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Phase Behavior of the Reactant and Products of Cyclohexane Oxidation in Compressed CO_2

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This work investigates the phase equilibrium behavior of the constituents involved in the reaction medium of cyclohexane oxidation to produce cyclohexanol and cyclohexanone in compressed carbon dioxide. For this purpose, high-pressure cloud point data for binary, ternary, and quaternary CO_2-containing systems with the reactant (cyclohexane) and the main products (cyclohexanol and cyclohexanone) were measured. The static synthetic method using a variable-volume view cell was employed for obtaining the experimental data in the temperature range of (293 to 343) K at several overall compositions and pressures up to 27 MPa. The experimental data were satisfactorily represented by the Peng−Robinson equation of state (PR-EoS) with the classical quadratic mixing rules.

Introduction

Supercritical fluids (SCFs) as reaction media have several advantages over conventional solvents, particularly regarding the effects of solvent parameters on reaction systems.[1] Relative to conventional solvents, SCFs have more favorable transport properties that can be fine-tuned near the critical point. Besides the well-known environmental advantages, one additional attractive feature of SCF as a medium for a variety of chemical reactions is that they can lower mass transfer limitations and allow better control of selectivity and reaction yield. Furthermore, it permits us to combine advantageously the reaction, separation, and purification steps.[2−5] In this sense, the use of supercritical carbon dioxide ($SCCO_2$) has become a natural and interesting possibility to replace organic (liquid) solvents in many chemical reactions, like the catalytic alkane oxidation.

The products from cyclohexane oxidation, cyclohexanol and cyclohexanone, are raw materials for adipic acid synthesis and precursors of nylon 6-polymers, with expressive industrial relevance.[6,7] Currently, oxidation of cyclohexane has been generally performed in liquid phase at (393 to 413) K and pressures greater than 2 MPa, with air or oxygen, catalyzed by transition metals or promoted by initiators and even without catalysts. However, oxidation in a compressed CO_2 medium is a cleaner process compared to organic solvents and may be an effective way to reduce byproducts as the reaction rates and conversions can be manipulated by adjusting the operating conditions of temperature and pressure and feed composition near the mixture critical point.[3,7,8]

The knowledge of phase behavior plays a fundamental role in determining appropriate regions to conduct one- or two-phase reactions.[9,10] In fact, reaction mixtures are usually complex systems because composition varies with conversion or reaction time, and therefore phase behavior and critical parameters also change with conversion. Thus, as mentioned by Zhang et al.,[7] negligence of phase behavior in reacting systems may lead to misinterpretation of the solvent effect. Moreover, temperature

Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexane (2)

T/K	P/MPa	σ/MPa[a]	transition type	T/K	P/MPa	σ/MPa	transition type
		$x_1 = 0.451$				$x_1 = 0.884$	
293	3.90	0.02	VLE-BP	293	4.82	0.03	VLE-BP
303	4.59	0.03	VLE-BP	303	5.86	0.06	VLE-BP
313	5.21	0.05	VLE-BP	313	7.08	0.03	VLE-BP
323	5.84	0.02	VLE-BP	323	8.28	0.02	VLE-BP
333	6.51	0.02	VLE-BP	333	9.53	0.01	VLE-BP
		$x_1 = 0.561$				$x_1 = 0.916$	
293	4.51	0.06	VLE-BP	293	5.13	0.02	VLE-BP
303	5.28	0.04	VLE-BP	303	6.30	0.04	VLE-BP
313	6.07	0.05	VLE-BP	313	7.49	0.03	VLE-BP
323	6.95	0.08	VLE-BP	323	8.76	0.05	VLE-BP
333	7.81	0.08	VLE-BP	333	9.75	0.05	VLE-BP
		$x_1 = 0.657$				$x_1 = 0.945$	
293	4.56	0.04	VLE-BP	293	5.24	0.10	VLE-BP
303	5.45	0.02	VLE-BP	303	6.36	0.08	VLE-BP
313	6.42	0.03	VLE-BP	313	7.64	0.09	VLE-BP
323	7.41	0.03	VLE-BP	323	8.74	0.02	VLE-BP
333	8.42	0.03	VLE-BP	333	9.70	0.01	VLE-DP
		$x_1 = 0.780$				$x_1 = 0.973$	
293	4.89	0.03	VLE-BP	293	5.45	0.06	VLE-BP
303	5.87	0.02	VLE-BP	303	6.44	0.01	VLE-BP
313	6.95	0.04	VLE-BP	313	7.56	0.01	VLE-BP
323	8.12	0.04	VLE-BP	323	8.66	0.02	VLE-DP
333	9.31	0.06	VLE-BP				
		$x_1 = 0.855$				$x_1 = 0.981$	
293	4.93	0.04	VLE-BP	293	5.33	0.04	VLE-BP
303	6.07	0.06	VLE-BP	303	6.41	0.06	VLE-BP
313	7.31	0.08	VLE-BP	313	7.47	0.03	VLE-DP
323	8.56	0.03	VLE-BP	323	8.51	0.16	VLE-DP
333	9.81	0.08	VLE-BP				

[a] Standard deviation.

