Phase Equilibrium for (Camphor + CO_2), (Camphor + Propane), and (Camphor + CO_2 + Propane)

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Phase equilibrium data for {camphor (1) + CO_2 (2)}, {camphor (1) + propane (3)}, and {camphor (1) + CO_2 (2) + propane (3)} were measured using a high-pressure variable-volume view cell and the synthetic static method; experiments were performed at temperatures of (304, 314, 324, 334, 344, 354, 364, 374, and 384) K. The phase transitions have been visually identified as bubble and dew points. The temperature and pressure uncertainties were 0.5 K and 0.07 MPa. The experimental data were described satisfactorily by the Peng−Robinson equation of state with vdW2 mixing rule. The binary interaction parameters (k_{12} and l_{12}) were estimated by heuristic optimization using the simulated annealing (SA) method. Propane considerably affected the phase behavior of camphor + CO_2 when used as a second solvent, resulting in pressures for the LV phase transition intermediate to the phase transition pressure of the binary systems investigated.

Introduction

Extraction methods using classical techniques such as hydrodistillation and organic solvents have been used for obtaining volatile oils. Nevertheless, such methods present some disadvantages including thermal degradation of the extracted products, residues of organic solvent, and low yield.[1] Supercritical fluid extraction (SFE) method is a viable alternative procedure presenting some advantages, such as operation at low temperature and products free of undesirable residues. The SFE process requires optimization in two steps: (i) in the extraction step, temperature and pressure are chosen to maximize the yield in extract or a selected target component; (ii) in the separation step, temperature and pressure are selected in order to minimize the solubility of the extract or target component in the supercritical fluid. In the extraction step, the system can be viewed as a pseudo-ternary system, formed by the cellulosic structure, the solute mixture, and the solvent as defined by Rodrigues et al.[2] In the separation step, the system is formed by the solute mixture, and the solvent can thus be treated as a pseudo-binary system. The determination of phase behavior of these pseudo-binary systems is indispensable for the design of separators. Carbon dioxide is the most utilized solvent for SFE. This substance is not toxic and has a low critical temperature, which allows it to be used for the extraction of substances in both food and pharmaceutical industries.[3,4] Moreover, CO_2 is not a pollutant for the environment. On the other hand, propane does not present many of these qualities, but it is a better solvent as compared to CO_2 for a number of substances.[5] Its low critical temperature and its similarity to organic compounds, as compared to CO_2, renders propane economically more advantageous in some separation processes.[3,6]

The extraction of chemical compounds from vegetable solid substrates, at both low and high pressures, is a very complex process due to the great differences of chemical structure, size, and polarity of the compounds. The knowledge of the phase equilibrium of natural extracts in supercritical fluid at high pressures, obtained from experimental measurements of binary data, is fundamental for determination of the optimal conditions that should be used for various separation processes. Therefore, obtaining equilibrium data for binary, ternary, and multicomponent systems is very convenient for process design. The equations of state (EOS) have been extensively used for a consistent description of phase equilibrium of several systems including systems containing natural extracts.[7−11] To determine the phase equilibrium of vegetable extracts at high pressures in supercritical fluid using EOS, it is necessary to establish the parameters of binary interaction of the various binary systems that form the mixture as well as the critical properties and the acentric factors of the more representative compounds in the multicomponent mixture denoted as the extract.

Camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one, CAS Registry No. 76-22-2)[12] is an oxygenated terpene ($C_{10}H_{16}O$) that is one of the major constituents of the volatile oil from lavender flowers (*Lavandula stoechas* sp. *Cariensis boiss*), camphor tree (*Cinnamomum camphora*), and rosemary (*Rosmarinus officinalis*). This substance is commonly used in the pharmaceutical, food, and perfume industries.[13,14] Thus, the knowledge of the phase behavior of camphor + carbon dioxide and camphor + propane can help the definition of SFE parameters, specifically in the separation step.

Recently, some scientists have applied heuristic optimization methods, such as the Simulated Annealing (SA) and Genetic Algorithm, for the modeling of phase equilibrium at high pressures.[15,16] According to Kundu et al.,[16] the SA method is more efficient to estimate parameters of thermodynamic models than the deterministic method of Levemberg−Maquart.

