

## The phase envelopes of alternative solvents (ionic liquid, CO<sub>2</sub>) and building blocks of biomass origin (lactic acid, propionic acid)

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### ABSTRACT

Solid–liquid, liquid–liquid and vapour–liquid equilibrium measurements for binary and ternary systems containing building blocks of biomass origin such as propionic acid, lactic acid and alternative solvents like carbon dioxide and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid have been carried out at 313.15 K. The binary solid–liquid and liquid–liquid equilibrium measurements were performed at ambient pressure. The vapour–liquid equilibrium was studied in the range of pressure from 3.54 to 12 MPa while ternary systems were examined at 9, 10 and 12 MPa. The samples from the coexisting phases were taken and the compositions of both liquid and vapour phases were determined experimentally. The three-phase system was observed for lactic acid + ionic liquid + CO<sub>2</sub> as well. The achieved results were correlated using the Peng–Robinson equation of state with the Mathias–Klotz–Prausnitz mixing rule. The set of interaction parameters for the employed equations of state and the mixing rule for the investigated systems were obtained.

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### 1. Introduction

In view of the progress of solvents in science and application, ionic liquids and supercritical fluids have been classified as “advanced fluids or 2nd generation green solvents” [1]. Supercritical fluids have been investigated over the last 30 years extensively because their properties can be varied over a wide range by changes in pressure and temperature. This led to the development of new applications in separation processes and in reaction technology [2]. For many chemical processes and separation operations that are conducted at high pressures, knowledge of the phase behaviour is of a special interest [3]. Other examples for the need of high pressure phase equilibrium data are simulation of petroleum reservoirs, enhanced oil recovery, the transportation and storage of natural gas, and the study of geological processes. In particular, the interest in supercritical fluid extraction processes has led to an increase in the number of publications concerning high pressure phase equilibrium data [4–6]. One of the examples of chemical reactions that can be positively

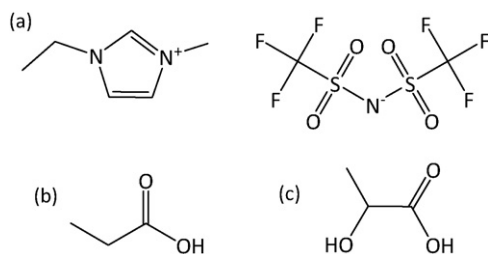
influenced by supercritical fluids is hydrogenation, in particular with the addition of supercritical carbon dioxide which enhances hydrogen transport to the liquid phase and the equilibrium concentrations of low volatile components in the gaseous phase [7,8].

Ionic liquids, a novel class of green solvents, have some unusual features such as low vapour pressure and excellent solvent power for both organic and inorganic compounds. Among the several applications predictable for ionic liquids in chemical reactions [9], homogeneous and biphasic transfer catalysts [10,11], separation processes [12] their use in processes with supercritical fluids [13] are one of the most exciting and the most frequently studied recently.

There are a lot of industrially relevant separation processes which involve carboxylic acids. For example, carboxylic acids obtained from renewable resources are broadly used as building blocks and they can be employed in the production of valuable products (i.e. nylon, biodegradable plastics and certain pharmaceuticals). They are also used as food preservatives and to derive other useful chemical species (e.g. esters). Furthermore, the amphiphatic properties of the carboxylic acids render them extremely useful in the formation of cleaning agents such as soaps and detergents [14]. Acids appear also frequently in an aqueous waste streams or as by-products of industrial operations because they represent stable oxidation products. To prevent pollution and an associated

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**Fig. 1.** Chemical structure of (a) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ ); (b) propionic acid; (c) lactic acid (2-hydroxypropionic acid).

impact on the environment, these acids must be removed and separated. Once this has been accomplished, the carboxylic acids may be purified (if required) and utilised in a number of the economically beneficial above-mentioned processes. Alternatively, they may be sold, thereby generating a profit from material that was previously disposed of waste.

The aim of this work is to present the vapour–liquid equilibrium (VLE) data for ternary systems of  $\text{CO}_2$ , 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ ) and carboxylic acids: propionic acid or lactic acid. Propionic and lactic acids were selected for this investigation due to being classified among the top value added chemicals from biomass, especially as candidates of the top 30 building blocks from sugar. Lactic acid belongs to a “family 2” responsible for hydrogenolysis to derivatives of sorbitol, or xylitol/arabinitol. Propionic acid acts as a secondary chemical being recognised as reagent, propionol, acrylate and producer of amines [15]. To the best of our knowledge, the VLE data for ternary systems containing carboxylic acid: lactic or propionic acid +  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}] + \text{CO}_2$  have never been published before. This work focuses on vapour–liquid phase equilibria of the ternary systems: lactic acid +  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}] + \text{CO}_2$  and propionic acid +  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}] + \text{CO}_2$ , and of the binary system consisting of  $\text{CO}_2$  + lactic acid. Additionally, solid–liquid and liquid–liquid equilibrium data for the  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$  + propionic acid or lactic acid are presented in this work.