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Table 2. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexanone (2)

T/K	P/MPa	σ/MPa	transition type	T/K	P/MPa	σ/MPa	transition type
$x_1 = 0.598$				$x_1 = 0.905$			
293	3.53	0.04	VLE-BP	293	5.00	0.09	VLE-BP
303	4.43	0.09	VLE-BP	303	6.22	0.04	VLE-BP
313	5.48	0.04	VLE-BP	313	7.58	0.02	VLE-BP
323	6.43	0.06	VLE-BP	323	9.15	0.06	VLE-BP
333	7.34	0.04	VLE-BP	333	10.77	0.01	VLE-BP
$x_1 = 0.691$				$x_1 = 0.952$			
293	4.58	0.07	VLE-BP	293	5.18	0.04	VLE-BP
303	5.51	0.06	VLE-BP	303	6.36	0.04	VLE-BP
313	6.57	0.02	VLE-BP	313	7.79	0.04	VLE-BP
323	7.83	0.04	VLE-BP	323	9.32	0.08	VLE-BP
333	8.96	0.05	VLE-BP	333	10.83	0.04	VLE-DP
$x_1 = 0.770$				$x_1 = 0.977$			
293	4.74	0.04	VLE-BP	293	5.25	0.07	VLE-BP
303	5.71	0.06	VLE-BP	303	6.52	0.06	VLE-BP
313	6.76	0.04	VLE-BP	313	7.91	0.06	VLE-BP
323	8.06	0.03	VLE-BP	323	9.25	0.03	VLE-DP
333	9.46	0.06	VLE-BP	333	10.68	0.04	VLE-DP
$x_1 = 0.839$				$x_1 = 0.991$			
293	4.87	0.09	VLE-BP	293	5.51	0.02	VLE-BP
303	5.98	0.04	VLE-BP	303	6.81	0.04	VLE-BP
313	7.34	0.01	VLE-BP	313	8.00	0.03	VLE-BP
323	8.80	0.01	VLE-BP	323	9.26	0.05	VLE-DP
333	10.35	0.04	VLE-BP	333	10.45	0.05	VLE-DP

Table 3. Experimental Phase Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexanol (2)

T/K	P/MPa	σ/MPa	transition type	T/K	P/MPa	σ/MPa	transition type
$x_1 = 0.202$				$x_1 = 0.694$			
303	5.33	0.09	VLE-BP	333	24.80	0.09	LLE
313	5.74	0.05	VLE-BP	343	22.01	0.06	LLE
323	6.16	0.04	VLE-BP	$x_1 = 0.774$			
333	6.47	0.09	VLE-BP	333	26.48	0.04	LLE
343	6.73	0.02	VLE-BP	343	23.21	0.09	LLE
$x_1 = 0.363$				$x_1 = 0.842$			
303	7.74	0.05	VLE-BP	303	6.92	0.02	VLLE
313	8.63	0.01	VLE-BP	333	26.26	0.04	LLE
323	9.37	0.01	VLE-BP	343	23.03	0.06	LLE
333	10.02	0.08	VLE-BP				
343	10.57	0.02	VLE-BP				
$x_1 = 0.432$				$x_1 = 0.901$			
303	15.66	0.05	LLE	303	6.91	0.02	VLLE
303	6.87	0.03	VLLE	333	22.69	0.03	LLE
313	11.67	0.09	LLE	343	21.04	0.08	LLE
323	11.37	0.05	LLE				
333	12.01	0.05	VLE				
343	12.65	0.08	VLE				
$x_1 = 0.493$				$x_1 = 0.953$			
313	18.11	0.11	LLE	303	19.50	0.03	LLE
323	14.28	0.01	LLE	303	6.77	0.04	VLLE
333	13.70	0.01	LLE	313	15.22	0.02	LLE
343	14.10	0.06	LLE	323	14.66	0.03	LLE
				333	15.14	0.03	LLE
				343	16.17	0.02	LLE
$x_1 = 0.551$				$x_1 = 0.977$			
303	6.78	0.03	VLLE	303	9.41	0.01	VLE-BP
313	25.26	0.15	LLE	313	10.14	0.02	LLE
323	20.99	0.06	LLE	323	11.62	0.01	LLE
333	17.48	0.09	LLE	333	13.07	0.02	LLE
342	16.62	0.08	LLE	343	14.21	0.06	LLE
$x_1 = 0.602$							
303	7.02	0.03	VLLE				
323	26.97	0.09	LLE				
333	21.55	0.09	LLE				
343	19.41	0.04	LLE				

and pressure may have a remarkable influence on product profile, selectivities, and reaction rates.[11]

