



Article

High-Pressure Phase Equilibrium Studies of Multicomponent (Alcohol-Water-Ionic Liquid-CO₂) Systems

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Received: 31 January 2020; Accepted: 22 February 2020; Published: 25 February 2020

Abstract: Selective water (by-product) separation from reaction mixtures stands as an important process intensification strategy for equilibrium-limited reactions. In this work, the possibility of using a high-pressure biphasic reaction media composed of a hydrophobic ionic liquid, 1-hexy-3-methylimidazolium tetracyanoborate, and carbon dioxide was explored for levulinic acid production from 1,4-butanediol. Vapour-liquid equilibrium measurements were performed for the binary (diol+CO₂), ternary (diol+CO₂+IL), and quaternary systems (diol+CO₂+IL+water), at 313.2 K and pressures up to 18 MPa. The static analytical method was used in a high-pressure phase equilibrium apparatus equipped with a visual sapphire cell. The capability of the quaternary system to perform physical water separation is discussed in this paper.

Keywords: 1,4-butanediol, 1,2-propanediol, carbon dioxide, tetracyanoborate ionic liquid, supercritical fluid, phase equilibrium, water repellent

1. Introduction

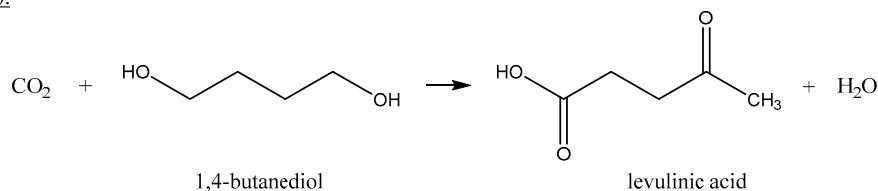
Production of chemicals from renewable sources, such as commodity sugars, lignocellulosic biomass, or algae, is a promising strategy to reduce the worldwide dependence on fossil-derived feedstocks. At the end of 2016, Novamont announced the opening of the world's first industrial plant dedicated to the production of 1,4-butanediol (1,4-BDO) directly from sugars and through the use of bacteria [1]. Applying the technology developed by Genomatica, based on the action of suitably engineered *Escherichia coli* strain [2,3], the biorefinery was designed to produce 30,000 tons per year of the low-impact bio-alcohol. Already, eight months after the grand opening, the company confirmed that the new plant has met all performance guarantees and runs as planned. 1,4-butanediol is a chemical intermediate which finds wide-scale industrial applications in the production of, e.g., elastic fibers, plastics, or solvents. Its key end-products are tetrahydrofuran (THF), polybutylene terephthalate (PBT), gamma-butyrolactone (GBL), and polyurethanes (PU), among others [4,5]. Until 2016 1,4-BDO was manufactured entirely from petroleum-based feedstocks such as acetylene, butane, propylene, and butadiene. The demand for 1,4-BDO in 2019 was roughly 4.3 million tons, resulting in a market worth approximately US\$5.7 billion. Given the increasing importance of this compound, it is estimated this market will reach more than US\$ 10.3 billion by 2025.

Climate change poses one of the most pressing challenges worldwide and is predominantly caused by an increasing release of greenhouse gases. Carbon dioxide, the most abundant waste gas, is predicted to become a cheap and readily available (in a compressed form) feedstock thanks to the

future implementation of carbon capture, usage and storage (CCUS) technologies. A wide window of opportunities will open for the captured carbon dioxide to be utilized as a raw material in the production of a variety of industrial products and applications.

CCUS is a fast-developing field and many critical reviews on this subject have already been published [6–11]. Recently, Roh et al. not only reviewed the carbon dioxide conversion processes currently under investigation in the literature, but also described relevant gaps and opportunities in the field, giving examples of potential pathways and reaction networks [11]. Based on these ideas, Putra et al. proposed a new route for a production of ethyl levulinate, an alternative fuel additive, from waste carbon dioxide and 1,4-butanediol [12]. This method comprises the synthesis of levulinic acid (a very important platform chemical itself [13]) from the reaction between carbon dioxide and diol, and subsequent esterification of the acid thus obtained with ethanol (Figure 1).

