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Liquid–liquid equilibria for the systems ethylene carbonate + ethylene glycol + glycerol; ethylene carbonate + glycerol carbonate + glycerol and ethylene carbonate + ethylene glycol + glycerol carbonate + glycerol at catalytic reacting temperatures

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ABSTRACT

The measurements of the liquid–liquid equilibria implied in the reaction system to yield glycerol carbonate from ethylene carbonate and glycerol were performed. First, data for the ternary systems consisting of ethylene carbonate + ethylene glycol + glycerol as well as ethylene carbonate + glycerol carbonate + glycerol at 313.2, 318.2 and 323.2 K and atmospheric pressure were acquired. Furthermore, the quaternary equilibrium involving both products of the reaction, i.e., ethylene carbonate + ethylene glycol + glycerol carbonate + glycerol, was evaluated under the same conditions. All the data experimental data were correlated with the NRTL model with root-mean square deviations of about 0.03 for all the systems tested.

Keywords: Glycerol carbonate; Ethylene carbonate; Ethylene glycol; Glycerol; Liquid–liquid equilibrium; NRTL

1. Introduction

The plethora of glycerol available as a consequence of the marked development of the biodiesel industry, particularly throughout the last decade, has provoked the need for the valorization of such formerly profitable by-product of the process. Under such scenario, intensive research has been undertaken in order to obtain valuable products from this promising resource (Pagliaro et al., 2009; Pagliaro and Rossi, 2008). Among the products subject to experimental efforts are solketal, 1,2-propanediol or glycerol carbonate (GC) (Behr et al., 2008; Zhou et al., 2008).

GC, systematically known as 4-(hydroxymethyl)-1,3-dioxolan-2-one has been addressed as a component with potential and promising applications in assorted fields. Among those can be mentioned its utilization as a general purpose solvent (Benoit et al., 2010; Lameiras et al., 2011), electrolyte liquid carrier in Li and Li-ion batteries (Chen et al., 2002), blowing agent in polyurethane foams formation (Gillis et al., 1997) or in gas separation membranes (Kovvali and Sirkar, 2002). Simultaneously, its usefulness as feedstock towards the synthesis of further relevant products has also been reported, particularly polymeric compounds (Iaych et al., 2011; Mouloungui and Pelet, 2001; Rokicki et al., 2005).

Multiple reactions have been reported in literature approaching the generation of GC in substitution of the formerly used phosgenation of glycerol. Pressurized addition of CO (Hu et al., 2010) and CO_2 to glycerol (Ezhova et al., 2012; George et al., 2009) (Gly) or its reaction with urea (Li et al., 2006; Rubio-Marcos et al., 2010) are among the examples. Transesterification of an organic carbonate with glycerol is one of the most followed routes and presents most advantageous operational aspects compared to the aforementioned reactions, for atmospheric pressure suffices and temperatures are significantly lower than those reported for the glycerolysis of urea (Sonnati et al., 2013). Aliphatic

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Nomenclature

Latin characters

HPLC	high-performance liquid chromatography
K	distribution ratio (as defined by Eq. (2))
LLE	liquid–liquid equilibria
NRTL	non-random two-liquid model
OF	objective function
Q	refers to the quaternary system {EC + EG + GC + Gly}
rmsd	root-mean square deviation
T1	refers to the ternary system {EC + EG + Gly}
T2	refers to the ternary system {EC + GC + Gly}

Greek symbols

α_{ij}	non-randomness binary interaction parameter as defined in the NRTL method
Δg_{ij}	binary interaction parameter as defined in the NRTL method

Components

EC	ethylene carbonate
EG	ethylene glycol
GC	glycerol carbonate
Gly	glycerol

Subscripts

I, II	relative to the glycerol-rich and ethylene carbonate-rich phases, respectively
2	in Eq. (2), relative to cosolvents EG (system T1), GC (system T2), EG + GC (system Q)

organic carbonates such as dimethyl carbonate (DMC) (Jiabo and Tao, 2010; Kim et al., 2007; Ochoa-Gomez et al., 2009) or diethyl carbonate (Alvarez et al., 2010; Patel et al., 2009) have been employed to such aim; however, the use of cyclic carbonates, such as ethylene carbonate (EC) has been paid less attention to, despite the by-product of the reaction being ethyleneglycol (EG), widely used as antifreeze to cite only an example (Climent et al., 2010; Cho et al., 2010).