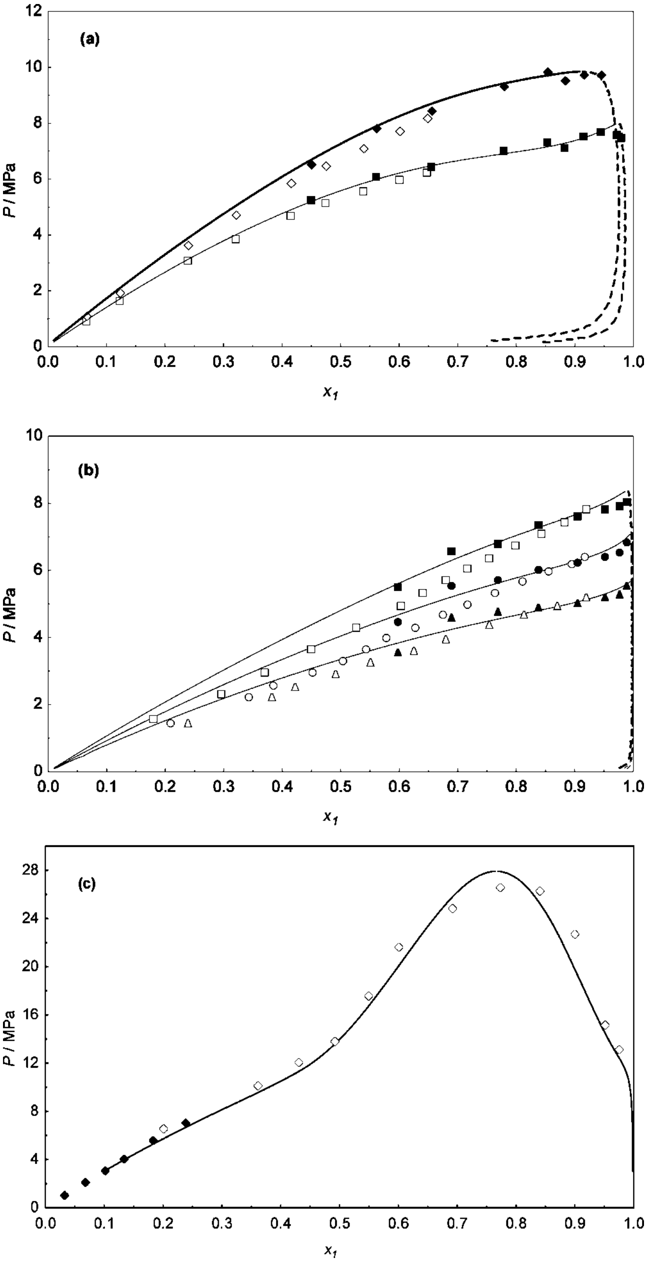

Figure 1. Comparison between binary P,x,y experimental data (VLE) obtained in this work and the literature. (a) Carbon dioxide (1) + cyclohexane (2): this work (■, 313 K; ◆, 333 K) and the literature[13] (□, 313 K; ◇, 333 K). (b) Carbon dioxide (1) + cyclohexanone (2): this work (▲, 293 K; ●, 303 K; ■, 313 K) and the literature[17] (△, 290.8 K; ○, 300.9 K; □, 310.15 K). (c) Carbon dioxide (1) + cyclohexanol (2): ◆, this work; ◇, literature[15] at 333 K. Continuous lines represent calculated values from the PR-EoS.

While appreciable material is available regarding phase equilibrium data of binary mixtures, experimental information of ternary and quaternary systems, especially related directly to the reaction systems, is scarce. Inspection of the literature reveals the existence of some experimental phase equilibrium or solubility data for CO_2 + cyclohexane[12−14] and CO_2 + products of the cyclohexane oxidation,[10,15−17] but most of them were obtained at high temperatures. Zhang and co-workers[7] reported values of critical temperature and pressure for a six-component (carbon dioxide, nitrogen, cyclohexane, cyclohexanol, cyclohexanone, water) reacting mixture of cyclohexane oxidation at temperatures nearly or above 400 K. However, no systematic study was found regarding the phase behavior of

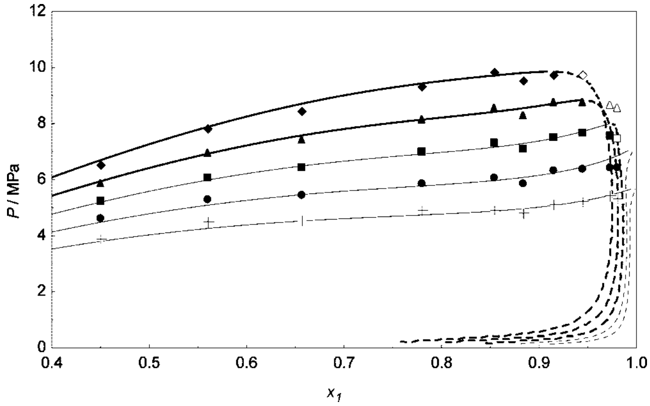

Figure 2. P,x,y data (VLE) for the binary system carbon dioxide (1) + cyclohexane (2) (+, BP at 293 K; ●, BP at 303 K; ■, BP at 313 K; □, DP at 313 K; ▲, BP at 323 K; Δ, DP at 323 K; ◆, BP at 333 K; ◇, DP at 333 K). Continuous lines denote calculated values from the PR-EoS: —, BP transitions; - - -, DP transitions.