1st step:



2nd step:

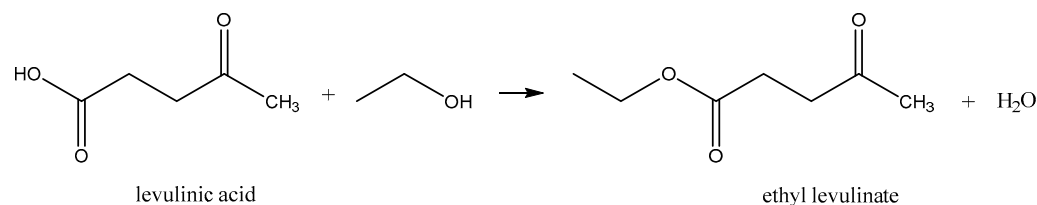


Figure 1. The two-step synthesis of ethyl levulinate from carbon dioxide and 1,4-butanediol.

The authors followed the technical evaluation of the process with an economic and sensitivity analysis and concluded that the process is always profitable provided the ethyl levulinate remains slightly more expensive than the 1,4-butanediol. Nevertheless, due to the lack of reaction data for the first step of levulinic acid formation, several assumptions must be considered. First, to be assured that the production process is commercially viable, it is imperative to find an efficient, eco-friendly, and cost-effective catalyst. Second, the reaction under consideration has a severe equilibrium limitation caused by the formation of high quantities of water, which should be removed from the reaction mixture. In their approach, Putra et al. envisaged a distillation operation [12]. In this work, in order to avoid this energy-intensive step, we investigate the possibility of performing the synthesis in a supercritical carbon dioxide-ionic liquid (CO₂+IL) system. Most ionic liquids can absorb high concentrations of carbon dioxide, while they are not soluble in dense carbon dioxide to any measurable extent [14]. As a consequence, the (CO₂+IL) binary systems are always biphasic with multiple options to adjust their solvent properties, e.g., changing pressure, temperature, or structure of ILs ions, which provides a versatile reaction and separation environment. Coupling ionic liquids with carbon dioxide further decreases the viscosity of the liquid phase, improving diffusivity and mass transfer of compounds [15,16], an important factor in the case of the highly viscous 1,4-butanediol [17]. In our approach we explore the hydrophobic nature of a particular ionic liquid, 1-hexyl-3-methylimidazolium tetracyanoborate [18,19], and investigate its feasibility to remove water from the liquid reaction mixture into the dense carbon dioxide phase, shifting the reaction equilibrium towards the product formation. This study is part of an on-going project in our laboratory and comprises the measurement of vapour-liquid equilibria of multicomponent systems under high carbon dioxide pressures, up to 18MPa, and temperature of 313.2 K.

2. Materials and Methods

2.1. Materials

Ionic liquid used in this work, 1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][B(CN)₄]) (≥ 98.0 % purity), was purchased from Merck KGaA, Darmstadt, Germany, and used without further purification (water content < 300 ppm). Carbon dioxide (99.98 % purity) was supplied by Air Liquide and also used as received. 1,4-butanediol and 1-butanol (GC internal standard) were supplied by Sigma-Aldrich, Algés, Portugal, with purity of 99 and more than 99.7%, respectively. Absolute anhydrous ethanol of 99.9% purity (Carlo Erba, Barcelona, Spain) was used only as a solvent in vapour-liquid equilibrium measurements to wash the lines, and in gas chromatography analysis. All alcohols were dried over molecular sieves with 0.3 nm pore diameter (Fluka), for at least 24h, prior to their use. Distilled water (Diwer Technologies Water max station Type I) was used to prepare particular samples of ternary or quaternary systems.

2.2. Apparatus and Experimental Procedure

A detailed and up-to-date description of the facility and methodology used to measure vapour-liquid equilibrium can be found in the work of Rebocho et al. [20]. Here, only an overview is given. The essence of the apparatus is a high-pressure cylinder-shaped sapphire cell (15 cm of height and 3.2 cm/1.9 cm of external/internal diameter). It is placed inside a thermostatic air bath with a window allowing visualisation of the internal volume. A high-power ventilator ensures a uniform distribution of heat and temperature is measured by the Hart Scientific temperature controller (model 2100) coupled with an RTD probe from the same supplier (model 2622). The pressure in the system is gauged by the Setra pressure transducer (model Model 204/C204), with an accuracy of determination of ± 0.007 MPa. The estimated temperature uncertainty is ± 0.1 K.

