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Phase Equilibrium Measurements for the System Fennel (*Foeniculum vulgare*) Extract + CO_2

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Phase equilibria data for the system formed by CO_2 (1) + fennel extract (2) were measured at pressures from (47.4 to 220.4) bar and temperatures of (303.0, 313.1, 323.1, and 333.0) K; CO_2 mole fraction varied from (0.4827 to 0.9966). The phase equilibrium experiments (cloud points) were performed using a high-pressure variable-volume view cell. The phase transitions were visually recorded as bubble or dew points. The fennel extract used in the present work was obtained by extraction with carbon dioxide. Liquid−vapor (LV) equilibria were observed at all temperatures for x_1 = (0.4827 to 0.7086). Liquid−liquid (LL) equilibria were observed for all temperatures at x_1 = (0.7178 to 0.7760) and x_1 = 0.9949, except at 333.0 K; LL transition was also observed at 303.0 K and x_1 = 0.9966. At 303.0 K, liquid−liquid−vapor (LLV) transitions were observed at x_1 = (0.8297, 0.9273, and 0.9949); at 313.1 K for x_1 = (0.9273 and 0.9949). At x_1 = 0.9966 and 303.0 K, LL and LLV were observed at (98.4 and 70.2) bar, respectively. The experimental data were fitted to the Peng−Robinson equation of state with the quadratic mixing rule using the simulated annealing minimization method. The model described quantitatively the experimental data.

Introduction

In supercritical fluid extraction (SFE) from solid substratum the step of extract/ solvent separation can be costly depending on the flash separator's pressure. For the optimization of the extraction process, the knowledge of the phase equilibrium data is required. When available, the equilibria data are used for the selection of the best conditions of pressure and temperature to be used in the separation step and/or for fractionated extraction.[1] Despite the reduction observed in the investment costs in the past decade, the manufacturing costs of SFE extracts are still considered prohibitive by many in industry. To achieve a reduction in these costs, it is mandatory to gather all the information related to a particular system. In that respect, the knowledge of phase equilibria can benefit the design of SFE systems, specifically in the separation step. Relevant data on phase equilibria of several binary and ternary systems of interest have been published in the literature.[2−4] The use of phase equilibria data for real systems, such as the mixture that forms fennel extract, is more appropriate for process design; nonetheless, this type of data is still scarcely available. Due to the variety and complexity of the chemical functional groups that form a natural extract, such as volatile oils, oleoresins, and the like, the phase equilibria of these systems generally is not trivial.[5−9] Nonetheless, the Peng−Robinson[10] equation of state (PR EOS) was capable of quantitatively describing the phase behavior of such systems as demonstrated by Souza et al.[9] for clove oil + CO_2: The clove oil obtained by SFE was treated as a pseudo-pure compound; its thermophysical properties were estimated by the Kay's[11] rule using the pure components properties estimated using the method of Constantinou and Gani;[12] the acentric factor was calculated with the Lee and Kesler method.[11]

The purposes of the present work were to measure the phase equilibrium for the system formed by CO_2 + fennel extract, to model the experimental data using the PR EOS coupled to the phase stability analysis, and to compare the phase equilibrium behavior predicted using the estimated parameters for a pseudo-binary system formed by CO_2 + SFE fennel extract; three pseudo-pure compounds denoted as FE_1, FE_2, and FE_3 were considered based on the compositions of fennel extracts published in the literature.

