid, the product was light protected to avoid/minimize any degradation [4,7,16,17].

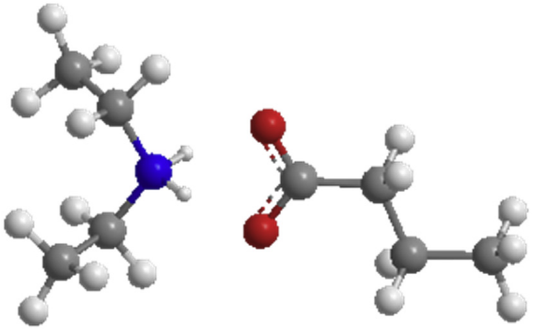

Fig. 1. [DEA][Bu] molecular structure.

2.2. NMR spectroscopy

The NMR spectra were acquired at 298 K on a Bruker Avance III 500 spectrometer operating at 11.75 T (500 MHz for ^1H), using D_2O as a solvent. The acquisition parameters were as follows: 64 and 1024 scans (NS), 64 and 32 k data points (TD), spectral windows (SWs) of 12.02 and 248.47 ppm, acquisition times (AQs) of 5.45 and 0.52 s, and relaxation delays (d1s) of 10 and 0.5 s for ^1H and ^{13}C, respectively. The results were analysed using Bruker TopSpin software. All ^1H NMR chemical shifts are given in δ (ppm) related to TMSP-d_4 signal at δ 0.00 as an internal reference.

2.3. Water content

The water content was determined with a Metrohm 831 Karl Fischer coulometer. The mass fraction water content and combined standard uncertainty (u_c) were estimated by GEU software [18], according to GUM [19].

2.4. FT-IR spectroscopy

The infrared absorption spectra (FT-IR) were obtained with a Shimadzu FT-IR configured to operate at medium and high frequencies (4000–400 cm^{-1}) using the ATR method with a resolution of 0.10 cm^{-1}. The KBr pellets used in the analyses were embedded with [DEA][Bu].

2.5. Density and sound speed

The measurements of density and sound speed were performed simultaneously on an Anton Paar DSA 5000. This equipment had two measuring cells: a cell with U-shape vibration tube, for the density measurements, and a pulse-echo cell for measuring the speed of sound. Both cells were equipped with Peltier elements for temperature control with an accuracy of ±0.01 K. In the calibration of the equipment, deionized water (<0.02 $\mu S.cm^{-1}$) was used and the values of density and speed of sound were compared with those available in the NIST databank [20] presenting uncertainties below ± 0.00002 $g.cm^{-3}$ for density and ±0.0004 $m.s^{-1}$ for the speed of sound.

2.6. Viscosity

Viscosity measurements were performed on an Anton Paar SVM 3000. It measured the viscosity by means of concentric rotary cylinders, which spun at a constant speed. The equipment analysis procedure followed the methodology described in ASTM D 445–01. The equipment was previously calibrated, and in this procedure, standard oils (provided by the manufacturer) of different viscosities were used. The analyses were performed with a temperature variation in the range of 283.15 K–373.15 K, and the calculated deviations for the calibration data were within the range reported by the manufacturer of 1.0%.