A typical experiment started with the removal of all gases from the system by means of a vacuum pump (Edwards, model RV3). A certain amount of liquid sample, with a known composition, was then loaded into the cell and heated up to the required temperature. After temperature was attained, carbon dioxide was compressed and slowly added to the cell up to the desired pressure. In order to accelerate equilibration of liquid and vapour phases, the entire content of the cell was mixed with a magnetic stirrer. Based on the experience gained in previous measurements performed in our laboratory [20–23], two hours are enough to reach equilibrium conditions. Once this happens, samples from gas and vapour phases were withdrawn through two HPLC valves into previously evacuated sample loops, and subsequently expanded to a low-pressure calibrated volume. The amount of CO₂ in each sample was calculated from the measurement of pressure after expansion. In order to ascertain the reproducibility of measurements all experiments were performed at least three times. The average standard deviation of the mole fraction of carbon dioxide is ± 0.0002 for the vapour phase and ± 0.031 for the liquid phase (the quaternary system).

Concentrations of water and alcohol were determined by Karl-Fischer coulometric titration method (Metrohm 831 Karl Fischer coulometer) and chromatography, respectively. The vapour phase samples were analysed in a gas chromatographer equipped with a flame ionization detector (GC-FID) and a ZB-1HT Inferno capillary column (15 m, 0.25 ID, 0.1 film). Helium gas served as the carrier gas and 1-butanol as the internal standard. Liquid phase samples were analysed by HPLC (DIONEX ICS3000) coupled with a refractive index detector, using silica-based Phenomenex Luna C8 column (250 mm $\times$ 4.6 mm, conditions: developing solvent: water/methanol = 70/30, 1 mL/min., 313.2 K). The quantity of the ionic liquid was calculated by volume difference between calibrated sampling loop and experimentally determined amounts of water, carbon dioxide, and diol. The average standard deviation of mole fractions of alcohol, water, and ionic liquid were up to ± 0.009 , ± 0.004 , and ± 0.019 , respectively, for the liquid phase, and ± 0.00005 and ± 0.0001 for the alcohol and water, respectively, in the gaseous phase.

3. Results and Discussion

In order to examine the feasibility of the ionic liquid [hmim][B(CN)₄] (1-hexyl-3-methylimidazolium tetracyanoborate), to work both as a reaction medium and a water-repellent, the phase behaviour of multicomponent systems under high CO₂ pressures was studied. The principal alcohol under investigation in this study was 1,4-butanediol. However, in order to verify the applicability of the proposed strategy to the conversion of different diols, experiments were also performed for 1,2-propanediol (1,2-PDO).

Table 1 presents the vapour-liquid equilibrium data for the quaternary system containing carbon dioxide, 1,4-butanediol, [hmim][B(CN)₄] and water. As expected, the solubility of carbon dioxide in the liquid phase increased with the increasing pressure. Since the system is composed of four components and presents two phases, it has 4 degrees of freedom. Furthermore, the initial concentration of water in the system was 50 mol% with respect to the alcohol to simulate the progress of the reaction. This value was selected assuming the theoretical 50% conversion of diol to levulinic acid. The ratio of ionic liquid to alcohol was set at 0.3 molar, and 1 by weight. The ionic liquid is expected to play a role of a water-repellent, making it possible to separate formed water from the reaction medium, but also of a solvent, bringing the substrates together by enhancing the solubility of gas in the liquid phase.

Table 1. Vapour-liquid equilibrium data for the quaternary (CO₂ +1,4 BDO +[hmim][B(CN)₄] +H₂O) system at 313.2 K¹.