Materials and Methods

Preparation and Characterization of the Fennel Extract. Fennel extract was obtained by supercritical extraction using fennel seeds cultivated under controlled conditions[13] and CO_2 (99.99 %, AGA, Campinas, Brazil) in a SFE unit (Applied Separations, Allentown, PA). The extract was obtained at 30 °C and 250 bar from fennel seeds harvested mature in December 2001 (seeds denoted as Fv_3 by Moura et al.[13]); the extraction conditions were chosen based on the kinetic studies of Moura et al.[13] The fennel extract (essential oil and part of the oleoresin) composition was determined using gas chromatography with a flame ionization detector (GC-FID) and a split injector (Shimadzu, model 17A, Kyoto, Japan) equipped with a capillary column of fused silica (DB-5; 30 m × 0.25 mm × 0.25 μm, J&W Scientific, Folsom, CA). The carrier gas (1.7 mL/min) was helium (99.9 %, White Martins Gases Industriais, Campinas, Brazil). The injector and detector temperatures were 240 and 280 °C, respectively. The following temperature programming was used: 50 °C (5

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Table 1. Composition of Fennel Extract Used in This Work[a]

component	mole fraction	T_b / K	T_c / K	P_c / bar	w	molar mass / kg·kmol^{-1}
fenchone	0.0109	509.9[b]	742.4[b]	30.9[b]	0.4057[b]	152.24
anethole	0.1714	486.4[b]	700.8[b]	29.9[b]	0.4469[b]	148.2
palmitic acid	0.0689	622.3[c]	780.4[c]	14.7[c]	1.0104[c]	253.43
palmitoliec acid	0.0115	607.0[c]	780.0[c]	14.2[c]	0.8669[c]	254.41
stearic acid	0.0278	648.1[c]	796.7[c]	13.3[c]	1.0861[c]	284.48
oleic acid	0.4701	625.5[c]	796.3[c]	12.4[c]	0.9245[c]	282.47
linoleic acid	0.2393	624.1[c]	796.0[c]	12.4[c]	0.7767[c]	280.45
fennel extract			778.0[d]	15.8[d]	0.8114[d]	255.29[d]
CO_2			304.2[e]	73.8[e]	0.22368[e]	44.01

[a] Thermophysical properties and acentric factors of the substances identified in the fennel extract components, of the pseudopure component denoted as fennel extract and of CO_2. The subscripts c and b refer to critical properties and normal boiling temperature. [b] Joback and Reid.[16] [c] Araújo and Meireles.[17] [d] The properties of the fennel extract were estimated by the Kay's rule except the critical pressure, which was estimated by the Prausnitz and Gunn's rule.[11] [e] Angus et al.[18]

min); 50 to 280 °C at 5 °C/min; 280 °C (5 min). The sample injected in the GC-FID system were fennel extracts (0.005 g) diluted in 1 mL of ethyl acetate (p.a., lot 55893, LabSynth, São Paulo, Brazil); 1 μL of sample was injected, and the sample split ratio was 1:30. The identification of the chemical constituents was based on the comparison of the retention index for SFE fennel extracts. The quantification was done using the external standard method[14] and the following standards: anethole (99 %, Aldrich, lot 06605HR, Milwaukee, WI), fenchone (98 %, Aldrich, lot 04416TS, Milwaukee, WI).

Phase Equilibrium Apparatus and Procedure. Phase equilibrium experiments (cloud points) were performed through a static method without sampling[15] in a high-pressure variable-volume view cell. The apparatus is very similar to the one used to measure the phase equilibria of CO_2 + clove oil,[9] and it is the equipment that was used to measure the phase equilibria of binary mixtures of CO_2 + acetonitrile, dichloromethane, carvone, and 1,2-limoneneoxide.[15] Phase transitions were visually recorded as bubble or dew points. Carbon dioxide, 99.99 % (AGA, Campinas, Brazil), was used. The temperature was measured with an uncertainty of ± 0.5 K. The amount of solvent charged was monitored by the change in the total volume of the transfer vessel of the pump. The uncertainty was ± 0.001 for the mole fraction. The cell content was continuously agitated with the aid of a magnetic stirrer and a Teflon-coated stirring bar. After the desired temperature was reached, the cell pressure was increased to the point of the observation of a single phase. At this point, the system was allowed to stabilize for at least 30 min, and the cell pressure was slowly decreased until the incipient formation of a new phase; after repetition of the experimental procedure at least three times, the equilibrium pressure was then recorded, leading to an uncertainty of ± 0.7 bar. After completing the test at a given temperature, the cell temperature was stabilized at a new value, and the experimental procedure was repeated. Experimental data were measured at (303.0, 313.1, 323.1, and 333.0) K.