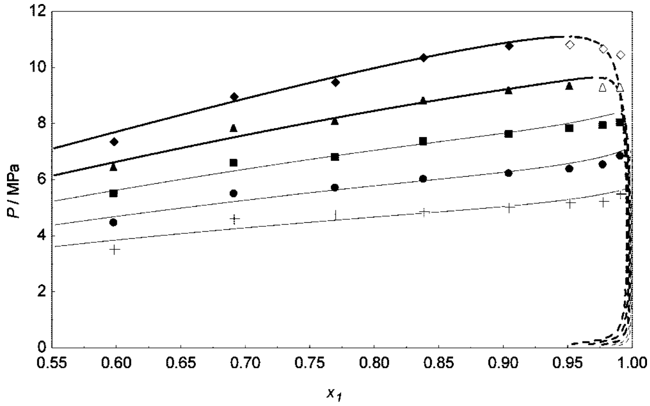

Figure 3. P,x,y data (VLE) for the binary system carbon dioxide (1) + cyclohexanone (2) (+, BP at 293 K; ●, BP at 303 K; ■, BP at 313 K; ▲, BP at 323 K; △, DP at 323 K; ◆, BP at 333 K; ◇, DP at 333 K). Continuous lines denote calculated values from the PR-EoS: —, BP transitions; - - -, DP transitions.

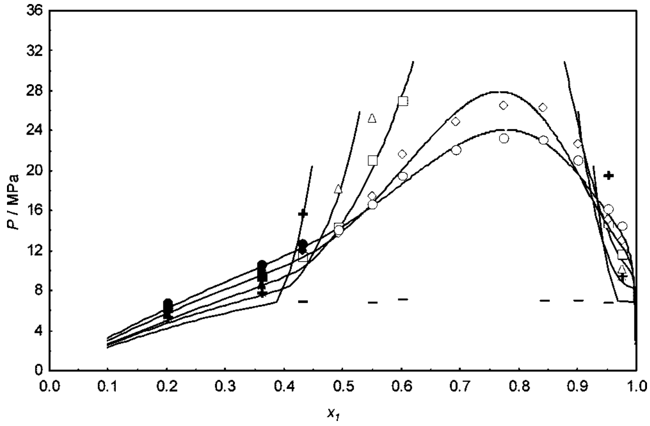

Figure 4. P,x,y data for the binary system carbon dioxide (1) + cyclohexanol (2) (*, VLE at 303 K; +, LLE at 303 K, −, VLLE at 303 K; ▲, VLE at 313 K; △, LLE at 313 K; ■, VLE at 323 K; □, LLE at 323 K; ◆, VLE at 333 K; ◇, LLE at 333 K; ●, VLE at 343 K; ○, LLE at 343 K). Continuous lines denote calculated values from the PR-EoS.

Table 4. Binary Interaction Parameters of the PR-EoS Fitted in This Work

system	$k_{12}\cdot 10^2$	$l_{12}\cdot 10^2$	N
CO_2 (1) + cyclohexane (2)	11.83	−3.59	36
CO_2 (1) + cyclohexanone (2)	4.95	−2.74	35
CO_2 (1) + cyclohexanol (2)	9.72	−6.44	30

Table 5. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexane (2) + Cyclohexanone (3)[a]

T/K	P/MPa	σ/MPa	transition type	T/K	P/MPa	σ/MPa	transition type
	$x_1 = 0.673$				$x_1 = 0.949$		
293	4.11	0.06	VLE-BP	293	5.10	0.01	VLE-BP
303	4.98	0.05	VLE-BP	303	6.34	0.06	VLE-BP
313	5.90	0.08	VLE-BP	313	7.70	0.04	VLE-BP
323	6.90	0.06	VLE-BP	323	9.01	0.01	VLE-BP
333	7.95	0.06	VLE-BP	333	10.18	0.01	VLE-DP
343	9.04	0.08	VLE-BP	343	11.56	0.03	VLE-DP
	$x_1 = 0.828$				$x_1 = 0.975$		
293	4.69	0.04	VLE-BP	293	5.40	0.06	VLE-BP
303	5.76	0.05	VLE-BP	303	6.62	0.05	VLE-BP
313	6.93	0.06	VLE-BP	313	7.98	0.04	VLE-BP
323	8.20	0.05	VLE-BP	323	9.05	0.08	VLE-BP
333	9.52	0.04	VLE-BP	333	10.14	0.01	VLE-DP
343	10.84	0.05	VLE-BP	343	10.51	0.03	VLE-DP

[a] Cyclohexane and cyclohexanone are in equimolar concentration in the mixture.

