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Phase behaviour of pseudoternary system (carbon dioxide + ω-pentadecalactone + dichloromethane) at different dichloromethane to ω-pentadecalactone mass ratios

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ABSTRACT

Experimental phase equilibrium data for the pseudoternary system involving (carbon dioxide + ω-pentadecalactone + dichloromethane) have been measured in order to provide fundamental information to conduct the polymerization reaction in supercritical carbon dioxide medium. The experiments were performed using a variable-volume view cell over the temperature range from 313 K to 343 K, system pressure between 3.6 MPa and 19.4 MPa and different mass ratios of dichloromethane to ω-pentadecalactone (0.5:1, 1:1 and 2:1). Phase transitions of vapour-liquid (bubble and dew point), liquid-liquid and vapour-liquid-liquid types were observed. The experimental results were modelled using the Peng-Robinson (PR) equation of state with the Wong-Sandler (PR-WS) mixing rule, providing a good representation of the experimental phase equilibrium data.

1. Introduction

Recently, the polymerization of macrolactones has been studied as an alternative for the synthesis of biodegradable polyesters [1–3]. Polyesters produced from macrolactones find useful applications in the biomedical area due to its good mechanical and biocompatible properties [4,5]. Among these polyesters, poly (ω-pentadecalactone) is a semicrystalline polymer obtained from monomers as pentadecanolide or ω-pentadecalactone (ω-PDL) [1].

The ω-pentadecalactone is a fragrance ingredient that can be used in many compounds. It can be found in large amounts in nature in *Angelica archangelica L.* root oil. The worldwide volume of use for ω-pentadecalactone is around (100–1000) metric tons per year [6,7]. The poly(ω-pentadecalactone) (PPDL) is a highly crystalline polyester having a melting point around 100 °C, and a long string of methylene groups, and therefore, showing similar structure to polyethylene [8]. Crystallization behaviour and mechanical properties of poly(ω-pentadecalactone) are similar to that of linear high density polyethylene (HDPE), with the advantage of being degradable due to the presence of hydrolysable ester bonds in the polymer backbone [3].

Several studies in the literature use toxic solvents for the reaction polymerization medium [8–11]. A good candidate for replacing these toxic solvent can be supercritical carbon dioxide ($scCO_2$), a low cost, non-toxic and non-flammable solvent [12]. $ScCO_2$ presents transport properties that can accelerate the mass transfer in enzymatic reactions and some studies show that the use of supercritical fluids can improve the stability and enzymatic activity after a pre-treatment prior the organic reaction [13,14]. In fact, the high pressure technology has gained much attention in the production process of biodegradable polymers such as polyesters catalyzed by enzymes [12,15–17].

In this context, the knowledge of phase behaviour involving the components (supercritical fluid, monomers, co-solvents, polymers) is very important in order to understand better the several aspects (mass transfer, particle size, polydispersity index, *etc.*) and for the analysis and proper interpretation of the polymerization reaction [18,19]. Very recently, high pressure phase equilibrium data of ω-pentadecalactone in supercritical carbon dioxide using chloroform as co-solvent have been reported by Rebelatto et al. [20] and Polloni et al. [21] investigated the enzyme-ring opening polymerization (e-ROP) of ω-pentadecalactone using supercritical

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carbon dioxide as solvent and dichloromethane and chloroform as co-solvents in the reaction media. Such authors observed that polymerization using dichloromethane as co-solvent showed higher reaction yields compared to those found when only $scCO_2$ was employed as solvent. Furthermore, dichloromethane has already been used successfully in the production of biodegradable materials [22,23].

In order to evaluate the system behaviour with the addition of another co-solvent, the objective of this work was to investigate the use of dichloromethane as co-solvent to the system (carbon dioxide + ω-pentadecalactone) at different dichloromethane to monomer mass ratios (0.5:1; 1:1 and 2:1). In addition, the PR-EoS with Wong-Sandler (PR-WS) mixing rule was employed to represent the experimental phase equilibrium data.

2. Experimental

2.1. Materials

The solvent carbon dioxide (0.999 mass fraction in the liquid phase) was purchased from White Martins S.A. (Brazil) and dichloromethane was used as a co-solvent (Sigma-Aldrich, United States of America, 0.998 mass fraction purity). The monomer ω-pentadecalactone, (1-oxa-2-cyclohexadecanone, (CAS number 106-02-5) was purchased from Sigma-Aldrich (United States of America, minimum fraction purity of 0.980), used without further purification and stored under nitrogen atmosphere. The water content was measured by the Karl Fischer titration method (Mettler Toledo, model DL 50) resulting in 2.1 wt% for the ω-pentadecalactone. Table 1 contains the molecular formula, provenance, purification method and purity of all components used in this work.

