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High-Pressure Vapor−Liquid Equilibrium Data for Systems Involving Carbon Dioxide + Organic Solvent + *β*-Carotene

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This work reports experimental phase equilibrium (transition points) data for the systems CO_2 + ethyl acetate, CO_2 + ethyl acetate + *β*-carotene, and CO_2 + ethanol + *β*-carotene at different concentrations of *β*-carotene in the organic (liquid) solvents. For this purpose, the static synthetic method, using a variable-volume view cell, was employed for obtaining the experimental data in the temperature range from (303 to 343) K and pressures up to 12 MPa. Vapor−liquid phase transitions were observed as bubble and dew points for all overall compositions investigated. In a general sense, it was experimentally observed that the addition of *β*-carotene leads to negligible changes in pressure transition values compared to CO_2 + solvent systems. The Peng−Robinson equation of state, with the classical van der Waals quadratic mixing rule, was employed for the thermodynamic modeling of the systems investigated with a satisfactory agreement between experiment and theory. It was also observed that the interaction parameters of *β*-carotene/organic solvent and *β*-carotene/CO_2 need not be considered for efficient prediction of phase behavior of the ternary systems.

Introduction

Over the past few years, functional foods have attracted increasing attention in the food industry due to their nutritional and physiological benefits. These kinds of foods usually contain compounds known as nutraceuticals or functional ingredients, which are used as a food supplement.[1] These nutraceuticals can occur naturally in food or can be added in a controlled dosage. A widely used class of nutraceutical compounds is that belonging to carotenoids, with *β*-carotene as one of the most important substances, having an essential role in the human diet due to its recognized antioxidant property and as a precursor of Vitamin A. In fact, it has been shown that ingestion of *β*-carotene may help prevent the occurrence of night blindness and some types of cancer, such as skin and liver.[2] Another interesting characteristic of *β*-carotene is the colorant power that varies from yellow to red.

Though synthetic chemical additives have been added during food manufacture, coherently with the current worldwide “green” image or “green” consumerism, the use of compounds from natural sources has become popular. Recently, several works have conducted the extraction of *β*-carotene from natural sources employing supercritical fluids, primarily carbon dioxide.[1−5] As a consequence of supercritical fluid technology, the *β*-carotene obtained is organic solvent-free. On the other hand, the resulting powder can present undesirable large particles and a broad particle size distribution. The large particle size reduces the pigment coloring because the size is inversely proportional to the coloring power. Furthermore, the large particle size distribution can make an encapsulation process with a biopolymer inefficient with consequent loss of important product properties.[6]

Several precipitation techniques using supercritical fluids have been proposed as an alternative to conventional methods such as organic solvents or spray drying.[7,8] The application of supercritical fluids as antisolvents for *β*-carotene precipitation is an attractive technique due to the very low solubility of this substance in the supercritical fluids.[9,10] Precipitation or coprecipitation of carotenoids and biopolymers using the supercritical antisolvent process was carried out by researchers who also investigated the effect of various parameters on the characteristics of the powder precipitated.[6,11,12]

For any precipitation process with sub- or supercritical fluids, there is a relationship between the observed phase behavior and the mechanism of kinetic nucleation and growth.[13] In this sense, the knowledge of phase behavior of the solute + solvent + antisolvent system plays an important role in an attempt to elucidate a particle formation mechanism and also to determine adequate operating conditions to conduct precipitation. In some cases, the phase behavior of the solvent/antisolvent system is modified by the presence of the solute, mainly in the case of polymers. In this specific case, the relationship of phase behavior with morphology of precipitated powder may be drastically affected when the phase behavior of the ternary system is not taken into account.