Table 6. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexanone (2) + Cyclohexanol (3)[a]

T/K	P/MPa	σ/MPa	transition type	T/K	P/MPa	σ/MPa	transition type
	$x_1 = 0.692$				$x_1 = 0.953$		
293	5.19	0.06	VLE-BP	293	5.34	0.05	VLE-BP
303	6.63	0.07	VLE-BP	303	6.75	0.06	VLE-BP
313	7.75	0.02	VLE-BP	313	8.04	0.04	VLE-BP
323	9.00	0.08	VLE-BP	323	10.03	0.06	VLE-BP
333	10.55	0.04	VLE-BP	333	11.97	0.08	VLE-DP
343	12.08	0.01	VLE-BP	343	13.67	0.01	VLE-DP
	$x_1 = 0.840$				$x_1 = 0.977$		
293	5.26	0.06	VLE-BP	293	5.45	0.01	VLE-BP
303	6.46	0.02	VLE-BP	303	6.66	0.08	VLE-BP
313	7.86	0.06	VLE-BP	313	7.94	0.03	VLE-BP
323	9.49	0.02	VLE-BP	323	9.45	0.06	VLE-BP
333	11.24	0.05	VLE-BP	333	10.92	0.02	VLE-DP
343	13.22	0.01	VLE-BP	343	12.20	0.03	VLE-DP

[a] Cyclohexanone and cyclohexanol are in equimolar concentration in the mixture.

binary, ternary, and quaternary systems of constituents of cyclohexane oxidation, particularly at relatively low temperatures. It should also be mentioned that the development of biomimetic catalysts has permitted us to conduct the cyclohexane reaction at low temperatures. For example, Olsen and coworkers[18] presented a study on the cyclohexane oxidation catalyzed by iron tetraphenylporphyrin in supercritical carbon dioxide using either *tert*-butyl-hydroperoxide (*t*-BuOOH) or hydrogen peroxide (H_2O_2) as terminal oxidants and found promising results.

In this context, this work is aimed at reporting phase equilibrium (cloud point) data for systems formed by the reactant (cyclohexane) and products of the cyclohexane oxidation (cyclohexanol and cyclohexanone) with compressed CO_2 in the temperature range of (293 to 343) K. The Peng−Robinson equation of state[19] is shown to satisfactorily represent the experimental data obtained.

Experimental Section and Modeling

Materials. Cyclohexane (99 %, Merck), cyclohexanone (99 %, Merck), cyclohexanol (99 %, Sigma-Aldrich), and CO_2 (99.9 %, liquid phase, AGA) were used without further purification.

Apparatus and Experimental Procedure. Phase equilibrium experiments were conducted employing the static synthetic method in a high-pressure variable-volume view cell. A detailed description of the experimental apparatus and procedure together

Table 7. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexane (2) + Cyclohexanol (3)[a]

T/K	P/MPa	σ/MPa	transition type	T/K	P/MPa	σ/MPa	transition type
$x_1 = 0.4730$				$x_1 = 0.8926$			
293	4.45	0.04	VLE-BP	293	11.92	0.06	LLE
303	5.26	0.01	VLE-BP	293	5.12	0.03	VLLE
313	6.09	0.01	VLE-BP	303	8.85	0.02	LLE
323	6.88	0.03	VLE-BP	303	6.31	0.03	VLLE
333	7.63	0.03	VLE-BP	313	8.85	0.01	LLE
343	8.36	0.02	VLE-BP	313	7.61	0.03	VLLE
$x_1 = 0.6750$				323	9.94	0.01	LLE
293	4.77	0.21	VLE-BP	323	8.99	0.02	VLLE
303	5.91	0.01	VLE-BP	333	11.35	0.02	VLE-DP
313	6.93	0.04	VLE-BP	343	12.69	0.01	VLE-DP
323	8.14	0.02	VLE-BP	$x_1 = 0.9219$			
333	9.44	0.03	VLE-BP	293	9.90	0.01	LLE
343	10.44	0.02	VLE-BP	293	5.10	0.01	VLLE
$x_1 = 0.7577$				303	8.01	0.02	LLE
293	6.39	0.28	LLE	303	6.39	0.03	VLLE
293	4.88	0.01	VLLE	313	8.69	0.04	LLE
303	5.99	0.07	VLE-BP	313	7.70	0.03	VLLE
313	7.16	0.01	VLE-BP	323	10.00	0.04	LLE
323	8.43	0.01	VLE-BP	323	8.99	0.02	VLLE
333	9.77	0.01	VLE-BP	333	11.48	0.02	VLE-DP
343	11.15	0.02	VLE-BP	343	12.82	0.06	VLE-DP
$x_1 = 0.7802$				$x_1 = 0.9494$			
293	8.08	0.04	LLE	293	6.04	0.03	LLE
293	4.89	0.01	VLLE	293	5.04	0.02	VLLE
303	6.03	0.01	VLE-BP	303	6.57	0.01	LLE
313	7.27	0.02	VLE-BP	303	6.29	0.01	VLLE
323	8.61	0.02	VLE-BP	313	8.10	0.02	LLE
333	10.00	0.01	VLE-BP	313	7.68	0.02	VLLE
343	11.44	0.03	VLE-BP	323	9.79	0.01	VLE-DP
$x_1 = 0.8290$				333	11.32	0.02	VLE-DP
293	12.03	0.01	LLE	343	12.56	0.01	VLE-DP
293	4.83	0.04	VLLE	$x_1 = 0.9754$			
303	7.75	0.01	LLE	293	5.37	0.03	VLE-BP
303	5.98	0.02	VLLE	303	6.70	0.01	VLE-BP
313	7.48	0.01	LLE	313	8.06	0.01	VLE-BP
$x_1 = 0.8290$				$x_1 = 0.9754$			
313	7.34	0.01	VLLE	323	9.70	0.03	VLE-DP
323	8.59	0.02	VLE-BP	333	11.04	0.05	VLE-DP
333	10.18	0.01	VLE-BP	343	12.02	0.04	VLE-DP
343	11.69	0.03	VLE-BP				
$x_1 = 0.8622$							
293	14.27	0.01	LLE				
293	4.95	0.01	VLLE				
303	9.19	0.01	LLE				
303	6.25	0.02	VLLE				
313	8.64	0.02	LLE				
313	7.51	0.03	VLLE				
323	9.58	0.02	LLE				
323	8.89	0.03	VLLE				
333	10.89	0.05	VLE-DP				
343	12.28	0.02	VLE-DP				