The goal of the present work is to study the liquid–liquid equilibrium (LLE) of the existing systems for the reaction between EC and Gly (represented in Fig. 1), namely: {EC + EG + Gly} (system T1 from this point forward); {EC + GC + Gly} (T2) and the quaternary system {EC + EG + GC + Gly} (Q).

The LLE for similar systems involving the presence of glycerol have already been researched by several authors. First, LLE studies involving its presence as part of the biodiesel production process have been made, covering the equilibria of ternary systems consisting of methylesters of diverse origins + glycerol + methanol (do Carmo et al., 2014; Lee et al., 2010) or ethanol (Basso et al., 2012; de Azevedo Rocha et al., 2014; do Carmo et al., 2014), of importance in the separation of the products of the process. On the other hand, a series of other papers have reported on the LLE existing in systems deriving from processes aimed at the valorization of glycerol. Equilibria among acetone + solketal + glycerol (Esteban et al., 2014a) or acetone + water + glycerol (Krishna et al., 1989) are of interest in the synthesis of solketal, another valuable product from glycerol. Also, ternary equilibria derived from the etherification of glycerol have been described, including different combinations of glycerol and mono-, di- and tri-tert-butylethers (Liu et al., 2014). Wang and Lu studied the system consisting of dimethyl carbonate + methanol + glycerol, also existing in another route to synthesize glycerol carbonate (Wang and Lu, 2012). More recently, this study was profoundly extended to cover the equilibria for the systems comprising dimethyl carbonate + glycerol carbonate + glycerol and the quaternary system dimethyl carbonate + methanol + glycerol carbonate + glycerol (Esteban et al., 2014b), much like it is herein proposed.

The effect of the separate and joint presence of the products will be assessed throughout the reaction initially consisting of an almost immiscible system evolving into a single phase system working with mixtures simulating the development of the reaction. The temperature interval selected for this study was 313.2 K, below which EC is in solid state, and 323.2 K temperature at which this reaction has been reported to take place (Climent et al., 2010). Assays were conducted at atmospheric pressure.

LLE data regression was realized utilizing the non-random two liquid (NRTL) model, common tool for fitting in all of the aforementioned references, with the corresponding binary interaction parameters being retrieved after satisfactory fitting.

2. Materials and methods

2.1. *Materials*

The following reagents were used throughout the experimental procedure: extra pure Gly (assay grade 99.88%) from Fischer Chemical; EG (99.8%, anhydrous) from Sigma–Aldrich; GC (purity ≥ 99.5%) from Sigma–Aldrich and EC (synthesis grade, purity > 99%), from Scharlau. Citric acid ACS reagent (purity ≥ 99.5%) by Sigma–Aldrich was employed as an internal standard in HPLC analyses.

2.2. *Apparatus and procedure*

Hermetically sealed 25 mL round-bottom flasks were used to perform LLE experiments. Agitation of the feed mixture was magnetic provided by an IKA Yellow Line TC3 heating and stirring device. Appropriate temperature (bath temperature control oscillation of ±0.05 K) for each experiment was reached by means of a glycerol bath heated.

Feed samples were weighted in a Kern and Sohn ABS-220-4 analytical balance with a precision of 0.0001 g. Energetic stirring of the different feeds was performed for 6 h, enough to ensure total mass transfer between the liquid phases after which separation of the light (Gly-rich, I) and heavy (EC-rich, II) phases was performed. First, settling of the phases was allowed for 3 h. After such period, separation of phases was ensured and even further aided using a thermostatic Sigma 4–16 K centrifuge in order to keep the adequate temperature. Samples were taken from each phase for analysis. Data were obtained by performing triplicate experiments.

2.3. *Analytical methodology*

Samples from each phase were diluted in a 5 g/L citric acid (internal standard) solution for HPLC analysis. Each component was analyzed with a JASCO 2000 series device, with a refraction index detector. A constant flow rate of 0.5 mL/min of acid Milli-Q water (0.005 N H_2SO_4) was used as mobile phase. Separation was realized using a Rezex ROA-Organic Acid H+ (8%) column (150 × 7.80 mm) at 60 °C.

3. Results and discussion

3.1. *LLE experimental data*

Tables 1–3 compile the global molar composition of each individual experiment. Three distinct cases were evaluated, namely: EG is the only cosolvent (system T1); only GC is present (system T2); and finally, both EG and GC are used