## 2. Experimental

### 2.1. Materials

Carbon dioxide was supplied by Air Liquide, with a stated purity of 99.998 mol%. Propionic acid (propanoic acid) with the stated purity 99 wt% was purchased from Sigma while lactic acid (2-hydroxypropionic acid) (purity: 99 wt%) was supplied by Fluka. Both acids were dried using 3 Å molecular sieves. The  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$  ionic liquid was obtained from Solchemar, Portugal, with the stated purity of 98 wt%. The IL was further thoroughly degassed, dried, and freed from any traces of volatile compounds by applying vacuum (0.1 Pa) at moderate temperature (60 °C). All the drying procedures were carried out for 48 h and the fresh samples of the components were used to prepare the solutions, always immediately prior to the measurements. The Karl–Fischer titrations revealed the water contents as follows: propionic acid – 680 ppm, lactic acid – 710 ppm,  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$  – 70 ppm.

The structure of investigated ionic liquid and both carboxylic acids is presented in Fig. 1.

### 2.2. Phase equilibria measurements

#### 2.2.1. Solid–liquid and liquid–liquid equilibrium apparatus and technique

Solid–liquid (SLE) and liquid–liquid equilibrium (LLE) experiments were performed in stirring-equipped, septum-closed conical Pyrex vials. A glass beaker of 2 L was used as a thermostat bath and was filled with ethanol (243–293 K), water (293–333 K) or silicon oil (333–413 K) as a thermostatic liquid. The temperature was monitored using a calibrated Pt100 temperature probe. All experiments were carried out at ambient pressure of 0.1 MPa using a visual method – observation by eye of turbidity (cloud point – LLE) that precedes phase separation and last crystal disappearance (SLE) that leads to single liquid phase formation. Experiments were carried out in a Pyrex-glass cell equipped with stirrer. The cell could be opened/closed by a Teflon valve at the end of a long, capillary thin (ID = 0.1 mm) neck. It allowed the cell to be deeply immersed in a temperature controlled bath, while at the same time diminishes losses due to evaporation. The solutions were prepared in the cell, adding the liquids through the neck using Hamilton syringes with lengthy needles – the liquid inside the cell always occupied almost its entire volume ( $\pm 0.5 \text{ cm}^3$ ). The compositions were measured gravimetrically, with a precision of  $\pm 2 \times 10^{-5}$  of the mole fraction.

In each LLE experiment, a heterogeneous solution was heated from room temperature until it (eventually) became homogenous. Then, starting from the one-phase region, the solution was cooled off and the temperature at which it became turbid was taken as a cloud point. In the case of SLE, upon heating, the temperature at which the last crystal disappeared was taken as the equilibrium one. Both heating and cooling processes were performed with continuous stirring, in three to four runs, with the last run being carried out very slowly (the rate of temperature change near the expected cloud point was no greater than  $5 \text{ K h}^{-1}$ ).

#### 2.2.2. Vapour–liquid equilibrium apparatus and technique

The most up-to-date version of the apparatus used in this experiment was described in detail in the literature [16,17]. The main part of the phase equilibrium apparatus is a sapphire cylindrical tube with the following dimensions: height – 15 cm, internal diameter – 1.9 cm, external diameter – 3.2 cm. The sapphire cell was placed inside an air bath and initially connected to the vacuum pump, to facilitate loading of  $7.0 \pm 0.1 \text{ mL}$  of the mixture of the investigated compound(s) into the sapphire tube. When ternary systems were studied, the mixtures were prepared directly before the experiment and kept in ice to eliminate or reduce the possible changes in the composition. Next,  $\text{CO}_2$  was loaded to the desired pressure. Stirring of the contents was performed with a magnetic stirrer. Temperature was measured with a platinum-resistance thermometer with an accuracy of 0.05 K using a temperature controller Hart Scientific 2100 (Fluke Hart Scientific). Pressure was measured with an accuracy of 0.1% and a precision of 0.1% by a digital manometer LEO2 (Keller UK Ltd.). In each experiment, time allowed for phases to reach equilibrium was about 2 h, corresponding to stirring for 1 h and a rest period of another hour. The equilibration time depends on the amount of the introduced  $\text{CO}_2$  and was determined on the basis of previous experiments performed in our laboratory [16,17]. A sample from either the top or the bottom phase was taken through a HPLC valve, into the sample loop. The volumes of the upper and bottom sample loops were identical and equal to  $100 \mu\text{L}$ . The content of the loops was expanded into the calibrated large volumes (474.9 mL). The expansion volumes include cold traps that ensure condensation of an acid. The pressure drop during sampling (between 0.1 and 0.4 MPa) was balanced by introduction of  $\text{CO}_2$  before the next sampling. The next sample was taken after the equilibration time of 1 h of mixing and 1 h of the separation of phases.

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