[a] Cyclohexane and cyclohexanol are in equimolar concentration in the mixture.

with the typical experimental uncertainties can be found elsewhere.[20−22] Briefly, the experimental apparatus consists of a variable-volume view cell, with a maximum internal volume of 27 mL, with two sapphire windows for visual observation, an absolute pressure transducer (Smar LD 301), with a precision of 0.03 MPa, a portable programmer (Smar, HT 201) for the pressure data acquisition, and a syringe pump (ISCO 260D).

Initially, a known mass of the solute (or mixture of solutes) was weighed on a precision scale balance (Gilbertini E254 with 0.0001 g accuracy) and loaded into the equilibrium cell. The cell was then flushed with low-pressure CO_2 to remove any residual air. The charge of a known volume of CO_2 was performed with the help of the syringe pump (resulting accuracy of 0.005 g in CO_2 loadings) until a desired global composition was achieved. On the basis of the uncertainty in CO_2 loading and other compound weightings, we estimate that the uncertainty in global mass fraction of the mixtures was lower than 0.005 %. Then, the cell content was kept at continuous agitation with the help of a magnetic stirrer and a Teflon-coated stirring bar. The temperature control was then turned on, and once the desired temperature was reached and controlled within 0.5 K, the pressure system was increased until the visualization of a one-phase system in the cell. In ternary and quaternary systems, solutes (cyclohexane, cyclohexanone, and cyclohexanol) were always fed in the mixture in an equimolar concentration. In this sense, for ternary systems $x_2 = x_3$, and for the quaternary system, $x_2 = x_3 = x_4$.

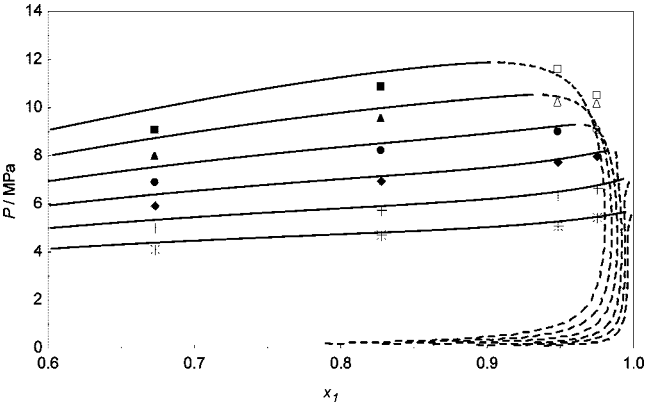

Figure 5. P,x,y data (VLE) for the ternary system carbon dioxide (1) + cyclohexane (2) + cyclohexanone (3) (*, BP at 293 K; +, BP at 303 K; ◆, BP at 313 K; ●, BP at 323 K; ○, DP at 323 K; ▲, BP at 333 K; △, DP at 333 K; ■, BP at 343 K; □, DP at 343 K). Continuous lines denote calculated values from the PR-EoS: —, BP transitions; - - -, DP transitions. Cyclohexane and cyclohexanone are in equimolar concentration in the mixture ($x_2 = x_3$).

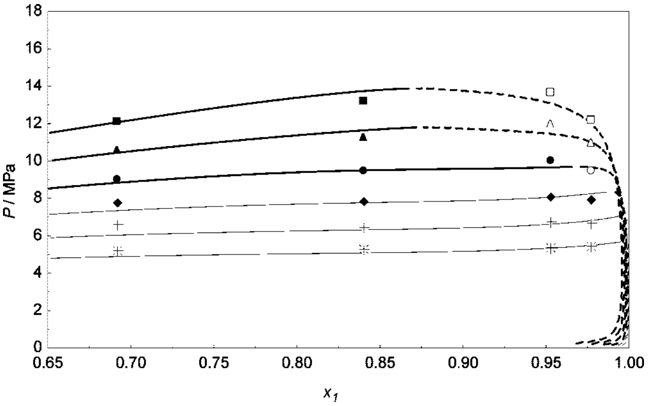

Figure 6. P,x,y data (VLE) for the ternary system carbon dioxide (1) + cyclohexanone (2) + cyclohexanol (3) (*, BP at 293 K; +, BP at 303 K; ◆, BP at 313 K; ●, BP at 323 K; ○, DP at 323 K; ▲, BP at 333 K; △, DP at 333 K; ■, BP at 343 K; □, DP at 343 K). Continuous lines denote calculated values from the PR-EoS: —, BP transitions; - - -, DP transitions. Cyclohexanone and cyclohexanol are in equimolar concentration in the mixture ($x_2 = x_3$).