Modeling of Experimental Data. The thermophysical properties and the acentric factor of the anethole and fenchone were estimated using the group contribution method of Joback and Reid;[16] the properties of fatty acids (oleic acid, palmitoleic acid, palmitic acid, stearic acid, and palmitoleic acid) were estimated by the methods selected by Araújo and Meireles.[17] The fennel extract was considered a pseudo pure component; its thermophysical properties and acentric factor were calculated using the Kay's rule,[11] except the critical pressure that was estimated by using the Prausnitz and Gunn's rule.[11] The thermophysical properties and the acentric factor of CO_2 were obtained in Angus et al.[18] The PR EOS, together with the van der Waals quadratic mixing rule (two adjustable parameters: k_{ij} and l_{ij}), was used to model the experimental data. However, at the temperatures where liquid−liquid−vapor (LLV) was observed, only the experimental data of liquid−liquid (LL) equilibrium were used to estimate the model parameters. The calculation procedure was the same as that of Souza et al.:[9] The phase stability analysis was performed using the minimization of the tangent plane distance of the Gibbs free energy;[19] the simulated annealing routine[20] was utilized. The modified procedure was validated using the examples of Hua et al.[21] and Stradi et al.[22] The results for the phase stability problem were used as the initialization for the flash calculation.

Table 2. Bubble Point and Dew Pressures of the System CO_2 (1) + Fennel Extract (2) at Specified Temperatures

		P/bar at *T*/K			
x_1	type of equilib[a]	303.0	313.1	323.1	333.0
0.4827	LV	47.4 ± 0.3	56.29 ± 0.2	64.0 ± 0.1	71.6 ± 0.1
0.5355	LV	53.8 ± 0.2	60.49 ± 0.3	69.8 ± 0.2	77.7 ± 0.1
0.5991	LV	65.9 ± 0.1	77.1 ± 0.1	88.0 ± 0.2	99.4 ± 0.1
0.6383	LV	64.6 ± 0.1	78.3 ± 0.1	92.6 ± 0.1	107.7 ± 0.5
0.6975	LV	72.1 ± 0.6	88.5 ± 0.1	105.9 ± 0.2	123.6 ± 0.2
0.7086	LV	70.21 ± 0.1	89.3 ± 0.1	110.0 ± 0.2	130.5 ± 0.1
0.7178	LL	82.8 ± 0.2	107.0 ± 0.2	127.5 ± 0.3	146.4 ± 0.2
0.7427	LL	99.3 ± 0.1	119.6 ± 0.1	138.3 ± 0.1	160.4 ± 0.3
0.7760	LL	174.3 ± 0.2	180.5 ± 0.3	194.4 ± 0.1	209.8 ± 0.4
0.8297	LLV	69.2 ± 0.4			
0.9273	LLV	69.4 ± 0.3	85.5 ± 0.1		
0.9949	LL	194.0 ± 0.1	205.2 ± 0.1	220.4 ± 0.2	-
0.9949	LLV	69.7 ± 0.6	80.2 ± 0.1		
0.9966	LL	98.4 ± 0.3			
0.9966	LLV	70.2 ± 0.1			

[a] LV, liquid−vapor; LL, liquid−liquid; LLV, liquid−liquid-vapor.