2.2. Phase equilibrium apparatus and procedure

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 [20,24–29] and was extensively validated [26,27].

For evaluation of the effect of dichloromethane on the phase behaviour of the system investigated, the pseudoternary system (carbon dioxide + ω-pentadecalactone + dichloromethane) was treated as a pseudobinary system {carbon dioxide (1) + ω-pentadecalactone (2)}, *i.e.*, in dichloromethane free-basis, at three different mass ratios of dichloromethane to ω-pentadecalactone. The experimental phase equilibrium data were obtained in the temperature range of 313 K to 343 K and pressures up to 19.4 MPa; the investigated mass ratio of dichloromethane to ω-pentadecalactone was kept constant at 0.5:1, 1:1 and 2:1, corresponding to the following mole ratios: 1.42:1, 2.83:1 and 5.66:1, respectively. The overall mass fraction (w'_1) of the pseudoternary system {carbon dioxide (1) + ω-pentadecalactone (2) + dichloromethane (3)}, in dichloromethane free-basis, was varied from 0.3524 to 0.9733; 0.3551 to 0.9735 and 0.3827 to 0.9478 for the mass ratios of dichloromethane to ω-pentadecalactone of 0.5:1, 1:1, 2:1, respectively.

3. Thermodynamic modelling

The thermodynamic model used to represent the experimental data obtained in this work was previously reported [23–25]. Thermodynamic modelling was performed with the Peng-Robinson equation of sate (PR-EoS) using the Wong-Sandler (WS) mixing rule [30]. For the calculation of mole excess Gibbs energy [$g^E = f(T,P,x)$] in the PR-WS model, it was adopted the NRTL activity coefficient model [30], fitting the following binary interaction parameters to the experimental data: Δg_{ij}, Δg_{ji}, α_{ij} and k_{ij} in the PR-WS model. Due to the considerable water content in the PDL – about 2.1 wt% or 22.25% on molar basis, it was chosen to consider the water present in the ω-pentadecalactone taking it into account as a component of the system in the modelling. Thus, the pseudoternary systems were considered quaternaries.

Binary interaction parameters were estimated for the quaternaries systems throughout minimizing a least square objective function (Eq. (1)) of experimental and calculated pressures using the Nelder-Mead Simplex method [31]. In order to calculate the saturation pressure of vapour-liquid (bubble or dew points) and liquid-liquid equilibrium, a FORTRAN computation code was implemented as presented by Ferrari et al. [32],

$$OF = \sum_{i=1}^{Nobs} \left(P_i^{exp} - P_i^{cal}\right)^2 \quad (1)$$

where *Nobs* denotes the number of observations, P^{cal} and P^{exp} represent the calculated and experimental pressure values, respectively.

The Lyndersen method [33] was used to calculate the critical properties of ω-pentadecalactone, and the acentric factor was estimated by the definition using recent experimental vapour pressure reported in the literature [34]. In addition to vapour pressure experimental data, the Antoine equation was employed to correlate the measured values,

$$\ln(P^{sat}/Pa) = A - B/(T/K + C) \quad (2)$$

where P^{sat} is the saturation pressure (Pa) at the temperature T (K), and A, B, and C are adjustable parameters (values given in Table 2). In this table is also reported the correlation coefficient, R, obtained by fitting Eq. (2) to the experimental data, through the minimization of the following objective function (OF):

$$OF = \sum_i \left[\ln\left(P^{exptl}\right) - \ln\left(P^{calcd}\right)\right]_i^2 \quad (3)$$

Pure component properties for carbon dioxide, dichloromethane, ω-pentadecalactone and water are presented in Table 3.

Thermodynamic modelling of quaternaries systems were performed fixing the previous binary parameters obtained from the ternary system (CO_2 + ω-pentadecalactone + water) (*i.e.*, binary

Table 2
Vapour-pressure Antoine's constants (Eq. (1)) for ω-pentadecalactone.

A[b]	B[b]	C[b]	R[a]
16.85246	3063.95	-142.864	0.999

[a] Correlation coefficient.
[b] Calculated from the experimental vapour pressure data [34].

Table 1
Chemical name, molecular formula, provenance, purification method and purity of the materials used (purity provided by suppliers).

Chemical Name	Molecular formula	Provenance	Purification method	Minimum mass fraction purity
[a]ω-pentadecalactone	$C_{15}H_{28}O_2$	Sigma-Aldrich	None	0.980
Dichloromethane	CH_2Cl_2	Sigma-Aldrich	None	0.998
Carbon dioxide	CO_2	White Martins S.A.	None	0.999

[a] 1-oxa-2-cyclohexadecanone.