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Table 1. Molar Mass M, Critical Temperature T_c, Pressure p_c, and Acentric Factor ω for the Compounds Used in This Work

	molar mass	T_c	P_c		
compound	kg·kmol^{-1}	K	MPa	ω	ref
camphor	152	701.36	2.946	0.3335	13
CO_2	44	304.21	7.383	0.2236	13
propane	44	369.80	4.250	0.153	19

The objectives of the present work were (i) to measure the phase equilibrium for {camphor (1) + CO_2 (2)}, {camphor (1) + propane (3)}, and {camphor (1) + CO_2 (2) + propane (3)} using the static synthetic method without sampling at the temperature of (304 to 354) K, (304 to 384) K, and (304 to 354) K, respectively, and (ii) to model the experimental data using the Peng−Robinson EOS[17] coupled to the quadratic mixing rule of van der Waals using binary interaction parameters estimated by the SA method described by Press et al.[18]

Materials and Methods

The phase equilibrium experiments were performed using camphor (99.5 % (mass), lot 53508, Vete, São Paulo, Brazil), CO_2 (99.9 % (mass), AGA, Erechim, Brazil), and propane (99 % (mass), White Martins, Erechim, Brazil).

Phase equilibrium was measured using the static method without sampling in a high-pressure variable-volume view cell. The equipment and experimental procedure used were previously described by Corazza et al.,[7,8] Moura et al.,[9] and Souza et al.[10] The phase transitions were visually identified as bubble or dew points. For a given temperature and solute mole fraction, the experimental procedure used to determine the phase transition pressure was repeated at least three times. An average value was considered for both transition temperature and transition pressure. The temperature and pressure uncertainties (standard deviations of mean values) were ± 0.5 K and ± 0.07 MPa. The experimental data were obtained at temperatures of (304 to 354) K for {camphor (1) + CO_2 (2)} and {camphor (1) + CO_2 (2) + propane (3)}; for {camphor (1) + propane (2)}, the experiments were carried out at temperatures of (304 to 384) K.

Modeling of the Experimental Data. The thermophysical properties and acentric factors for camphor and CO_2 were obtained from Akgün et al.[13] The thermophysical properties and acentric factor for propane were obtained from Reid et al.[19] The binary interaction parameters, k_{ij} and l_{ij}, of the Peng−Robinson[17] EOS were estimated using the procedure described by Corazza et al.[20] The SA method, as described by Press et al.,[18] was used to minimize the objective function (OF) given in eq 1:

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

where P_i^{exp} is the saturation pressure of the i observation and P_i^{calcd} is the calculated pressure for the i observation. NOBS is the number of experimental observations used in the modeling.

Results and Discussion

The critical properties and acentric factors for camphor (1), CO_2 (2), and propane (3) are listed in Table 1. The bubble and cloud points measured for {camphor (1) + CO_2 (2)} are listed in Table 2. For the isotherm at a temperature of 304 K, only bubble point transitions were observed. For the isotherms at temperatures of (314 to 354) K, bubble point transitions were observed for all mole fractions, except for $x_2 > 0.9$.

Table 2. Mole Fraction x_2, Pressure P, and Temperature T for the LV Equilibrium in {Camphor (1) + CO_2 (2)}[a]

	P/MPa					
x_2	T = 304 K	T = 314 K	T = 324 K	T = 334 K	T = 344 K	T = 354 K
0.9907	7.28	8.65^{DP}	9.88^{DP}	12.06^{DP}	12.59^{DP}	
0.9759	6.82	8.47	10.04^{DP}	11.95^{DP}	13.46^{DP}	14.94^{DP}
0.9618	6.49	8.30	10.01	11.82^{DP}	13.75^{DP}	15.43^{DP}
0.9558	6.85	8.16	9.93	11.78^{DP}	13.58^{DP}	15.71^{DP}
0.9264	6.55	8.04	9.90	11.91	13.87	15.61^{DP}
0.8873	6.66	8.03	9.85	11.70	13.65	15.55
0.8558	6.11	7.70	9.42	11.43	13.39	15.28
0.8054	6.47	7.64	9.21	10.85	12.62	14.37
0.7487	5.97	7.17	8.55	10.03	11.51	13.04
0.6482	5.14	6.02	7.17	8.33	9.44	10.69
0.5716	4.49	5.53	6.25	7.25	8.14	9.16
0.4472	3.42	3.98	4.59	5.53	6.15	6.83
0.3955				4.90	5.33	6.09
0.3160					4.29	4.91