The approach based on pseudobinary diagrams neglects the equilibrium involving the third component (solute), thus assuming that the solute precipitates in the entire antisolvent composition range. In some cases, however, part of the solute can remain dissolved in the solvent and can be lost at the exit of the precipitation chamber. In particular, the cosolvency effect can occur when a mixture of two compounds, organic solvent + solute, is more soluble in a supercritical solvent than the individual (isolated) components.[14] The cosolvency effect of

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CO_2 has been studied for the systems CO_2 + ethanol + griseofulvin, CO_2 + acetone + griseofulvin,[15] and CO_2 + 1-propanol + salicylic acid.[16]

In this context, the aim of the present work is to report phase equilibrium (transition points) data for the ternary systems CO_2 + ethanol + β-carotene and CO_2 + ethyl acetate + β-carotene, at different concentrations of β-carotene in the organic solvent, and for the binary system CO_2 + ethyl acetate. The ternary systems were predicted with the Peng−Robinson equation of state (PR-EoS) using only binary system information. Experimental data together with modeling results may constitute relevant information for the precipitation of β-carotene using the supercritical antisolvent process.

Experimental

Materials. Ethyl acetate (99.5 %) was purchased from Quimex (Brazil), and ethanol (99.5 %) was obtained from Merck (Germany). Type-I synthetic *trans*-β-carotene with a minimum purity of 95 % was purchased from Sigma-Aldrich (USA), and carbon dioxide (99.9 % in liquid phase) was supplied by White Martins S.A. All materials were used as received, without any further purification. The organic stock solutions were prepared using two distinct concentrations of β-carotene in ethanol (0.096 $g\cdot L^{-1}$ and 0.3033 $g\cdot L^{-1}$) and one in ethyl acetate (0.3380 $g\cdot L^{-1}$).

Apparatus and Experimental 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 used in a variety of studies.[17−20] 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). The equilibrium cell contains a movable piston, which permits pressure control inside the cell. Phase transitions were recorded visually through manipulation of the pressure by the syringe pump using the solvent as a pneumatic fluid.

Initially, a known mass of the solute (either the organic solvent or a mixture of β-carotene + organic solvent) 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 weighings, 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. At this point, the system was kept for at least 30 min to allow stabilization, and then the pressure was slowly decreased, typically at a rate of (0.1 to 0.3) $MPa\cdot min^{-1}$, until incipient formation of a new phase. This procedure was repeated at least three times for each temperature and global composition. After completion of the measurement at a given temperature, the cell temperature was established at a new value and the experimental procedure was repeated.

Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Ethanol (2) + β-Carotene (3) at a β-Carotene Concentration of 0.096 $g\cdot L^{-1}$ in Ethanol (CO_2-Free Basis)

T / K	P / MPa	σ[a] / MPa	transition type	T / K	P / MPa	σ[a] / MPa	transition type
	$x_1 = 0.208$				$x_1 = 0.795$		
303	3.12	0.02	BP	303	6.32	0.01	BP
313	3.61	0.01	BP	313	7.41	0.01	BP
323	4.10	0.03	BP	323	8.92	0.02	BP
333	4.66	0.02	BP	333	10.21	0.02	BP
343	5.14	0.02	BP	343	11.43	0.01	BP
	$x_1 = 0.421$				$x_1 = 0.904$		
303	5.42	0.01	BP	303	6.32	0.01	BP
313	6.34	0.01	BP	313	7.54	0.01	BP
323	7.23	0.02	BP	323	8.92	0.01	BP
333	8.01	0.01	BP	333	10.10	0.09	BP
343	8.92	0.01	BP	343	11.23	0.01	DP
	$x_1 = 0.610$				$x_1 = 0.956$		
303	5.90	0.01	BP	303	6.67	0.02	BP
313	7.12	0.02	BP	313	8.08	0.01	BP
323	8.45	0.01	BP	323	9.04	0.01	BP
333	9.67	0.02	BP	333	9.73	0.04	DP
343	10.82	0.02	BP				

[a] Experimental standard deviation.

Table 2. Experimental Vapor−Liquid Equilibrium Data for the System Carbon Dioxide (1) + Ethanol (2) + β-Carotene (3) at a β-Carotene Concentration of 0.303 $g\cdot L^{-1}$ in Ethanol (CO_2-Free Basis)

T / K	P / MPa	σ[a] / MPa	transition type	T / K	P / MPa	σ[a] / MPa	transition type
	$x_1 = 0.628$				$x_1 = 0.904$		
303	5.80	0.02	BP	303	6.25	0.02	BP
313	7.11	0.01	BP	313	7.68	0.01	BP
323	8.46	0.01	BP	323	8.91	0.01	BP
333	9.74	0.03	BP	333	10.03	0.02	BP
343	10.90	0.03	BP	343	11.14	0.03	BP
	$x_1 = 0.806$				$x_1 = 0.952$		
303	6.22	0.02	BP	303	6.26	0.01	BP
313	7.54	0.01	BP	313	7.77	0.01	BP
323	8.92	0.02	BP	323	8.66	0.02	DP
333	10.44	0.04	BP				
343	11.73	0.01	BP				

[a] Experimental standard deviation.

