

DETERMINATION EQUILIBRIUM DATA LIQUID-VAPOR FOR HIGH PRESSURE SYSTEMS INVOLVING CARBON DIOXIDE + SOLKETAL + OLEIC ACID

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ABSTRACT – This paper reports experimental phase equilibrium data for the systems {CO₂(1)+ solketal(2)} and {CO₂(1) + solketal(2) + oleic acid(3)}. The phase transition pressures measurements for ternary mixtures were carried out by injecting a known amount of carbon dioxide into a mixture with fixed molar ratios of the two other components [0.75 solketal + 0.25 oleic acid]. A variable-volume cell with front window was used for obtaining experimental data. The temperature range from 308 to 338 K and pressures up to 20 MPa was obtained. Bubble point conditions were measured for the binary system {CO₂(1) + solketal(2)}, whereas bubble and dew point conditions were measured for the ternary system {CO₂(1) + solketal(2) + oleic acid(3)}.

1. INTRODUÇÃO

Monoacyl glycerides (MAGs) can be used as emulsifiers and stabilizers in the food and pharmaceutical industries (Camacho *et al.*, 2006; Sein *et al.*, 2002). These substances have a polar headgroup and a nonpolar hydrocarbon chain, and they show amphiphilic properties (Ganem-Quintanar *et al.*, 2000). Among their desirable properties as food emulsifiers, they are nontoxic, biodegradable, and biocompatible (Chen *et al.*, 1999; Kulkarni *et al.*, 2011). Their production usually occurs by glycerolysis of glycerol and oil, fat, or fatty acid (Hartel, 2008) via esterification of free fatty acids (FFAs) with glycerol (Macierzanka and Szelag, 2004) or by the hydrolysis of triglycerides in the presence of a chemical catalyst. These molecules are composed of two distinct parts: one that is soluble in a specific fluid (lyophilic) and one that is insoluble (lyophobic) (Holmberg *et al.*, 2003).

Monoolein (a monoglyceride of oleic acid) is one such MAG. In recent decades, the number of works involving its production increased considerably, certainly connected to the many industrial applications of this lipid, as also reflected in the large number of patents reported (Kulkarni *et al.*, 2011). Glycerol, which is used in the synthesis of monoolein, is a nontoxic, biodegradable compound whose relevance as a chemical is recognized worldwide, with many applications in the pharmaceutical, polymer, and food sectors (Wang *et al.*, 2001; Jerome *et al.*, 2008). Glycerol is a byproduct of the transesterification of oils for biodiesel production and is widely available. As the biodiesel industry grows, there will be more glycerol than the existing market can absorb (Ortiz *et al.*,

2013; Ozorio *et al.*, 2012). Thus, many current studies are focused on transforming glycerol into other chemicals by various catalytic processes. One of them is the acetalization of glycerol for production of 1,2-isopropylidene glycerol, also known as solketal (Reddy *et al.*, 2011). Solketal is a primary alcohol in which the formed acetal blocks the central hydroxyl group and one of the terminal hydroxyl groups (Monti *et al.*, 2008). It is used in the synthesis of many compounds, such as monoglycerides, diglycerides, glyceryl phosphates, and prostaglandins (Itabaiana *et al.*, 2012; Machado *et al.*, 2011; Molinari *et al.*, 2007). Solketal production can also occur in good yields by condensation reactions of glycerol and acetate using a homogeneous acid catalyst (Suriyaprapadilok and Kitiyanan, 2011) using heterogeneous catalysts (Ferreira *et al.*, 2010) and under supercritical conditions (Royon *et al.*, 2011). Several authors have sought alternative production methods via reactions in the absence of solvents, using clinoptilolite zeolite as a catalyst at elevated temperatures (Akgul and Karabakan, 2010), enzymatic esterification by lipase immobilized on *Penicillium camemberti* SiO₂-PVA in a continuous packed-bed reactor (Freitas *et al.*, 2011) and noncatalytic reaction in supercritical CO₂ (Moquin and Temelli, 2008). All of these authors used glycerol and oleic acid as substrates for the reaction.