Thermodynamic Modeling. The isofugacity approach together with the Peng−Robinson equation of state (PR-EoS) with the van der Waals quadratic mixing rule with two adjustable parameters, k_{ij} and l_{ij}, was used in the phase equilibrium calculations. The binary interaction parameters were optimized using the simulated annealing algorithm,[23,24] through bubble point calculations, where the following objective function (ψ) was minimized

$$\psi = \sum_{i=1}^{N} (P_i^{\text{calcd}} - P_i^{\text{exptl}})^2 \qquad (1)$$

where P_i^{calcd} and P_i^{exptl} denote calculated and experimental pressure values, respectively, and N is the number of experimental data points.

The critical properties and acentric factors of pure compounds were taken from the literature,[25] with the exception of the last parameter for cyclohexanone, which was estimated by the Constantinou and Gani group contribution method.[26]

Results and Discussion

Tables 1 to 3 present the binary phase equilibrium data formed by carbon dioxide with the reactant and products of the cyclohexane oxidation. In these tables is also shown the individual uncertainties of each measurement (taken from replication of experimental runs) and the type of phase transition observed: bubble point (BP) or dew point (DP) transition. Figure 1a,b, and c provides a comparison with literature information regarding the phase behavior for these binary systems, from which a satisfactory agreement of the results of this work with the literature data can be observed.

One can observe from Figures 2 and 3, respectively, for the systems CO_2 + cyclohexane and CO_2 + cyclohexanone, that only vapor−liquid equilibria (VLE) with bubble or dew point transitions were recorded. Conversely, as depicted in Figure 4, a more complex behavior was found for CO_2 + cyclohexanol, with the appearance of biphasic VLE, liquid−liquid equilibrium (LLE), and three-phase VLLE systems, for which the data set seems to be coherent with available literature data.[15] Table 4 presents the binary interaction parameters estimated from the data of the three binary systems investigated. One may consider that for all the binary systems the PR-EoS was capable of satisfactorily correlating the experimental phase equilibrium data.

Tables 5 to 7 and Figures 5 to 7 present the results for the ternary systems where it can be noticed that, except for carbon dioxide + cyclohexane + cyclohexanol, only VLE transitions and a reasonable agreement between experimental and calculated values were verified. It is interesting to take a look at the PT projection for this system at two compositions, shown in Figure 8, where lines for LL transitions present a decrease in pressure as the temperature is shifted to higher values. This phenomenon can be explained in terms of U-LCST phase transitions.

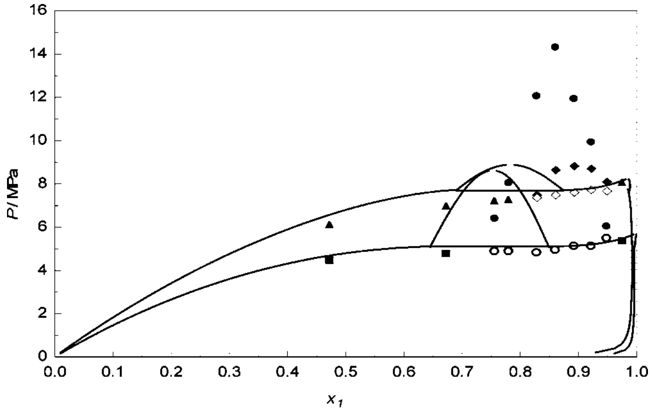

Figure 7. P,x,y data for the ternary system carbon dioxide (1) + cyclohexane (2) + cyclohexanol (3) (■, VLE at 293 K; ●, LLE at 293 K; ○, VLLE at 293 K; ▲, VLE at 313 K; ◆, LLE at 313 K; ◇, VLLE at 313 K). Continuous lines denote calculated values from the PR-EoS. Cyclohexane and cyclohexanol are in equimolar concentration in the mixture ($x_2 = x_3$).