P/MPa	x _{CO2}	x _{1,4-BDO}	x _{IL}	x _{H2O}	y _{CO2}	y _{1,4-BDO}	y _{IL}	y _{H2O}
8	0.324	0.072	0.475	0.129	0.9870	nd	nd	0.0130
10	0.438	0.047	0.396	0.119	0.9842	nd	nd	0.0158
12	0.467	0.042	0.391	0.100	0.9817	nd	nd	0.0183
14	0.551	0.028	0.353	0.067	0.9819	0.00198	nd	0.0161
16	0.616	0.017	0.310	0.057	0.9856	0.00183	nd	0.0126
18	0.646	0.014	0.299	0.041	0.9837	0.00179	nd	0.0145

¹ molar ratio of IL to diol = 0.3, molar ratio of H₂O to diol = 0.5; nd – not detected; u(T) = 0.1 K, u(P) = 0.007 MPa, u(x_{CO2}) = 0.031, u(x_{1,4-BDO}) = 0.009, u(x_{H2O}) = 0.004, u(x_{IL}) = 0.019, u(y_{CO2}) = 0.0002, u(y_{1,4-BDO}) = 0.00005, u(y_{H2O}) = 0.0001.

Tetracyanoborate-based ionic liquids have been proven to have a high, up to 80 mol %, capacity for carbon dioxide dissolution [24]. However, has already been shown, the presence of water can influence the solubility of carbon dioxide in the ionic liquid, depending on the ionic liquid-water affinity (hydrophobic vs. hydrophilic) [25]. Moreover, a small addition of water may lead to a significant change in the phase behaviour of the system containing ionic liquid, alcohol and carbon dioxide, leading to a phase separation [26].

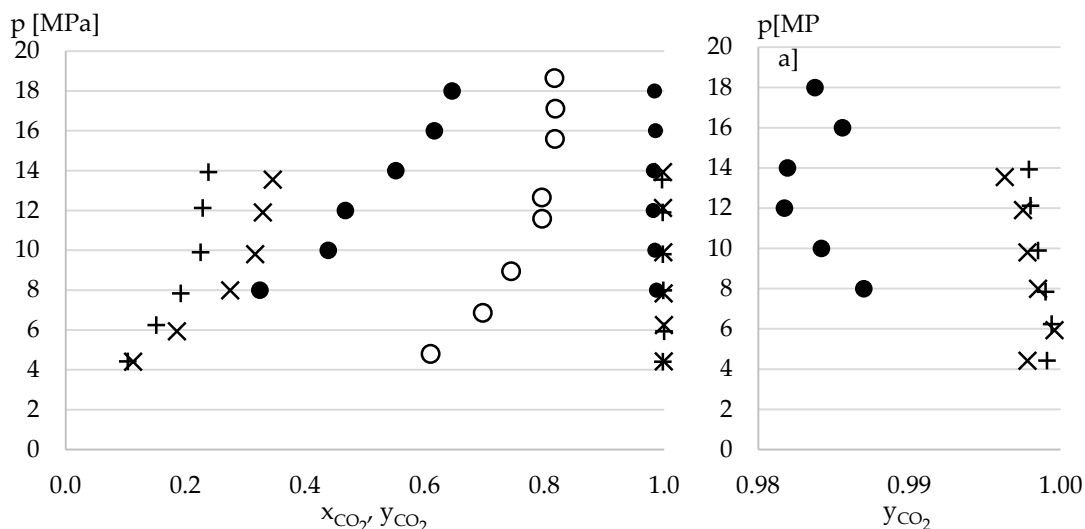


Figure 2. Vapour-liquid equilibrium studies for the quaternary •, $\text{CO}_2 + 1,4\text{-BDO} + [\text{hmim}][\text{B}(\text{CN})_4] + \text{H}_2\text{O}$ [this work] and binary ×, $\text{CO}_2 + 1,2\text{-BDO}$ and +, $\text{CO}_2 + 1,3\text{-BDO}$ (Reproduced with permission from [27] Copyright Elsevier, 2004), ○, $\text{CO}_2 + [\text{hmim}][\text{B}(\text{CN})_4]$ (Reproduced with permission from [24] Copyright Elsevier, 2016) systems, at 313,15 K; the right hand side represents an enlargement of the gas phase regime.

