Fluid Phase Equilibria xxx (2016) 1–10

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

High pressure vapor-liquid equilibria for binary methane and protic ionic liquid based on propionate anions

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ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form
21 March 2016
Accepted 25 March 2016
Available online xxx

Keywords:
Protic ionic liquids
Methane
High pressure
Equilibrium
Henry's law constant

ABSTRACT

Sour gases and methane separation has been studied for many years and ionic liquids (ILs) could be used to promote their separation. Protic ionic liquids based on substitute amines and carboxilate anions were reported to be selective to methane/carbon dioxide separation. However, the methane + ILs phase equilibria data, which is required to design gas separation, are scarce on the open literature. This study report the high pressure phase transition data for methane + *N*-methyl-2-hydroxyethylammonium propanoate, bis(2-hydroxyethyl)ammonium propanoate, or 2-hydroxyethylammonium propanoate. The binary system methane + *N*-methyl-2-hydroxyethylammonium propanoate was compared to literature experimental data. The structures and purities of ILs were confirmed by ^{1}H NMR, ^{13}C NMR, HSQC and HMBC NMR studies. Water content were measured by Karl Fischer coulometer measurements. The phase transitions have been classified as bubble points and studied at four temperatures from 333.1 to 363.1 K and pressures from 4 to 16 MPa. The experimental data were obtained using the static-synthetic visual method by a variable-volume cell unit. VLE transitions have been classified as bubble points. Henry's law constants were estimated and compared with other ILs and organic solvents. Experimental data for CH4 + + *N*-methyl-2-hydroxyethylammonium propanoate system were correlated using the three-parametric Redlich − Kwong − Peng − Robinson equation of state (RKPR-EoS) coupled to cubic van der Waals mixing rules (regarding the composition) and temperature dependence for the interaction energy parameter (CMR-T).

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1. Introduction

Carbon dioxide and methane separation technologies are required for the optimal production of natural gas from reservoirs because it contains large quantities of acid gases, such as the brazilian pre-salt area. Furthermore, gas miscible in oil as CO_2 or N_2 are injected in oil reservoirs to increase oil or gas recovery. Biogas also has a high CO_2 content (38–40%) [1]. Removal of acid gases as carbon dioxide increases the caloric content of natural gas and reduces corrosion in gas pipelines. Several studies had shown that ionic liquids can be used to promote this separation [2–7].

Most of the studies conducted in ionic liquids are based on imidazolium cation and to a lesser extent in phosphonium, trialkylamines or alkyl pyridinium [3,7]. Recently, protic ionic liquids (PILs) has been the focus of several studies due to its low cost, and simplified synthesis [4,5,8–14]. These PILs can usually be synthetized through a simple acid-base Brönsted reaction, where a proton from the acid is transferred to the base (typically an amine) [4,5]. Another important feature is the small levels of toxicity when compared to aprotic ionic liquids [15–17], even though more complex is the amine higher is the toxicity [16,17]. Pure substituted alkanolamine carboxylates are thermically stable up to 340 K (onset temperature for *N*-methyl-2-hydroxypropanoate is 342 K) [12,13]. These compounds are liquid with a segregated nanostructure [18,19] with micellar characteristic [10,20].

Carvalho and Coutinho [21] showed that the *N*-methyl-2-hydroxypropanoate has a good selectivity to separate CH_4/CO_2 and states that this kind of PILs could be an interesting alternative to be applied in processes to separate sour gases such as CO_2, H_2S and SO_2 from hydrocarbon streams. Most of these PILs had not been fully studied. Recently, studies have been reported on the synthesis,

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http://dx.doi.org/10.1016/j.fluid.2016.03.021
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Please cite this article in press as: L.M.C. Oliveira, et al., High pressure vapor-liquid equilibria for binary methane and protic ionic liquid based on propionate anions, Fluid Phase Equilibria (2016), http://dx.doi.org/10.1016/j.fluid.2016.03.021

physico-chemical and structural characterization of protic ionic liquids (PILs) [5,8–14]. However, there still several ILs whose equilibria phase data hadn't been reported yet.

In this work, the phase transition of methane + *N*-methyl-2-hydroxyethylammonium propionate (m2HEAPr), bis(2-hydroxyethyl)ammonium propanoate (BHEAPr), or 2-hydroxyethylammonium propionate (2HEAPr) were studied. The experimental method was the visual static synthetic method using a variable-volume cell unit. The experimental procedure was validated with the binary data of methanol + methane and ethanol + methane and compared to experimental data for these systems [22,23]. These data were included in the supporting information. The only data on these mixtures found was for the binary system methane + m-2HEAPr [20] which were compared to the obtained data. The binary systems methane + BHEAPr or 2HEAPr are new on the open literature.

The methane concentration range analysed was from 0.01 to 0.08 mol fraction. All systems studied were measured at temperatures ranging from (333.1 to 363.1) K and pressure up to 150 bar. Henry's law constants were estimated and compared with other ILs and organic solvents.