Results and Discussion

Table 1 shows the composition of fennel extract in terms of mole fraction of the substances quantified by GC-FID; the thermophysical properties of the substances that form the fennel extract, of the pseudo-pure component denoted as fennel extract, and of CO_2 are also shown. Despite the structural differences between anethole and fenchone, their estimated thermophysical properties are quite similar. Table 2 shows the bubble and dew points measured for the system CO_2 + fennel extract. Liquid−vapor (LV) equilibria were observed at all temperatures for x_1 = (0.4827 to 0.7086). LL equilibria were observed for all temperatures at x_1 = (0.7178 to 0.7760) and x_1 = 0.9949, except at 333.0 K; LL transition was also observed at 303.0 K and x_1 = 0.996. LLV transitions were observed at 303.0 K and x_1 = (0.8297, 0.9273, and 0.9949) and also at 313.1 K and x_1 =

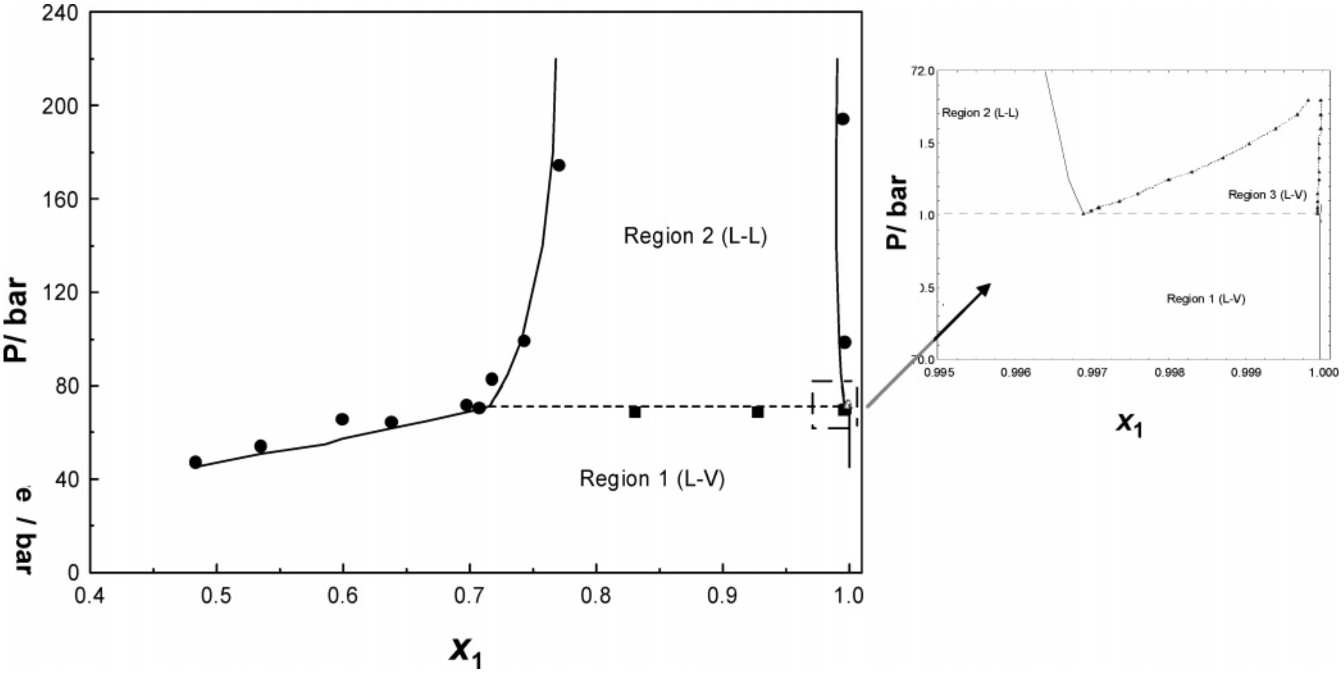

Figure 1. *P*−*x*−*y* plot for CO_2 + fennel extract at 303.0 K: ●, LL or LV; ■, L-L-V; — and - -, model. The inset was obtained by calculation using the optimized set of binary interaction parameters and the stability test.