Carbon dioxide has been explored as supercritical solvent for the extraction of bioactive materials and the synthesis of new products as it has mild critical temperature and critical pressure and is nontoxic and nonflammable (Marr and Gamse, 2010; Akin and Temelli, 2012; Al-Darmaki *et al.*, 2011). The solubility of reactants is an important factor for the occurrence of a chemical reaction. Therefore, knowing the effect of temperature, pressure, and composition on the phase behavior of a reaction system is key for determining the most favorable process conditions (Hong *et al.*, 2010; Laudani *et al.*, 2009). In particular, obtaining monoolein through esterification in supercritical CO₂ using solketal as the substrate instead of glycerol has not been investigated to date.

To deepen the understanding of this new monoolein synthesis technique, it is important to have phase equilibrium data for selected binary and ternary systems. Thus, this paper reports equilibrium data for the binary system {carbon dioxide (1) + solketal (2)} and the ternary system {carbon dioxide (1) + solketal (2) + oleic acid (3)} measured over the temperature range from (308 to 338) K.

2. EXPERIMENTAL SECTION

2.1. Material

Oleic acid (mass fraction 0.99) was purchased from Vetec (Brazil). (R,S)-1,2-isopropylidene glycerol (solketal) (mass fraction 0.98) was purchased from Sigma-Aldrich. Carbon dioxide (mass fraction 0.999 in the liquid phase) was obtained from White Martins S.A. (Osasco, SP, Brazil). All substances were used without any pretreatment.

2.2. Phase Equilibrium Apparatus and Experimental Procedure

Experimental data were measured in a high-pressure variable-volume cell with front and side windows by the static synthetic method. The apparatus and methodology have been described in previous work (Pinto *et al.*, 2011; Giufrida *et al.*, 2011; Mazzer *et al.*, 2012; Santos *et al.*, 2012; Pinto

et al., 2013; Prado *et al.*, 2011). On the basis of analysis of the propagation of errors reported in the work of Rodrigues-Reartes *et al.* (2009) using the uncertainties in the masses introduced into the phase equilibrium cell, it was possible to calculate the maximum uncertainty in the values of the mole fraction of carbon dioxide, which was not higher than 0.001. On the basis of three repetitions of each experimental point, the standard deviations in pressure were estimated to be in the range (0.01 to 0.05) MPa. The temperature controller was connected to a thermocouple (T type, accuracy of ± 1.0 K) that was in contact with the system inside the cell. The desired temperature was controlled to within 0.5 K.

3. EXPERIMENTAL RESULTS

Figure 1 compares phase equilibrium data for the $\{\text{CO}_2$ (1) + ethanol (2) $\}$ system at (303 and 313) K from the literature (Secuianu *et al.*, 2008; Chiu *et al.*, 2008; Chang *et al.*, 1998; Joung *et al.*, 2001) with data measured in the equilibrium cell used in this work. The good agreement between the present measurements and the literature values shows the reproducibility of the experimental apparatus.

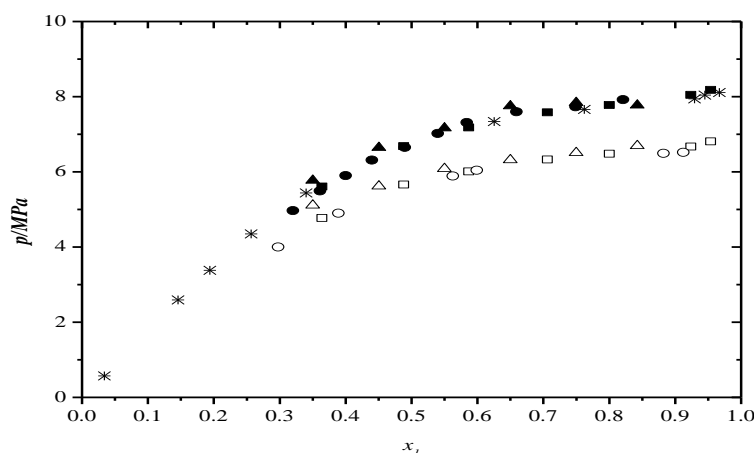


Figure 1 – Experimental pressure–composition diagram for the system $\{\text{CO}_2$ (1) + ethanol (2) $\}$ under vapor–liquid equilibrium conditions at 303.15 K (VLE-BP) (\triangle , this work; \circ , Secuianu *et al.*; \square , Chiu *et al.*) and 313.15 K (\blacktriangle , this work; \bullet , Chang *et al.*; \blacksquare , Chiu *et al.*; $*$, Joung *et al.*).