Results and Discussion

Stock solutions with different concentrations of β-carotene in ethanol and ethyl acetate were prepared for the measurement of phase equilibrium data with CO_2. For the ternary system CO_2 (1) + ethanol (2) + β-carotene (3), two different concentrations of β-carotene in ethanol were used (0.096 $g\cdot L^{-1}$ and 0.303 $g\cdot L^{-1}$), whereas for CO_2 (1) + ethyl acetate (2) + β-carotene (3), the concentration of β-carotene in ethyl acetate adopted was 0.338 $g\cdot L^{-1}$. On the basis of the balance weighing error and diluting procedure, we estimated that the solution concentration uncertainty is lower than 0.0005 $g\cdot L^{-1}$.

Tables 1 and 2 present, respectively, the results for the ternary system CO_2 + ethanol + β-carotene at the two investigated concentrations of β-carotene, where one can notice the occurrence of only biphasic vapor−liquid coexistence curves.

Phase behavior for the binary system CO_2 (1) + ethyl acetate (2) was investigated aiming at comparing the results obtained with the ternary system CO_2 (1) + ethyl acetate (2) + β-carotene (3) and also due to the lack of experimental information about this binary system in the temperature range investigated in this

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Binary System Carbon Dioxide (1) + Ethyl Acetate (2)

T / K	P / MPa	σ^a / MPa	transition type	T / K	P / MPa	σ^a / MPa	transition type
	$x_1 = 0.461$				$x_1 = 0.936$		
303	2.51	0.01	BP	303	6.02	0.01	BP
313	3.13	0.01	BP	313	7.24	0.01	BP
323	3.67	0.01	BP	323	8.56	0.02	BP
333	4.18	0.02	BP	333	9.22	0.02	BP
343	4.66	0.02	BP	343	10.13	0.02	DP
	$x_1 = 0.666$				$x_1 = 0.969$		
303	3.92	0.01	BP	303	6.22	0.02	BP
313	4.74	0.01	BP	313	7.58	0.02	BP
323	5.63	0.02	BP	323	8.89	0.02	DP
333	6.34	0.02	BP				
343	7.16	0.03	BP				
	$x_1 = 0.823$						
303	5.02	0.01	BP				
313	6.04	0.01	BP				
323	7.13	0.01	BP				
333	8.24	0.02	BP				
343	9.27	0.02	BP				

[a] Experimental standard deviation.

Table 4. Experimental Phase Equilibrium Data for the System Carbon Dioxide (1) + Ethyl Acetate (2) + β-Carotene (3) at a β-Carotene Concentration of 0.338 g·L^{-1} in Ethyl Acetate (CO$_2$-Free Basis)

T / K	P / MPa	σ^a / MPa	transition type	T / K	P / MPa	σ^a / MPa	transition type
	$x_1 = 0.462$				$x_1 = 0.824$		
303	2.52	0.01	BP	303	5.02	0.01	BP
313	3.01	0.01	BP	313	6.12	0.02	BP
323	3.54	0.01	BP	323	7.13	0.01	BP
333	4.06	0.02	BP	333	8.22	0.01	BP
343	4.52	0.03	BP	343	9.24	0.02	BP
	$x_1 = 0.668$				$x_1 = 0.951$		
303	3.77	0.01	BP	303	6.22	0.01	BP
313	4.72	0.01	BP	313	7.64	0.01	BP
323	5.51	0.02	BP	323	8.68	0.02	BP
333	6.34	0.02	BP	333	9.42	0.02	DP
343	7.16	0.02	BP	343	10.88	0.02	DP

[a] Experimental standard deviation.