[a] DP, dew point. Points without subscripts are bubble points (BP).

Table 3. Mole Fraction x_3, Pressure P, and Temperature T Obtained for the LV Equilibrium in {Camphor (1) + Propane (3)}[a]

	P/MPa								
x_3	T = 304 K	T = 314 K	T = 324 K	T = 334 K	T = 344 K	T = 354 K	T = 364 K	T = 374K	T = 384 K
0.9943	1.25	1.57	1.94	2.38	2.86	3.40	4.00	4.50^{DP}	4.89^{DP}
0.9907	1.20	1.54	1.93	2.36	2.84	3.39	3.98	4.50	4.77^{DP}
0.8451	1.14	1.40	1.76	2.14	2.57	3.05	3.57	4.12	4.69
0.7461	1.28	1.55	1.84	2.19	2.57	2.98	3.46	3.88	4.39
0.5753	1.08	1.33	1.57	1.92	2.29	2.58	2.97	3.35	3.70
0.5129	1.00	1.30	1.56	1.81	2.17	2.41	2.60	2.91	3.31
0.4306				1.64	1.98	2.19	2.40	2.63	2.84
0.2980							1.98	2.15	2.28

[a] DP, dew point. Points without subscripts are bubble points (BP).

Table 4. Mole Fractions x_2 and x_3, Pressure P, and Temperature T Obtained for the LV Equilibrium of {Camphor (1) + CO_2 (2) + Propane (3)}[a]

			P/ MPa					
x_1	x_2	x_3	T = 304 K	T = 314 K	T = 324 K	T = 334 K	T = 344 K	T = 354 K
0.0494	0.2330	0.7176	2.40	2.71	3.66	4.34	4.79	5.53
0.0566	0.3960	0.5474	3.81	4.54	5.29	6.09	6.94	7.77
0.0568	0.6767	0.2665	4.82	6.12	7.25	8.7	10.09	11.38^{DP}
0.0630	0.8896	0.0474	6.77	8.03	9.82	11.57	13.32	15.02^{DP}
0.1105	0.7007	0.1888	4.98	6.78	7.99	9.25	11.19	12.61

[a] DP, dew point. Points without subscripts are bubble points (BP).

Table 3 lists the experimental data for {camphor (1) + propane (3)}. At temperatures of (304 to 364) K, only bubble points were observed. For temperatures of (374 to 384) K, dew points were observed for $x_3 > 0.99$. This system showed phase transition pressures lower than those of {camphor (1) + CO_2 (2)}.

Table 4 lists the equilibrium data obtained for {camphor (1) + CO_2 (2) + propane (3)}. For temperatures of (304 to 344) K, only bubble points were observed, while both bubble and dew points were found for temperature of 354 K at x_2 = (0.8896 and 0.6767) and at x_3 = (0.0474 and 0.2665). For this ternary system, the transition pressures were intermediate to the transition pressures measured for {camphor (1) + CO_2 (2)} and {camphor (1) + propane (3)}.

The binary interaction parameters are shown in Table 5. These parameters were estimated using the experimental data obtained at temperature of (304 to 384) K.

Figure 1 compares experimental and calculated phase equilibrium diagrams for {camphor (1) + CO_2 (2)} for isotherms at temperatures of (304 to 354) K. Figure 2 presents experimental and calculated results for temperatures of (314, 324, and 334) K for {camphor (1) + CO_2 (2)}; the data reported by

Table 5. Values of the Fitted Binary Interaction Parameters for the PR-EOS[17]

systems	k_{12} (10^2)	l_{12} (10^2)	OF[a]	NOBS[b]
CO_2 + camphor	5.4695	−0.6598	187.54	48
propane + camphor	10.3920	1.3507	77.88	46
CO_2 + propane[c]	16.5100	3.9030	4.37	14

[a] OF, objective function final value. [b] NOBS, number of experimental observations used for parameter fitting. [c] Ref 20.