As can be seen in Figure 2, even though the comparison is not straightforward due to a different number of components, the mixture of $[\text{hmim}][\text{B}(\text{CN})_4]$ and 1,4-butanediol in the quaternary system is able to dissolve lower, but still considerable, amounts of carbon dioxide in the liquid phase when compared to the binary ($\text{IL} + \text{CO}_2$) system [24]. In addition to the quaternary system, the binary ($\text{CO}_2 + 1,4\text{-BDO}$) and ternary ($\text{CO}_2 + 1,4\text{-BDO} + [\text{hmim}][\text{B}(\text{CN})_4]$) systems were studied. Unfortunately, it was impossible to take representative liquid samples from these systems due to the high viscosity of 1,4-butanediol.

The vapour-liquid equilibrium data for the ternary ($\text{CO}_2 + 1,4\text{-BDO} + [\text{hmim}][\text{B}(\text{CN})_4]$) system is given in Table 2. The analysis of the gas phase of the binary ($\text{CO}_2 + 1,4\text{-butanediol}$) system revealed that no alcohol passes to this phase in the studied pressure range. Inomata et al. [27] investigated the phase behaviour of isomers, e.g., 1,2- and 1,3-butanediol, and showed that (1,2-butanediol + CO_2) mixture has a smaller coexistence region (as seen in Figure 2). The authors suggested that 1,3-butanediol has less affinity for carbon dioxide due to the two hydroxyl groups located at both ends of the molecule having a larger effective surface area in comparison with $-\text{OH}$ groups of 1,2-butanediol. The term “effective surface area” was introduced in their work in order to distinguish between the behaviour of isomers using the modified group contribution equation of state. The new parameter takes into account the connecting positions of the group species, and not only their type and number, as usually considered by group contribution prediction methods. The longer distance between hydroxyl groups in 1,4-butanediol may suggest the even smaller affinity for CO_2 and explain the absence of this polyhydric alcohol in the gas phase under the conditions studied.

Table 1. Vapour-liquid equilibrium data for the ternary (CO_2 +1,4-BDO+[hmim][B(CN)₄]) system at 313.2 K¹ (data presented refer to the gas phase)

P/MPa	y _{CO2}	y _{1,4-BDO}	y _{IL}
8	1.0000	nd	nd
10	1.0000	nd	nd
12	1.0000	nd	nd
14	1.0000	nd	nd
16	0.9883	0.01168	nd
18	0.9921	0.00795	nd

¹ molar ratio of IL to diol = 0.3; nd – not detected; u(T) = 0.1 K, u(P) = 0.007 MPa, u(y_{CO2}) = 0.0002, u(y_{1,4-BDO}) = 0.00005.

In order to check the versatility of the proposed strategy, analogous vapour-liquid equilibrium measurements were performed for a diol that is more soluble in the dense carbon dioxide phase, i.e., 1,2-propanediol (1,2-PDO). Chyliński et al. [28] studied the solubility of 1,2-propanediol in the gas phase of the binary (CO_2 +1,2-PDO) system in the temperature range 311–333 K and pressures up to 8 MPa. The measured solubility was not higher than 0.04 mol% fraction. Knez and co-workers investigated the solubility at three, higher temperatures (398.2, 423.2 and 453.2 K) and pressures ranging from 2.5 to 55 MPa [29]. The authors determined that the solubility of 1,2-propanediol equals, on average, approximately 20 mol%. Table 3 reports the gas phase mole fractions of particular components obtained in this work for the quaternary (CO_2 +1,2-PDO+[hmim][B(CN)₄]+H₂O) system, at 313.2 K.

Table 2. Vapour-liquid equilibrium data for the quaternary (CO_2 +1,2-PDO+[hmim][B(CN)₄]+H₂O) system at 313.2 K¹ (data presented refer to the gas phase)

P/MPa	y _{CO2}	y _{1,4-BDO}	y _{H2O}
8	0.9877	nd	0.0123
10	0.9744	0.00148	0.0242
12	0.9657	0.00201	0.0324
14	0.9852	0.00239	0.0125
16	0.9806	0.00265	0.0168
18	0.9828	0.00296	0.0142

¹ molar ratio of IL to diol = 0.3, molar ratio of H₂O to diol = 0.5; nd – not detected; u(T) = 0.1 K, u(P) = 0.007 MPa, u(y_{CO2}) = 0.0002, u(y_{1,4-BDO}) = 0.00005, u(y_{H2O}) = 0.0001.