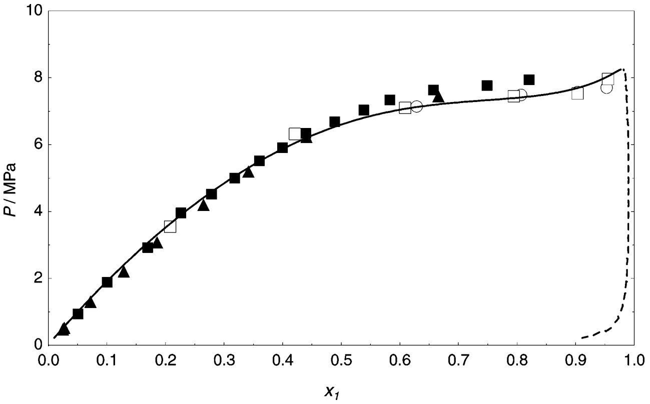

Figure 1. P,x,y VLE data for the ternary system carbon dioxide (1) + ethanol (2) + β-carotene (3) of this work and literature binary experimental data at approximately 313 K: □, ternary system at a β-carotene concentration in ethanol of 0.096 g·L^{-1}; ○, ternary system at a β-carotene concentration in ethanol of 0.303 g·L^{-1}; ■, carbon dioxide (1) + ethanol (2) binary system from Chang et al.;[21] ▲, carbon dioxide + ethanol binary system from Galicia Luna et al.[22] Lines denote calculated values from the PR-EoS: —, BP transitions; ---, DP transitions.

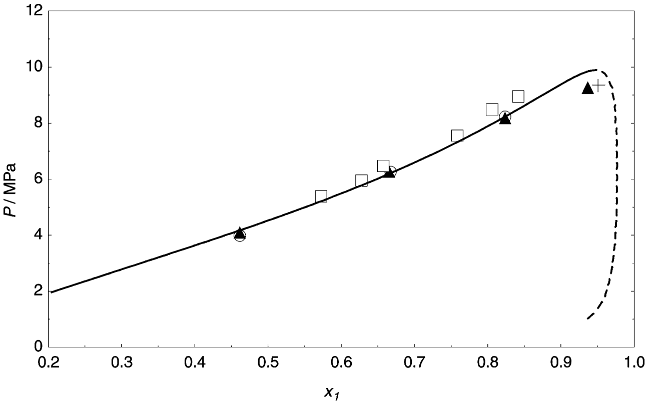

Figure 2. P,x,y VLE data for the ternary system carbon dioxide (1) + ethyl acetate (2) + β-carotene (3) of this work at a β-carotene concentration in ethyl acetate of 0.338 g·L^{-1} and literature experimental data at approximately 333 K: ▲, binary system CO$_2$ (1) + ethyl acetate (2) of this work; ○, ternary system−bubble point transitions, + ternary system−dew point transition; □, binary system from Tayan et al.[23] Lines denote calculated values from the PR-EoS: —, BP transitions; ---, DP transitions.

Table 5. Binary Interaction Parameters Fitted in This Work for the Systems CO$_2$ (1) + Ethanol (2) and CO$_2$ (1) + Ethyl Acetate (2)

system	k_{12}	l_{12}
CO$_2$ (1) + ethanol (2)	0.0703	−0.0262
CO$_2$ (1) + ethyl acetate (2)	−0.0373	−0.0639

work. Tables 3 and 4 present the experimental results for these systems, where again only vapor−liquid transitions were experimentally observed.

Figure 1 provides a comparison in the pressure−composition diagram between experimental data obtained in this work for the ternary system CO$_2$ + ethanol + β-carotene at the two β-carotene concentrations and binary data from the literature at 313 K.[21,22] Figure 2 presents a comparison involving experimental data for the ternary CO$_2$ + ethyl acetate + β-carotene and the binary CO$_2$ + ethyl acetate systems measured in this work and literature data at 333 K.[23]

In Figure 1, it can be seen that the presence of solute at the two concentrations investigated does not lead to significant changes in the pressure transitions when compared to the binary system. Similarly, in Figure 2, the same behavior is verified; i.e., the addition of β-carotene to the binary system CO$_2$ + ethyl acetate does not modify the vapor−liquid region for the β-carotene concentration investigated in this work.