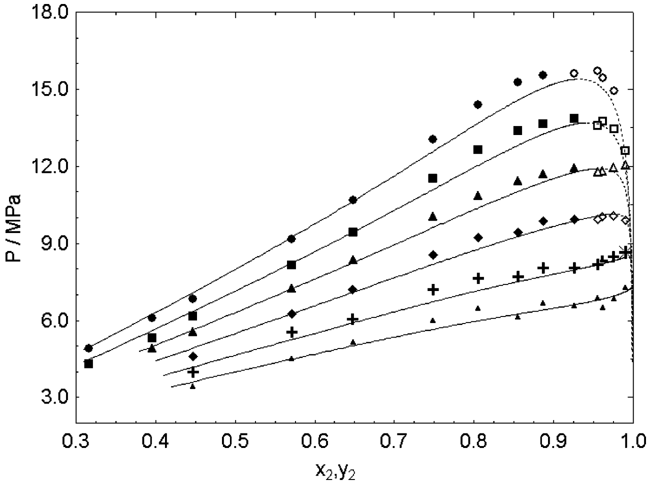

Figure 1. *P*−*x*−*y* plot for camphor (1) + CO_2 (2). Experimental data: ●, BP and ○, DP at 354 K; ■, BP and □, DP at 344 K; ▲, BP and △, DP at 334 K; ♦, BP and ◊, DP at 324 K; +, BP and ∗, DP at 314 K; small solid triangle, BP 314 K. PR-EOS model: —, liquid; - -, vapor.

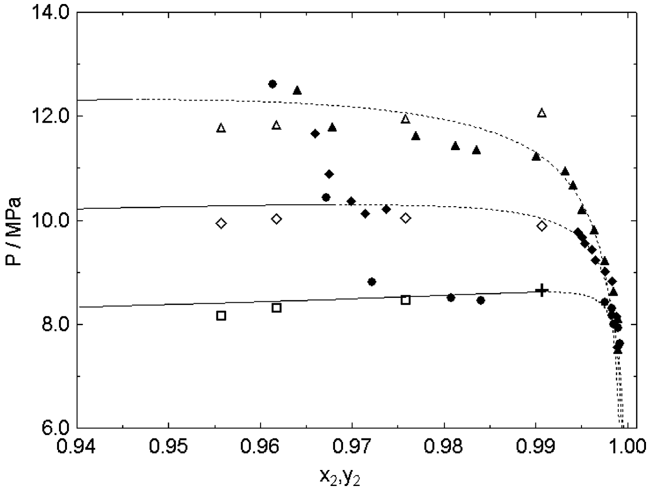

Figure 2. *P*−*x*−*y* plot for camphor (1) + CO_2 (2). Comparison to literature data at 314 K, 324 K, and 334 K: ●, DP at 334 K; ▲, DP at 324 K; △, BP and ◊, DP at 314 K. PR-EoS model: —, liquid; - -, vapor. Literature[13]: □, at 313 K; +, at 323 K; ♦, at 333 K.

Akgün et al.[13] are also shown in Figure 2 for comparison. These authors measured the phase equilibrium of (camphor + CO_2) using the static analytic method without visualization at temperatures of (313, 323, and 333) K; equilibrium data were reported as solid−fluid transition. Nonetheless, in the present work liquid−vapor transitions were visually observed and predicted by the thermodynamic model. Pure camphor is a solid at the conditions of temperature of 304 to 354 K; nonetheless, it dissolves readily when in contact with carbon dioxide or propane. In the view cell prior to any measuring, a homogeneous phase was observed while no solid phase was visually detected. Then, for the temperature and pressure of each experiment small bubbles (reported as bubble point) or small droplets (reported as dew point) were observed. Figure 3 compares experimental