Table 3. Values of the Fitted Binary Interaction Parameters

T/K	NU[a]	k_{12}	l_{12}	FO[b]
303.0	9	0.081629	−0.015712	216.48
313.1	9	0.077072	−0.029862	124.99
323.1	9	0.085056	−0.018230	140.46
333.0	9	0.090279	−0.012040	130.86

[a] NU, number of experimental points used in the parameters' fitting. [b] FO, objective function.

(0.9273 and 0.9949). At $x_1 = 0.9849$ and 303.0 K, LL and LLV were observed at 98.4 and 70.2 bar, respectively. Table 3 shows the parameters fitted to the PR EOS for the system CO_2 + fennel extract for temperatures of (303.0, 313.1, 323.1, and 333.0) K. The values are very close to each other. Nonetheless, fitting all data simultaneously regardless of the temperature gave a poor fit. Therefore, the system CO_2 + fennel extract could be adequately described by the PR EOS considering that the binary parameters are highly dependent on temperature.

The comparisons between experimental and calculated phase equilibria are shown in Figures 1 to 4 for (303.0, 323.1, 333.0, and 313.1) K, respectively. Figure 1 shows that, using the equilibrium stability test, the model correctly described the LLV region experimentally observed. The inset of Figure 1 shows the tri-phase region calculated using the PR EOS and the stability test. At 303.0 K, the model predicted the occurrence of LLV at 71.0 bar and $x_{1,L1} = 0.7149$ and $x_{1,L2} = 0.9969$, and $x_{1,V} = 0.999945$, conditions very close to the experimental values (Table 2).

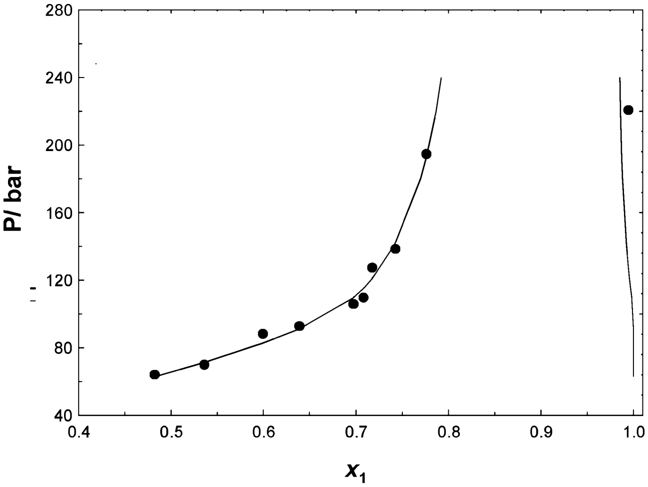

Figure 2. *P*−*x*−*y* plot for CO_2 + fennel extract at 323.1 K: ●, LL; and —, model.

Damjanovic et al.[23] compared the composition of fennel extract (SFE) with that of the volatile oil (that is, the extract obtained by hydrodistillation). The reported compositions are different from that of the present work. These authors reported anethole as being the major compound of the extracts at all conditions; in the present work, anethole was the major compound of the volatile fraction of fennel extracts. Additionally, the fatty acids, myristic acid (tetradecanoic acid) and palmitic acid (hexadecanoic acid), were detected by these authors, while in the present work, myristic acid was not detected in fennel extracts despite the detection of other fatty acids such as linoleic, palmitoleic, and stearic acids. To investigate the effects of the composition on the calculations of phase behavior for the system CO_2 + fennel extract, the data of Damjanovic et al.[23] were used to estimate the critical properties and the acentric factor of three pseudo-components denoted as (FE_1, FE_2, and FE_3) corresponding to the compositions of the fennel extracts obtained at 313.2 K and at pressures of (80, 100, and 150) bar (Table 4); the thermophysical properties and the acentric factors of (FE_1, FE_2, and FE_3) are in Table 5. Using the binary interaction parameters obtained in the present work, phase stability calculations were performed for the binary systems formed by CO_2 + the pseudo-components FE_1, FE_2, and FE_3. Figure 4 shows that the phase behavior of the system fennel extract + CO_2 can be of type IV (for the pseudo-pure component, which thermophysical properties were estimated using the composition of the fennel extract of the present work) or type III (for the pseudo-pure components, which thermophysical properties were obtained using the compositions of the fennel extracts reported by Damjanovic et al.[23]) according with the classification of van Konynenburg and Scott.[24]