In Figure 3 it can be seen that for both quaternary systems, (CO_2 +1,4-BDO +[hmim][B(CN)₄]+H₂O) and (CO_2 +1,2-PDO+[hmim][B(CN)₄]+H₂O), the amount of water that passes to the light gas phase is higher than that data presented in the literature for the binary (CO_2 +H₂O) system [30]. Thus, the presence of ionic liquid and alcohol influences positively the removal of water from the liquid phase. For the purpose of comparison, the values plotted in Figure reflect the ratio of the water-to-carbon dioxide sampled, at particular conditions, from the gas phase. The initial compositions of the systems investigated comprise the same amounts of diol, ionic liquid, and water.

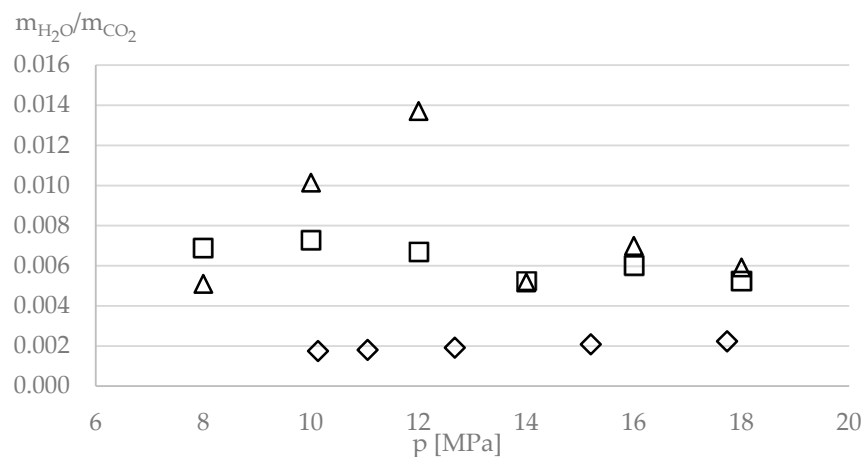


Figure 3. The relative amount of water in the gas phase for the quaternary □, (CO₂ + 1,4-BDO + [hmim][B(CN)₄] + H₂O) or Δ, (CO₂ + 1,2-PDO + [hmim][B(CN)₄] + H₂O) [this work], and the binary ◇, (CO₂+H₂O) (Reproduced with permission from [30] Copyright Elsevier, 1992) systems, at 313.2 K.

Unfortunately, the addition of 50 mol% (with respect to the diol) of water (a polar co-solvent) to the system simultaneously co-extracts the diol to the gas phase. Surprisingly, even the addition of a pure ionic liquid to the 1,4-butanediol causes some removal of the alcohol (only at pressures equal or higher than 16 MPa) from the liquid phase in the ternary (CO₂ + 1,4-BDO + [hmim][B(CN)₄]) mixture (see Table 1). This is an undesired effect for the alcohol transformation that takes place in the liquid phase. Figure 4 shows the composition of diols in the vapour phase for both quaternary systems and the literature data for the binary (CO₂+1,2-PDO) one [28]. Again, for the purpose of comparison, the values plotted reflect the ratio of alcohol-to-carbon dioxide, sampled at particular conditions from the gas phase. Both quaternary systems studied had similar initial compositions concerning the amounts of diol, ionic liquid, and water.