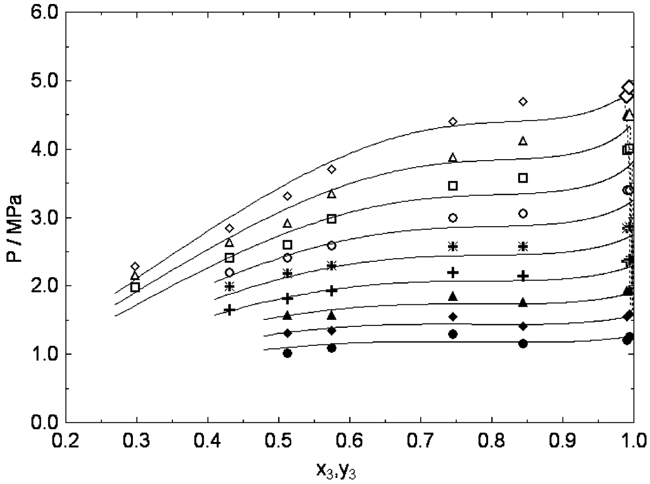

Figure 3. *P*−*x*−*y* plot for camphor (1) + propane (3). Experimental data: ◊, BP and smaller ◊, DP at 384 K; △, BP and smaller △, DP at 374 K; □, BP at 364 K; ○, BP at 354 K; ∗, BP at 344 K; +, BP at 334 K; ▲, BP at 324 K; ♦, BP at 314 K; ○, BP at 304 K. PR-EOS model: —, liquid; - -, vapor.

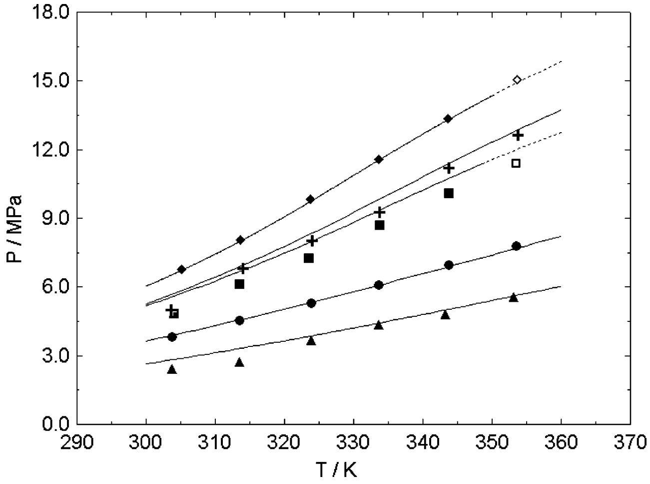

Figure 4. *P*−*T* diagram for the system camphor (1) + CO_2 (2) + propane (3). Isopleths for mole fraction. **C1**: $z_2 = 0.6767$ and $z_3 = 0.2665$ ♦, BP and ♦, DP. **C2**: $z_2 = 0.3960$ and $z_3 = 0.5474$ +, BP. **C3**: $z_2 = 0.8896$ and $z_3 = 0.0474$ ■, BP and □, DP. **C4**: $z_2 = 0.2330$ and $z_3 = 0.7176$ ●, BP. **C5**: $z_2 = 0.7007$ and $z_3 = 0.1888$ ▲, BP. PR-EOS model: —, liquid; - -, vapor.

and calculated data for the isotherms of (304 to 384) K for the system camphor + propane. The *P*−*T* diagram for the ternary system is shown in Figure 4; the isopleths for this system were calculated using the information for binary systems reported here. The binary interaction parameters for CO_2 + propane were taken from Corazza et al.[20]

Conclusions

It can be concluded that the use of propane as a second solvent considerably affected the phase behavior of the system camphor + CO_2 shifting the phase transition pressures to intermediate values in comparison to the investigated binary systems. The Peng−Robinson EOS coupled to the van der Waals mixing rule (vdW2) was capable of qualitatively describing the binary and ternary systems studied using the interaction parameters obtained by the SA method.

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