Taking into account this experimental evidence, binary phase equilibrium data obtained in this work for the system CO$_2$ (1) + ethyl acetate (2) were modeled using the PR-EoS with the van der Waals quadratic mixing rule (vdW2). Afterward, the interaction parameters were employed in predicting the behavior of the ternary system. For CO$_2$ (1) + ethanol (2), the binary interaction parameters of PR-EoS were obtained by fitting the experimental data available in the literature in the temperature range of (291 to 373) K.[22,24] The simulated annealing algorithm[25−27] was employed for the parameter estimation of the PR-EoS through the minimization of experimental and calculated pressure transition values from the vapor−liquid equilibrium (VLE) data

$$\mathrm{OF} = \sum_{i}^{\mathrm{NOBS}} (P_i^{\mathrm{calcd}} - P_i^{\mathrm{exptl}})^2 \qquad (1)$$

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

Table 5 presents the estimated binary interaction parameters for the systems CO$_2$ (1) + ethanol (2) and CO$_2$ (1) + ethyl

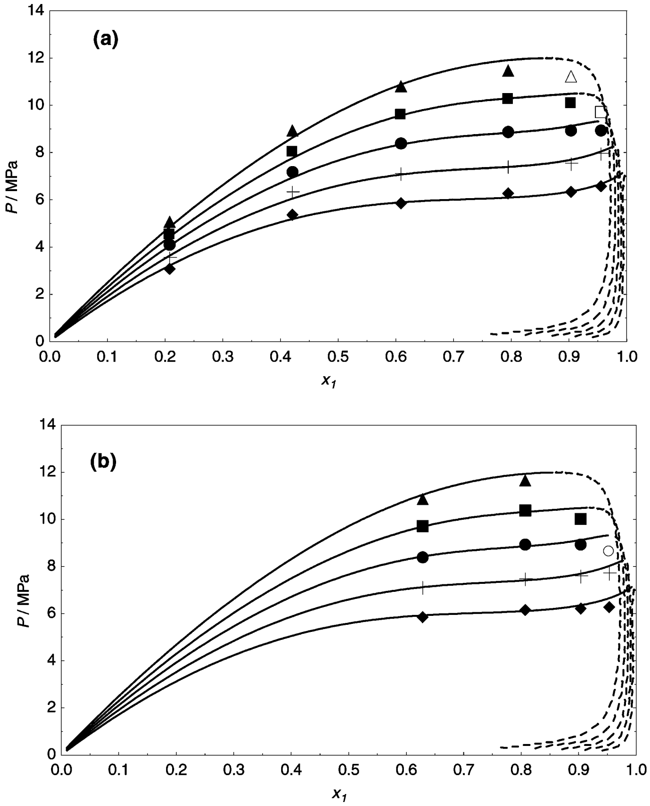

Figure 3. *P*,*x*,*y* VLE diagram for the system carbon dioxide (1) + ethanol (2) + β-carotene (3) at a β-carotene concentration in ethanol of (a) 0.096 g·L^{-1} (◆, BP at 303 K; +, BP at 313 K; ●, BP at 323 K; ■, BP at 333 K; □, DP at 333 K; ▲, BP at 343 K; △, DP at 343 K) and (b) 0.303 g·L^{-1} (◆, BP at 303 K; +, BP at 313 K; ●, BP at 323 K; ○, DP at 323 K; ■, BP at 333 K; ▲, BP at 343 K). Lines denote calculated values from the PR-EoS: —, BP transitions; ---, DP transitions.

acetate (2). The binary interaction parameters for β-carotene + CO_2, β-carotene + ethanol, and β-carotene + ethyl acetate were set to zero.

Figure 3 depicts the VLE experimental data and thermodynamic modeling for the ternary system CO_2 (1) + ethanol (2) + β-carotene (3) for β-carotene concentration in ethanol of 0.096 g·L^{-1} and 0.303 g·L^{-1} (CO_2-free basis).