To understand solubility behavior in multicomponent systems, it is necessary to study the solubility of each component. Table 1 presents phase equilibrium data obtained in this work for the binary system $\{\text{CO}_2$ (1) + solketal (2) $\}$ at values of the global CO_2 mole fraction (x_1) ranging from 0.35 to 1. Table 2 and Figure 2 present phase equilibrium data for the ternary system $\{\text{CO}_2$ (1) + solketal (2) + oleic acid (3) $\}$ at values of the global CO_2 mole fraction (x_1) ranging from 0.55 to 1 at temperatures of (308, 318, 328, and 338) K. The solketal:oleic acid molar ratio was constant and equal to 3:1. [0.75 solketal + 0.25 oleic acid] in all of these ternary systems, for which bubble point conditions were measured. Tables 1 and 2 present the experimental data in terms of the mole fractions of CO_2 (x_1) and solketal (x_2), the phase transition pressure (p) with standard uncertainty $u(p)$ of replicated pressure measurements, and the transition type (BP, bubble point; DP, dew point).

Table 1 – Phase equilibrium VLE data for the binary system {CO₂(1) + solketal(2)}.

x_1	p/MPa	u/MPa^a	Transition type ^b	x_1	p/MPa	σ/MPa^a	Transition type ^b
$T = 308 \text{ K}$				$T = 318 \text{ K}$			
0.35	3.23	0.0265	VLE (BP)	0.35	3.45	0.0153	VLE (BP)
0.45	4.07	0.0208	VLE (BP)	0.45	4.36	0.0173	VLE (BP)
0.55	4.01	0.0153	VLE (BP)	0.55	5.24	0.0306	VLE (BP)
0.65	4.85	0.0462	VLE (BP)	0.65	6.35	0.0289	VLE (BP)
0.75	5.25	0.03	VLE (BP)	0.75	7.65	0.0351	VLE (BP)
0.85	6.16	0.02	VLE (BP)	0.85	8.29	0.0153	VLE (BP)
$T = 328 \text{ K}$				$T = 338 \text{ K}$			
0.35	3.99	0.0289	VLE (BP)	0.35	4.40	0.0116	VLE (BP)
0.45	5.14	0.0173	VLE (BP)	0.45	6.07	0.0173	VLE (BP)
0.55	6.18	0.0346	VLE (BP)	0.55	7.13	0.0153	VLE (BP)
0.65	7.50	0.0322	VLE (BP)	0.65	8.87	0.0208	VLE (BP)
0.75	9.13	0.0404	VLE (BP)	0.75	10.34	0.0458	VLE (BP)
0.85	9.93	0.0208	VLE (BP)	0.85	12.14	0.04	VLE (BP)

^a $u(T) = 0.5 \text{ K}$, $u(x) = 0.001$. ^b(BP, bubble points).

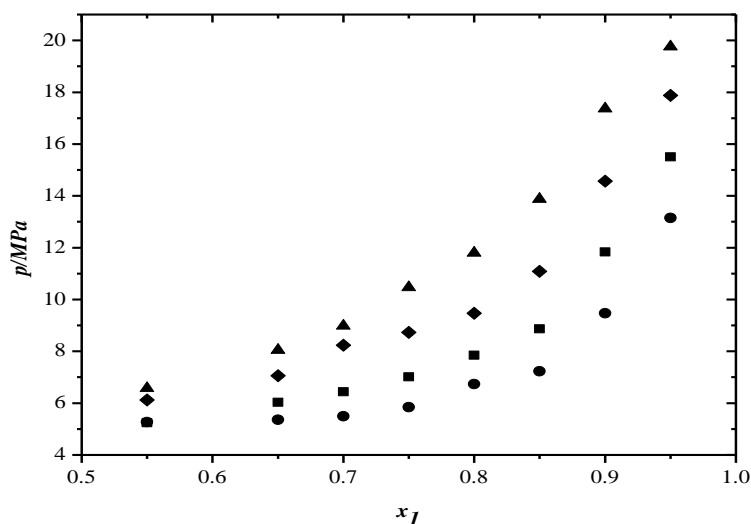


Figure 2 – Pressure-composition diagram for the system {CO₂(1) + [0.75 solketal(2) + 0.25 oleic acid(3)]} at T = 308 K (●); 318 K (■); 328 K (◆); 338 K (▲).

