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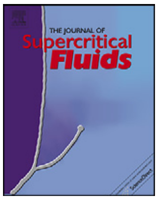

High-pressure phase equilibrium data for the L-lactic acid + (propane + ethanol) and the L-lactic acid + (carbon dioxide + ethanol) systems

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ABSTRACT

Biodegradable polymers have received increased attention due to their potential applications in the medicine and food industries; in particular, poly(L-lactic acid) (PLA) is of primary importance because of its biocompatibility and resorbable features. Recently, the synthesis of this biopolymer through the enzyme-catalyzed ring-opening polymerization of L-lactic acid in a compressed fluid has been considered promising. The aim of this work was to report the phase equilibrium data (cloud points) of the L-lactic acid + (propane + ethanol) and the L-lactic acid + (carbon dioxide + ethanol) systems. The phase equilibrium experiments were conducted in a variable-volume view cell employing the static synthetic method. These experiments were conducted in the temperature range of 323.15–353.15 K and at pressures up to 25 MPa; the mass ratio of ethanol to either CO_2 or propane was maintained at 1:9. The L-lactic acid + (propane + ethanol) system exhibited vapor–liquid, liquid–liquid and vapor–liquid–liquid transitions, whereas the L-lactic acid + (carbon dioxide + ethanol) system only exhibited liquid–liquid type transitions.

1. Introduction

The production of high-purity biodegradable polymers is an important issue because of the relevant applications of these polymers in the medicine and food industries. In particular, poly(L-lactic acid) (PLA) is of primary importance mainly due to the biocompatibility and resorbable features of this polymer [1]. Lactic acid, which is used as a raw material in the synthesis of PLA, is one of the simplest chiral molecules and is usually found as a mixture of two stereoisomers (L- and D-lactic acid) [2,3].

Another route for PLA synthesis comprises the ring-opening polymerization of lactide, which is the cyclic diester of lactic acid, i.e., 2-hydroxypropionic acid, at high pressures [4,5]. In fact, high-pressure (supercritical fluid) technology has recently gained increased attention in the design of processes that produce biodegradable polymers, such as the synthesis of polyesters [6] and poly(L-lactide) microspheres [7], the lipase-catalyzed synthesis of poly(L-lactide) [8], the polymerization of ε-caprolactone [9–11], the chemoenzymatic synthesis of poly(ε-caprolactone-*block*-methyl methacrylate) [12] and the production of PDLLA/HA composite foams [13].

Knowledge of the phase equilibria of the reaction system, which is composed of the monomer, the biodegradable polymer and the supercritical/compressed solvent, as well as the possible presence of a co-solvent, plays a crucial role in the development and optimization of the polymerization reaction because the location of the phase boundary of the system is important for the establishment of appropriate reaction conditions [14,15].

The use of compressed gases as solvents for enzyme-catalyzed reactions may be a promising route for the complete elimination of solvent traces from reaction products and can be advantageous in terms of energy consumption, easier product recovery, adjustable solvation ability and the reduction of side reactions. It is well known that carbon dioxide is used as the solvent in many applications, but its non-polarity may lead to a very poor solubility of monomers and polymers. In addition, the hydrophilic characteristics of CO_2 over wide pressure ranges may negatively affect the activity of enzymes [16–20]. Nevertheless, it has been shown that pressurized propane may be suitable as a reaction medium for enzyme-catalyzed bioconversions because near-critical propane presents a dielectric constant that is comparable to that of CO_2 [21] and because the phase transition pressures that are generally found in systems composed of high-molecular-weight compounds and propane are much lower than those found in systems that include CO_2 [22,23].

Phase equilibrium data of the L-lactide monomer and of L-lactic-acid-based polymers of low molecular weight in supercritical

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carbon dioxide have been reported [24,25]. However, to our knowledge, data on the phase behavior of L-lactic acid and carbon dioxide in the presence of a co-solvent are not found in the literature. Taking into account the fact that the addition of a co-solvent may considerably decrease the phase transition pressures and enhance the mass transfer of the system, ethanol was used as a co-solvent in this work because it is a “green”, food-grade GRAS solvent that can be produced from renewable sources. Consequently, this study investigates the phase equilibrium behavior of the L-lactic acid + (propane + ethanol) and the L-lactic acid + (carbon dioxide + ethanol) systems.

2. Experimental

2.1. Materials

L-lactic acid (CAS # 79-33-4) was purchased from Sigma–Aldrich (minimum purity of 98%), used without further purification and stored under a nitrogen atmosphere. The monomer water content was measured using the Karl Fischer titration method (Mettler Toledo Model DL 50) and found to be 1.068 wt.%. The solvents used were carbon dioxide (mass fraction purity of 99.9% in the liquid phase) and propane (99.5% purity), both of which were purchased from White Martins S.A. Ethanol was used as a co-solvent (Vetec, 99.8% purity).