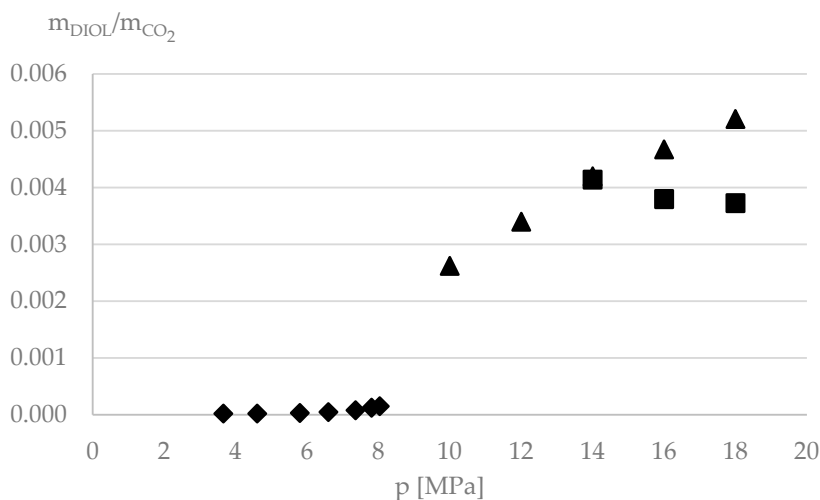


Figure 4. The relative amount of alcohol in the gas phase for the quaternary ■, (CO₂ + 1,4-BDO + [hmim][B(CN)₄] + H₂O) or ▲, (CO₂ + 1,2-PDO + [hmim][B(CN)₄] + H₂O) [this work], and binary ◆, (CO₂+1,2-PDO) (Reproduced with permission from [28] Copyright Elsevier, 1998) systems, at 313.2 K.

Optimum conditions for alcohol conversion are those in which diol and water are in different phases. In Figure 5, for each of the alcohols investigated such favourable reaction conditions are shaded in grey. For the quaternary (CO₂ + 1,4-BDO + [hmim][B(CN)₄] + H₂O) system at 313.2 K and pressures below 14 MPa, 1,4-butanediol remains in the liquid phase and the undesired by-product

(water) is expelled to the gas phase, positively shifting the reaction equilibrium. For the quaternary ($\text{CO}_2 + 1,2\text{-PDO} + [\text{hmim}][\text{B}(\text{CN})_4] + \text{H}_2\text{O}$) system these conditions exist at the same temperature for pressures lower than 10 MPa.

