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High pressure vapor-liquid equilibria for binary protic ionic liquids + methane or carbon dioxide

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ABSTRACT

This study reports the high pressure phase transition data for both methane and carbon dioxide and two large protic ionic liquids: N-methyl-2-hydroxyethylammonium propanoate [m-2HEA][Pr] and bis(2-hydroxyethyl) ammonium butanoate [BHEA][Bu]. The experimental data were obtained using the static-synthetic visual method by a variable-volume cell unit. The apparatus and experimental methodology were validated by methane + N-methyl-2-hydroxyethylammonium propanoate equilibrium data. The low deviation between the data indicates the experimental data is consistent with previous literature. Structure and purity of ILs were confirmed by FT-IR spectroscopy, ^{1}H and ^{13}C NMR studies. Water contents were measured by Karl Fischer volumetric measurements. NMRs and water contents analyses were performed on samples collected before and after the experiments. The phase transitions were classified as bubble points and studied at five temperatures from 313.1 to 353.1 K and pressures up to 20 MPa. Experimental data were correlated using the three-parametric Redlich Kwong – Peng Robinson equation of state (RKPR-EoS) coupled to mixing rules van der Waals type, cubic regarding the composition, and temperature dependence for the interaction energy parameter (CMR-T). Henry's law constants and ideal CO_2/CH_4 selectivities were calculated from this model and compared to other ILs ones.

1. Introduction

Carbon dioxide and methane separation has been studied for many years but it is still a challenge. Several ionic liquids (ILs) have shown great potential to be applied on CO_2 capture from several gas streams [1–11]. Its negligible vapor pressure, high solubility to organic compounds and high thermal stability are some of the ILs unique properties. These characteristics can be explained as result of a well-balanced mixture of Coulomb and dispersion intermolecular bounds, which can be tuned by going from aprotic to protic ionic liquids [12].

Protic ionic liquids (PILs) are formed by an equimolar combination of a Brønsted acid and a Brønsted base. The key difference between aprotic and protic ILs is the presence of proton-donor and proton-acceptor sites which can be used to build up a hydrogen-bonded network [5,6,13], which grants the PILs unique properties. The upsides of PILs are lower synthesis cost, lower toxicity and an easier production route than the aprotic ones [5,6,14–18]. Previous papers studied the phase equilibria of PILs + CO_2 or CH_4 and showed promising results [1,8].

In the present study, two large PILs were tested on binary methane or carbon dioxide high pressure phase equilibria: N-methyl-2-hydroxyethylammonium propanoate [m-2HEA][Pr], and bis(2-hydroxyethyl) ammonium butanoate [BHEA][Bu]. Carvalho and Coutinho estimated the ideal CO_2/CH_4 selectivities of several ILs, including the [m-2HEA][Pr] [1]. These parameters were estimated through Henry's law constants, obtained from CH_4 + IL experimental phase equilibria and an empirical correlation for CO_2 + ILs phase equilibria. In the present study, the [m-2HEA][Pr] + CO_2 phase equilibrium was obtained experimentally and the [m-2HEA][Pr] + CH_4 phase equilibrium was used to validate the methodology and apparatus. The [BHEA][Bu] was chosen to study the effect of the structure on the binary phase equilibria with CO_2 and CH_4. There were used a more polar cation where the methyl radical was substituted by a second hydroxyethyl radical and a less polar anion with one more methylene group.

Experimental data were correlated using two models: Carvalho and Coutinho's correlation [1], an empirical model for CO_2 solubility in nonvolatile solvents based on its molecular weight; the three-parametric Redlich-Kwong-Peng-Robinson EoS (RKPR-EoS) given by Cismondi and Mollerup [19] coupled to mixing rules van der Waals type,