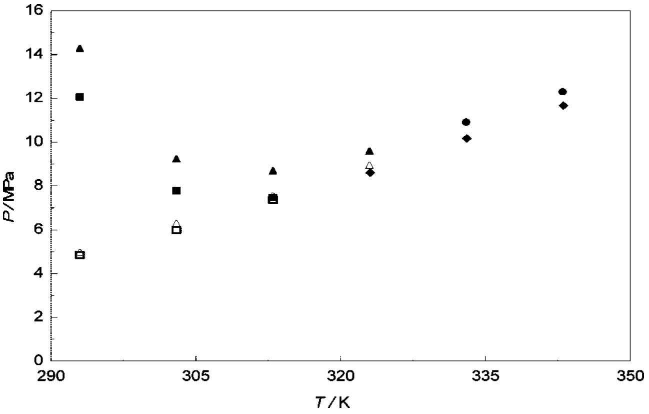

Figure 8. $P-T$ data for the ternary system carbon dioxide (1) + cyclohexane (2) + cyclohexanol (3) at selected CO_2 molar fractions: 0.8290 (◆, VLE; ■, LLE; □, VLLE) and 0.8662 (●, VLE; ▲, LLE; △, VLLE). Cyclohexane and cyclohexanol are in equimolar concentration in the mixture ($x_2 = x_3$).

Table 8. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Cyclohexane (2) + Cyclohexanone (3) + Cyclohexanol (4)[a]

T/K	P/MPa	σ/MPa	transition type	T/K	P/MPa	σ/MPa	transition type
	$x_1 = 0.680$				$x_1 = 0.950$		
293	4.48	0.06	VLE-BP	293	5.26	0.04	VLE-BP
303	5.50	0.06	VLE-BP	303	6.45	0.05	VLE-BP
313	6.69	0.06	VLE-BP	313	7.79	0.02	VLE-BP
323	7.60	0.04	VLE-BP	323	9.14	0.05	VLE-BP
333	8.70	0.04	VLE-BP	333	10.70	0.03	VLE-DP
343	9.86	0.06	VLE-BP	343	12.20	0.02	VLE-DP
	$x_1 = 0.830$				$x_1 = 0.976$		
293	4.85	0.04	VLE-BP	293	5.32	0.04	VLE-BP
303	5.92	0.06	VLE-BP	303	6.61	0.06	VLE-BP
313	7.21	0.07	VLE-BP	313	7.88	0.07	VLE-BP
323	8.53	0.01	VLE-BP	323	9.19	0.03	VLE-DP
333	10.01	0.02	VLE-BP	333	10.63	0.01	VLE-DP
343	11.51	0.03	VLE-BP	343	11.85	0.04	VLE-DP

[a] Cyclohexane, cyclohexanone, and cyclohexanol are in equimolar concentration in the mixture.

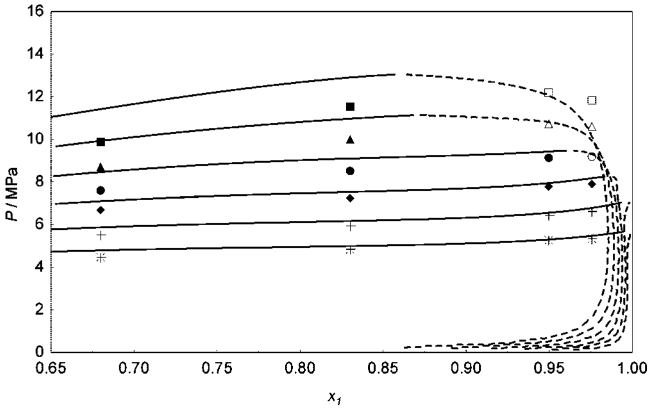

Figure 9. P,x,y data (VLE) for the quaternary system carbon dioxide (1) + cyclohexane (2) + cyclohexanone (3) + cyclohexanol (4) (*, BP at 293 K; +, BP at 303 K; ◆, BP at 313 K; ●, BP at 323 K; ○, DP at 323 K; ▲, BP at 333 K; △, DP at 333 K; ■, BP at 343 K; □, DP at 343 K). Continuous lines denote calculated values from the PR-EoS: —, BP transitions; - - -, DP transitions. Cyclohexane, cyclohexanol, and cyclohexanone are in equimolar concentration in the mixture ($x_2 = x_3 = x_4$).

The U-LCST behavior can be understood as a result of two opposite effects. The first provokes a decrease in pressure transition with increasing temperature. This transition type is referred to as UCST and is a consequence of energetic interactions between solutes and solvent. The second phenomenon is a result of differences in thermal expansion coefficients between solutes and solvent, and the resulting pressure transition curve is labeled LCST. The U-LCST behavior is commonly found in systems that present a large difference in molecular weight.[27,28] Results for the quaternary system are presented in Table 8 and Figure 9, for which only VLE transitions were experimentally verified and an acceptable representation of measured data was achieved with the PR-EoS. It may be worth mentioning that results for multicomponent systems were predicted using EoS cross parameters obtained from binary data information.

Conclusions

Phase equilibrium measurements for binary, ternary, and quaternary systems formed by carbon dioxide with the products of the cyclohexane oxidation were reported in this work and satisfactorily modeled with the PR-EoS in the temperature range of (293 to 343) K and pressures up to 27 MPa. The appearance of two-phase, vapor—liquid and liquid—liquid, and three-phase, vapor—liquid—liquid, equilibrium systems was experimentally observed with registered bubble and dew point phase transitions. Experimental information gathered in this work may be of relevance in conducting the cyclohexane oxidation in pressurized carbon dioxide.

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