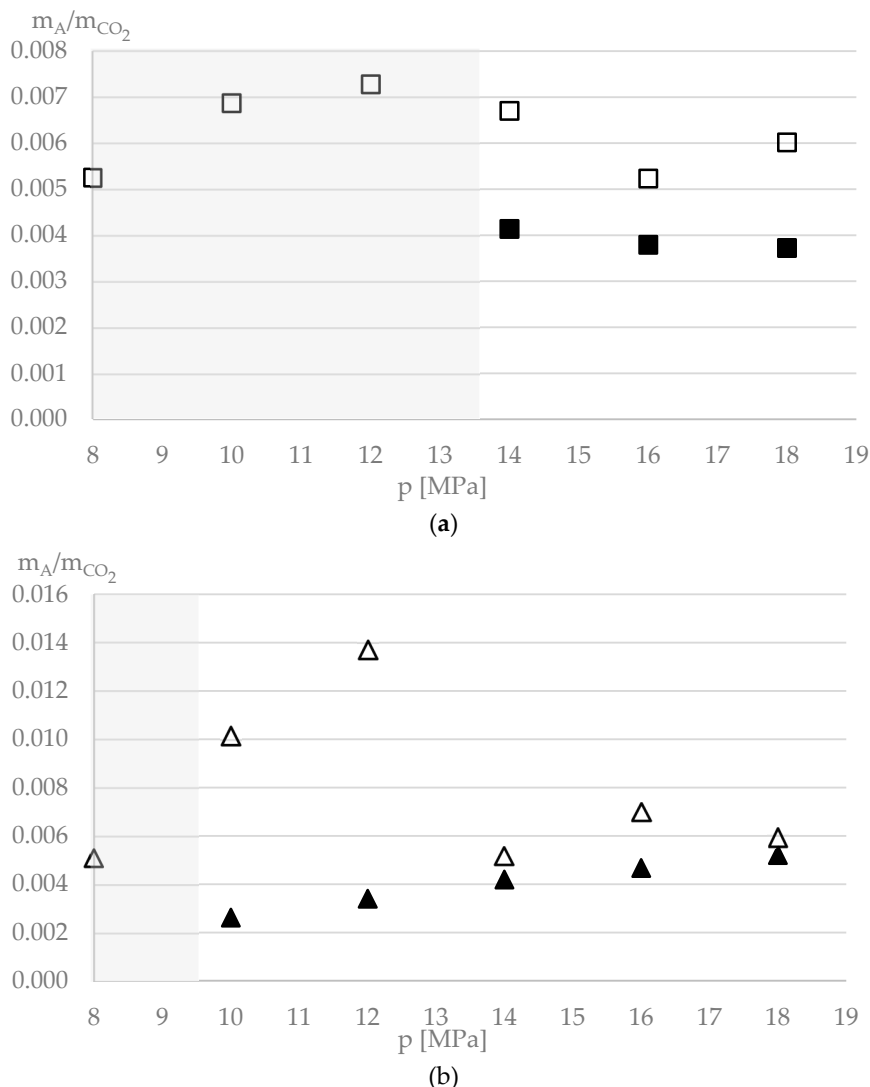


Figure 5. The relative amount of water vs. diol (m_A) in the gas phase of the quaternaries (a) ($\text{CO}_2 + 1,4\text{-BDO} + [\text{hmim}][\text{B}(\text{CN})_4] + \text{H}_2\text{O}$) or (b) ($\text{CO}_2 + 1,2\text{-PDO} + [\text{hmim}][\text{B}(\text{CN})_4] + \text{H}_2\text{O}$) systems at 313.2 K; ■, 1,4-BDO and □, H_2O ; ▲, 1,2-PDO and △, H_2O .

The results obtained in this study serve as a proof of concept that it is possible to use $[\text{hmim}][\text{B}(\text{CN})_4]$ as a reaction medium and water-repellent at the same time. The combination of high-pressure carbon dioxide with ionic liquid can potentially prevent the use of expensive distillation operation in levulinic acid synthesis from 1,4 BDO. In a continuous mode of operation, additional benefits emerge from an unusual, highly asymmetrical phase behaviour of the biphasic ($\text{CO}_2 + \text{IL}$) system. The desired product can be continuously extracted, in this particular case together with water, without any solvent cross-contamination keeping ionic liquid with a catalyst inside a reactor for reutilisation [31,32]. The approach presented certainly still requires an economic evaluation. Although it looks very promising, an overall cost associated with the usage of large volumes of ionic liquid may limit its application. Nonetheless, it is expected that the cost of ionic liquids will steadily decrease, along with the increasing demand for them. Plus, in ($\text{CO}_2 + \text{IL}$) systems ionic liquid can be easily recycled and reused, minimising the relevance of its initial cost.

4. Conclusions

This work proposes a high-pressure biphasic (CO₂+hydrophobic IL) system as an effective reaction media for carrying out levulinic acid production from biomass-derived 1,4-butanediol. The reaction under investigation has a severe equilibrium limitation caused by the formation of high quantities of water as a by-product. Vapour-liquid equilibrium results now obtained for the quaternary systems (diol + IL + CO₂ + water) show a considerable increase in the water mol fraction of the CO₂ rich-gaseous phase. Tetracyanoborate-based ionic liquid proved to be capable of simultaneously enhancing the carbon dioxide concentration in a liquid phase and acting as a water-repellent agent.

Author Contributions: M.E. Zakrzewska and A.V.M. Nunes conceived and designed the experiments; M.E. Zakrzewska and A.B. Paninho performed the experiments; M.E. Zakrzewska, A.V.M. Nunes and M.F.C. Guedes da Silva analyzed the data; M.E. Zakrzewska wrote the paper and A.V.M. Nunes and M.F.C. Guedes da Silva revised it; A.V.M. Nunes and M.F.C. Guedes da Silva acquired the financial support for the project. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Fundação para a Ciência e Tecnologia FCT/MCTES through project PTDC/EQU-EPQ/31926/2017, UID/QUI/50006/2019 of Associate Laboratory for Green Chemistry- LAQV and UIDB/00100/2020 of Centro de Química Estrutural. A.V.M. Nunes is thankful to FCT/MCTES for contract IF/01374/2014. M.E. Zakrzewska is thankful to FCT/MCTES for the postdoctoral grant SFRH/BPD/122655/2016. The NMR spectrometers at FCT NOVA are part of Rede Nacional de RMN (PTNMR), supported by Fundação para a Ciência e a Tecnologia (ROTEIRO/0031/2013 - PINFRA/22161/2016) (co-financed by FEDER through COMPETE 2020, POCI, and PORL and FCT through PIDDAC).

Conflict of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results

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