It can be verified from Figure 3 that the PR-EoS with the vdW2 mixing rule was able to satisfactorily predict the phase behavior of the ternary system using only binary information. Figure 4 presents the VLE experimental data and the thermodynamic modeling for the binary system CO_2 (1) + ethyl acetate (2) and for the ternary system CO_2 (1) + ethyl acetate (2) + β-carotene (3). In this case, on the basis of the results obtained for the system CO_2 (1) + ethanol (2) + β-carotene (3), the concentration of β-carotene in ethyl acetate was fixed to 0.338 g·L^{-1}.

It can be observed from Figure 4a that the model is capable of satisfactorily correlating the experimental data for the binary system. As shown in Figure 4b, the thermodynamic model was also able to predict with good accuracy the experimental data for the ternary system CO_2 (1) + ethyl acetate (2) + β-carotene (3). One should however call attention to the fact that the approach used here for thermodynamic modeling may be strictly valid for the β-carotene concentration range investigated.

Conclusions

Phase equilibrium measurements for the binary system CO_2 + ethyl acetate and for the ternary systems CO_2 + ethyl acetate + β-carotene and CO_2 + ethanol + β-carotene were reported in this work and modeled with the PR-EoS with quadratic mixing rules. It was experimentally observed that the addition of β-carotene to the binary systems does not lead to changes in transition pressures. The approach employed to predict phase equilibrium data of ternary systems using only binary information proved to be reliable, affording satisfactory agreement between experiment and theory. Results obtained in this work may be relevant for those interested in processing β-carotene using an innovative high-pressure antisolvent technique.

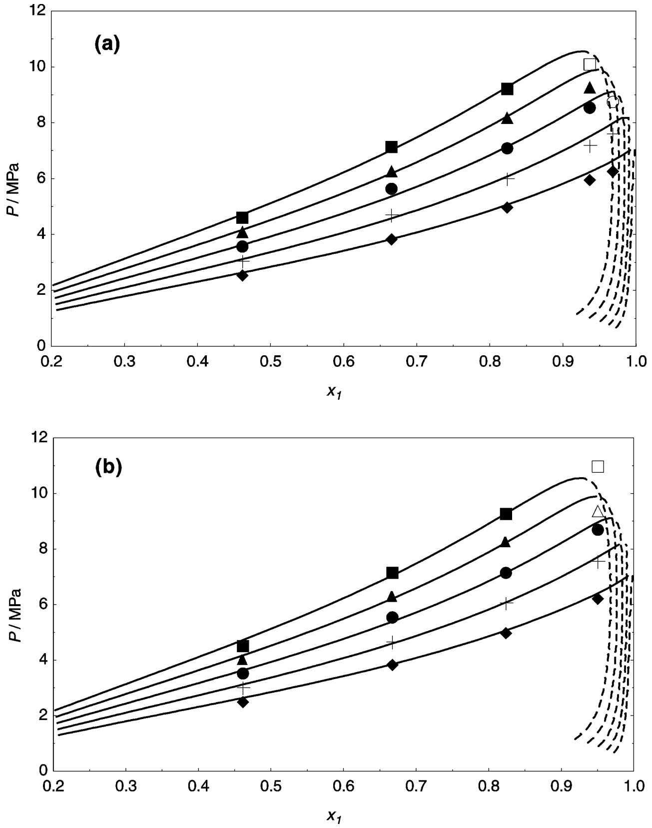

Figure 4. *P*,*x*,*y* VLE diagram of (a) the binary system carbon dioxide (1) + ethyl acetate (2) (◆, BP at 303 K; +, BP at 313 K; ●, BP at 323 K; ○, DP at 323 K; ▲, BP at 333 K; ■, BP at 343 K; □, DP at 343 K) and (b) the ternary system carbon dioxide (1) + ethyl acetate (2) +β-carotene (3) at a β-carotene concentration in ethyl acetate of 0.338 g·mL^{-1} (◆, BP at 303 K; +, BP at 313 K; ●, BP at 323 K; ▲, BP at 333 K; △, DP at 333 K; ■, BP at 343 K; □, DP at 343 K). Lines denote calculated values from the PR-EoS: —, BP transitions; ---, DP transitions.

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