Table 2 – Phase equilibrium VLE data for the ternary system {CO₂(1) + [0.75 solketal(2) + 0.25 oleic acid(3)]}.

x_1	x_2	p/MPa ^a	σ/MPa	Transition type	x_1	x_2	p/MPa ^a	σ/MPa	Transition type
$T = 308 \text{ K}$					$T = 318 \text{ K}$				

0.55	0.33	5.27	0.0153	VLE (BP)	0.55	0.33	5.24	0.0322	VLE (BP)
0.65	0.26	5.36	0.0404	VLE (BP)	0.65	0.26	6.03	0.0265	VLE (BP)
0.70	0.22	5.49	0.0361	VLE (BP)	0.70	0.22	6.44	0.0116	VLE (BP)
0.75	0.18	5.84	0.0361	VLE (BP)	0.75	0.18	7.01	0.0458	VLE (BP)
0.80	0.15	6.73	0.02	VLE (BP)	0.80	0.15	7.85	0.0252	VLE (BP)
0.85	0.11	7.23	0.0520	VLE (BP)	0.85	0.11	8.87	0.0116	VLE (BP)
0.90	0.07	9.47	0.0200	VLE (DP)	0.90	0.07	11.83	0.0379	VLE (DP)
0.95	0.04	13.15	0.0252	VLE (DP)	0.95	0.04	15.50	0.0116	VLE (DP)
<i>T = 328 K</i>					<i>T = 338 K</i>				
0.55	0.33	6.12	0.0500	VLE (BP)	0.55	0.33	6.57	0.0208	VLE (BP)
0.65	0.26	7.06	0.0351	VLE (BP)	0.65	0.26	8.05	0.0300	VLE (BP)
0.70	0.22	8.24	0.0351	VLE (BP)	0.70	0.22	8.98	0.0289	VLE (BP)
0.75	0.18	8.73	0.0200	VLE (BP)	0.75	0.18	10.47	0.0361	VLE (BP)
0.80	0.15	9.47	0.0379	VLE (BP)	0.80	0.15	11.80	0.0173	VLE (BP)
0.85	0.11	11.09	0.0153	VLE (BP)	0.85	0.11	13.88	0.0764	VLE (BP)
0.90	0.07	14.57	0	VLE (DP)	0.90	0.07	17.37	0.0557	VLE (DP)
0.95	0.04	17.88	0.0520	VLE (DP)	0.95	0.04	19.76	0.0321	VLE (DP)

Figure 3 compares the data for the binary and ternary systems of solketal at 308 and 338 K. The phase transition pressure at 308 K is higher for the ternary system {CO₂ (1) + [0.75 solketal (2) + 0.25 oleic acid (3)]} than for the binary system {CO₂ (1) + solketal (2)}, except for the liquid mole fraction of CO₂ equal to 0.85. At 338 K, the binary system has phase transition pressures slightly higher than those of the ternary system for liquid mole fractions of CO₂ lower than 0.75. de CO₂ (x₁) valores 0,35-1.

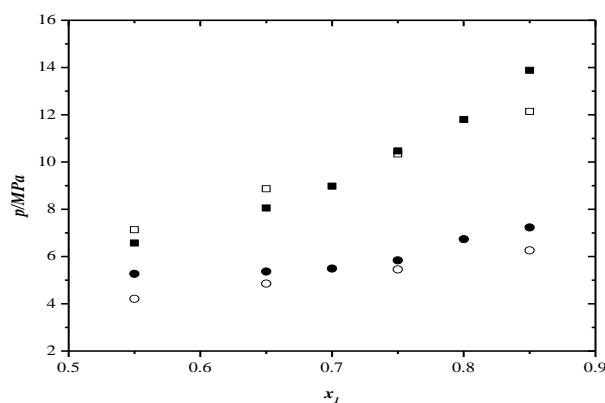


Figure 3 – Pressure-composition diagram comparison between systems {CO₂(1) + solketal(2)} at T = 308 K (○); 338 K (□) and {CO₂(1) + [0.75 solketal(2) + 0.25 oleic acid(3)]} at T = 308 K (●); 338 K (■).

4. CONCLUSÕES

This work has reported phase equilibrium measurements for the {CO₂ (1) + solketal (2)} and

{CO₂ (1) + [0.75 solketal (2) + 0.25 oleic acid (3)]} systems at temperatures from (308 to 338) K. Oleic acid and solketal exhibit excellent solubility in CO₂, a factor that favors the reaction to form monoacyl glycerides from oleic acid. The reported experimental data are important information for developing esterification processes under supercritical conditions, including the synthesis of monooleins by solketal esterification.

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