Experimental data were correlated using a three-parameter RKPR-EoS given by Cismondi and Mollerup [24], coupled to cubic van der Waals mixing rules (regarding the composition) [25]. In addition, a dependence on the temperature is used for the interaction energy parameter. The relationship between energy interaction parameter and temperature is given by Cismondi et al. [26,27]. The RKPR-EoS [24] and the CMR-T [25] were used to correlate equilibrium data in wide ranges pressure and temperature for highly asymmetric binary systems, such as the CO_2 + n-alkanes series [23,24] obtaining satisfactory results. So far, both RKPR-EoS and CMR-T were not used to correlate experimental data of systems involving ionic liquids. The objective of this modeling was to test the capability of the RKPR-EoS and CMR-T to correlate experimental data of binary systems formed by an ionic liquid.

2. Material and methods

2.1. ILs synthesizing method

The *N*-methyl-2-hydroxyethylammonium propionate (m-2HEAPr); bis(2-hydroxyethylammonium) propionate (BHEAPr) and 2-hydroxyethylammonium propionate (2HEAPr) were obtained by the reactions of propionic acid and a 2-(Methylamino)ethanol, bis(2-amino)ethanol and 2-(amino)ethanol, respectively. These precursors were used with no further purification methods. The characteristics of the materials used are showed in Table 1. The molecular structure of the ILs are showed in Fig. 1.

The synthesis of the ILs, a very common route, is explained in other studies [4,10]. 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. After the acid addition, the stirring was continued for 24 h at room temperature (~293 K). In order to decrease the reagents content and moisture, the IL were exposed to a moderate vacuum (20 kPa) 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 [4,10].

2.2. NMR spectroscopy and water content

The final water content was determined with a Metrohm 831 Karl Fischer coulometer, indicating a water mass fraction, standard deviation (σ) and uncertainty (u) (Table 2). According to the literature [28] the water content is one of the factors that directly influence the viscosity due protic ionic liquids have hygroscopic characteristics.

The NMR spectrum were obtained at a Bruker Nuclear magnetic resonance spectrometer (model AVANCE III 9.4 T). Deuterated chloroform was used as solvent for m2HEAPr and deuterated water was used as solvent for 2HEAPr and BHEAPr the results were analysed at Mestre-C software (*Mestrelab Research Inc.*) [29].

The ionic liquids were dried under high vacuum (10^{-4} Pa), for a period never smaller than 48 h, and the structure and purity checked by ^{1}H NMR both before and after the measurements. The obtained spectra showed the correct structure and there were not observed in trace contamination NMR spectra, confirming its purity. Main impurity present is water which was quantified by karl-fischer titration.

Table 3 presents the analysis of ^{1}H and ^{13}C NMR spectra of the ILs studied. The ^{1}H NMR spectrum of the LI m2HEAPr (Fig. 2) showed signal for two methyl groups as a singlet at δ 2.64 and δ quadruplet at 2.20, indicating the presence of an amino group attached to more non blinded (H-5′) and the other in the beta position to a carboxylate group. The observed multiplets at δ 3.03 and δ 3.84 are assigned to the methylene groups H-2′ and H-3′. The signal observed at δ 2.20 as quartet was attributed to hydrogen alpha to the carboxyl group. The presence of the amine hydrogens has been confirmed by displacement with singlet at δ 8.06.

The chemical shifts of the carbons were observed by HSQC spectrum analysis (Fig. 3), which allowed the assignment of the methylene C-2′ (δ 51.6) and C-3′ (δ 57.1) and methyl C-3 (δ 10.7) and C-5′ (δ 33.0).

The hydrogens H-2 methylene (δ 2.20) showed correlation in the HMBC (Fig. 4) with the carboxyl in the δ 181.9 $_2J$. It also observed the correlation of H-2′ (δ 3.03) with C-3′ (δ 57.1) to $_2J$ and C-5′ (δ 33.0) to $_3J$. The signal at δ 2.6 H-5′, $_3J$ also correlates with the C-2′ (δ 51.6) confirming the presence of more shielded methylenic group next to the amine group.

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

Phase equilibria experiments were carried out employing a

Table 1
Suppliers and purities of chemicals in this research.

Chemical name	Supplier	Mass fraction purity	Checked by manufactures	Further purification
2-hydroxyethylamine	Sigma Aldrich	0.990	NMR, FT-IR[b]	None
Bis(2-hydroxyethyl)amine	Sigma Aldrich	0.990	NMR, FT-IR[b]	None
Propanoic acid	Sigma Aldrich	0.995	GC[a]	None
Methane	White Martins	0.995	GC[a]	None
N-methyl-2-hydroxyethylamine	Sigma Aldrich	0.990	NMR, FT-IR[b]	None

[a] Gas chromatography by the supplier.
[b] Nuclear Magnetic Resonance and Fourier Transform Infrared Spectroscopy by the supplier.

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