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Nomenclature

[amim][dca]	1-allyl-3-methylimidazolium dicyanamide
[bmpip][Tf_2N]	1-butyl-1-methylpiperidinium bis(tri fluoromethylsulfonyl)imide
[bmpyrr][dca]	1-butyl-1-methylpyrrolidinium dicyanamide
[emim][dep]	1-ethyl-3-methylimidazolium diethylphosphate
[hmpy][Tf_2N]	1-hexyl-3-methylpyridinium(tri fluoromethylsulfonyl)imide
[hmim][Tf_2N]	1-hexyl-3-methylimidazolium(tri fluoromethylsulfonyl)imide
[bmim][PF_6]	1-*n*-butyl-3-methylimidazolium hexafluorophosphate
[cprop][Tf_2N]	1,2,3-tris(diethylamino)cyclopropenylium bis(tri fluoromethylsulfonyl) imide
[cprop][dca]	1,2,3-tris-(diethylamino)cyclopropenylium dicya namide
[BHEA][Bu]	butanoate bis (2-hydroxyethyl)ammonium
CO_2	carbon dioxide
u_c	combined uncertainty
R^2	determination coefficient
FT-IR	Fourier transform infrared spectroscopy
GC	gas chromatography
h	hour
ILs	ionic liquids
CH_4	methane
[toa][Tf_2N]	methyltrioctylammonium bis(tri fluoromethylsulfonyl) imide
x	mole fraction
N_2	nitrogen
NMR	nuclear magnetic resonance
%	percentage
[m-2HEA][Pr]	propionate N-methyl-(2-hydroxyethyl)ammonium
P	pressure
MPa	pressure unit, mega pascals
PILs	protic ionic liquids
T	temperature
K	temperature unit, kelvin
[tes][Tf_2N]	triethylsulfonium bis(trifluoromethylsulfonyl)imide
[thtdp][phos]	trihexyltetradecylphosphonium bis-(2,4,4-tri methylpentyl) phosphinate
[thtdp][dca]	trihexyltetradecylphosphonium dicyanamide
VLE	vapor–liquid equilibrium
ML	volume unit, milliliter

cubic regarding the composition, and temperature dependence for the interaction energy parameter (CMR-T).

2. Material and methods

2.1. ILs synthesizing method

The [m-2HEA][Pr] (Fig. 1a) and [BHEA][Bu] (Fig. 1b) were obtained by the reactions of propanoic and butanoic acids with, N-methyl-2-hydroxyethylamine and bis(2-hydroxyethyl) amine, respectively. These precursors were used with no further purification methods. The characteristics of the materials used are shown in Table 1.

The synthesis of the ILs, a common routine, is explained in other studies [5,15]. Briefly, the reactor was a three-necked glass flask connected to a reflux condenser, a PT-100 temperature probe and a dropping funnel, all mounted inside a thermal bath at 283.1 K. The organic acid was added dropwise to the flask containing the amine precursor. Intense stirring (ca. 450 rpm) was used to promote a better heat exchange and to avoid hot spots that might favors unwanted reactions. In order 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 a continuous stirring. During the step of purification and storage of ionic liquids, they were light protected, to avoid any degradation [5,16].

2.2. NMR spectroscopy and water content

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 solvent. The acquisition parameters were: 64 and 1024 scans (NS), 64 and 32k data points (TD), spectral window (SW) of 12.02 and 248.47 ppm, acquisition time (AQ) of 5.45 and 0.54 s, and relaxation delay (d1) of 10 and 0.5 s for ^1H and ^{13}C, respectively. The results were analyzed at Bruker TopSpin software. All ^1H NMR chemical shifts are given in δ (ppm) related to TMSP-d_4 signal at δ 0.00 as internal reference.

The ionic liquids were dried under high vacuum (10^{-4} Pa), for a period of at least 48 h, and the structure and purity checked by ^1H NMR and ^{13}C NMR both before and after the experiments on VLE cell.

The water contents were determined with a Metrohm 831 Karl Fischer coulometer before and after the phase equilibria experiments. Mass fraction water content and combined standard uncertainty (u_c), estimated by GEU software [20] according to GUM [21].

2.3. FT-IR spectroscopy

The infrared absorption spectra (FT-IR) were obtained with a Shimadzu FT-IR configured to operate at medium and high frequency (4000–900 cm^{-1}) using the ATR method with resolution of 0.10 cm^{-1}. The KBr pellets used on the analyses were embedded with ILs.

2.4. Static-synthetic visual method in a variable volume cell

Phase equilibria experiments were carried out employing a static-synthetic visual method in a high pressure variable-volume view cell. VLE transitions have been classified as bubble points. Both the apparatus and the methodology followed were fully described in previous works [6,8,11,22–26], and shown to be adequate to accurately measure vapor–liquid phase equilibria in a wide range of pressure and temperature.

Briefly, the experimental apparatus consists in a variable volume

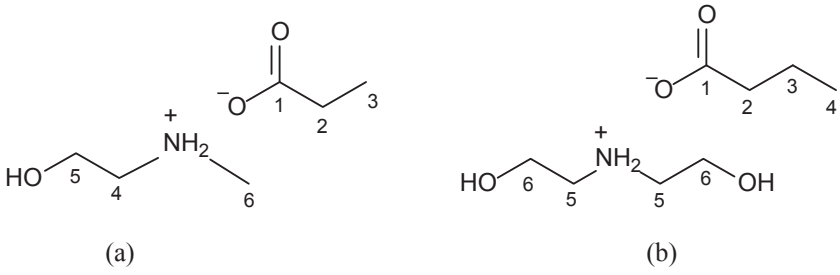

Fig. 1. ILs structures: (a) [m-2HEA][Pr]; (b) [BHEA][Bu].