2.2. Phase equilibrium apparatus and procedure

The phase equilibrium experiments were conducted employing the static synthetic method in a high-pressure variable-volume view cell. The experimental apparatus and procedure have been described in detail in a variety of studies [14,15,26–31] and extensively validated [32–34]. The experimental apparatus was employed to conduct the experiments in the temperature range of 323.15–353.15 K and at pressures up to 25 MPa; the mass ratio of ethanol to either CO_2 or propane was maintained constant at 1:9. The overall mass fraction of the (CO_2 + ethanol) mixture was varied from 0.930 to 0.990 at intervals of 0.010, whereas the overall mass fraction of the (propane + ethanol) mixture was varied from 0.950 to 0.990 at intervals of 0.005. The uncertainty in the pressure measurements was approximately 0.03 MPa, whereas the uncertainty in the temperature of the mixture inside the cell was 0.1 K. Based on the uncertainty in the CO_2 and propane loadings and in the heaviest weighing of the compounds, the uncertainty in the global composition of the mixture was estimated to be lower than 0.5% of the total weight.

3. Results and discussion

Fig. 1 presents the pressure–temperature diagram obtained for the (propane + ethanol) + L-lactic acid system for overall mass fractions of the (ethanol + propane) mixture of 0.950 and 0.955. As shown in the figure, this system was found to exhibit both vapor-liquid-liquid (VLLE) and liquid–liquid (LLE) phase transitions (Table 1). In addition, an increase in the temperature clearly leads to a reduction in the LLE immiscibility region and the transition pressure values with a progressive disappearance of the three-phase VLLE coexistence curve. This behavior is characteristic of UCST (Upper Critical Solution Temperature) phase transitions, in which an increase in the temperature leads to a decrease in the pressure transition values. Moreover, some scattering in the VLLE data is expected because uncertainties in the pressure measurements are unavoidable.

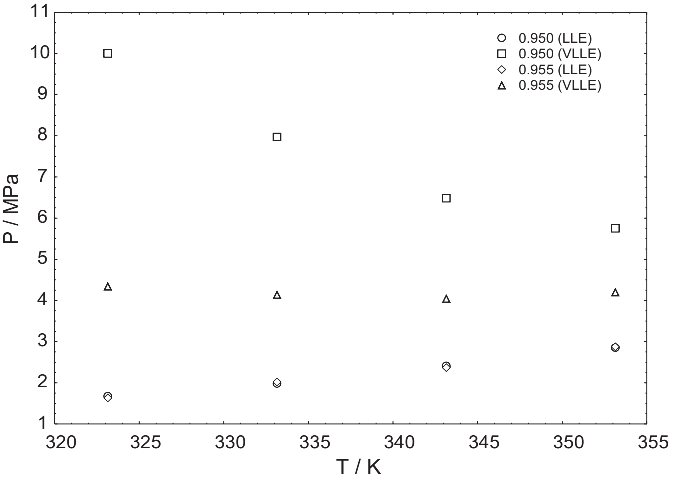

Fig. 1. Pressure–temperature diagram of the (propane + ethanol) + L-lactic acid system for overall mass fractions of the (propane + ethanol) mixture of 0.950 and 0.955.

Fig. 2 shows the pressure–temperature diagram of the (propane + ethanol) + L-lactic acid system for overall mass fractions of the (ethanol + propane) mixture between 0.960 and 0.990. As shown in the figure, vapor–liquid bubble point (VLE-BP) transitions (Table 1), which are characterized by the formation of bubbles from the mixture in the top of the equilibrium cell during depressurization, were recorded. The figure also shows that an increase in the temperature results in an increase in the system pressure.

Fig. 3 depicts the pressure–composition diagram for the (propane + ethanol) + L-lactic acid system in the temperature range of 323.15–353.15 and at pressures up to 10 MPa. As shown, all of the overall mass fraction of the solvent mixture (propane + ethanol) exhibits the presence of a vapor–liquid bubble point (VLE-BP) phase transition. An acceptable scattering of the pressure values was also observed in the VLLE data.

As shown in Figs. 4 and 5, the behavior of the (carbon dioxide + ethanol) + L-lactic acid system was also investigated in the temperature range of 323.15–353.15 K and at pressures up to approximately 25 MPa. As shown, the liquid–liquid phase separation (Table 2) is characterized by a carbon dioxide-rich phase, which is thus poor in monomer, and an organic-solvent-rich phase (monomer-rich phase). In this system, which exhibits LCST behavior, an increase in the temperature results in the expansion of the system. In simple terms, the anti-solvent action of carbon dioxide

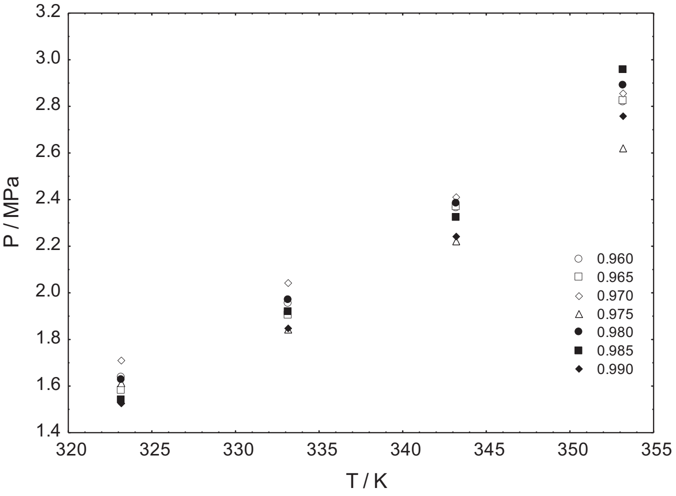

Fig. 2. Pressure–temperature diagram of the (propane + ethanol) + L-lactic acid system for overall mass fractions of the (propane + ethanol) mixture of 0.960 and 0.990 (VLE-BP).