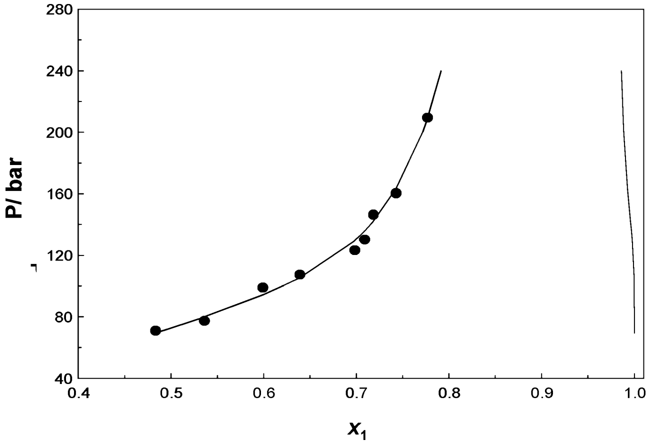

Figure 3. $P-x-y$ plot for CO_2 + fennel extract at 333.0: ●, LL; and —, model.

Table 4. Composition (Mole Fraction) of the Fennel Extracts Obtained by Damjanovic et al.[23] at 313.1 K and Pressures of (80, 100, and 150) bar

substances identified in fennel extracts by ref 23	mole fraction at P/bar		
	80	100	150
α-pinene	0.0047	0.0025	0.0034
camphene	0.0009	0.0008	0.0006
sabinene	0.0021	0.0020	0.0029
myrcene	0.0046	0.0047	0.0041
α-phellandrene	0.0015	0.0013	0.0012
p-cymene	0.0001	0.0006	trace
D-limonene	0.0069	0.0060	0.0045
1,8-cineole	0.0071	0.0020	0.0025
β-ocimene	trace	trace	trace
γ-terpinene	0.0053	0.0041	0.0064
fenchone	0.1030	0.1142	0.0935
camphor	trace	trace	trace
terpinen-4-ol	0.0007	0.0009	trace
methyl chavicol	0.0685	0.0694	0.0631
cis-anethole	trace	trace	trace
anisaldehyde	0.0006	0.0006	trace
trans-anethole	0.7554	0.7542	0.7342
germacrene D	0.0023	0.0018	0.0098
tetradecanoic acid	0.0009	0.0009	0.0069
hexadecainoic acid	0.0043	0.0039	0.0087
tetradecane	0.0159	0.0121	0.0114
1,2-benzenedicarboxylic acid, dioctyl ester	0.0007	0.0014	0.0027
pentadecane	0.0006	0.0005	0.0066
pentacosane	0.0005	0.0005	0.0050
1-hexadecanol	0.0025	0.0025	0.0062
hexacosane	0.0010	0.0010	0.0035
1-octadecanol	0.0021	0.0020	0.0083
7-octadecanone	0.0077	0.0101	0.0147

Table 5. Thermophysical Properties of the Pseudo-Components[a]

	pseudo-components properties		
	FE_1	FE_2	FE_3
T_b/K	503.7	509.8	515.7
T_c/K	713.9	722.2	722.9
P_c/bar	27.2	27.4	25.1
V_c/m³/mol	$506.9 \cdot 10^{-6}$	$513.5 \cdot 10^{-6}$	$552.0 \cdot 10^{-6}$
Z_c	0.2322	0.2344	0.2309
w	0.4817	0.4881	0.5159

[a] The properties of the pseudo-components were estimated by the Kay's rule except the critical pressures, which were estimated by the Prausnitz and Gunn's rule.[11]

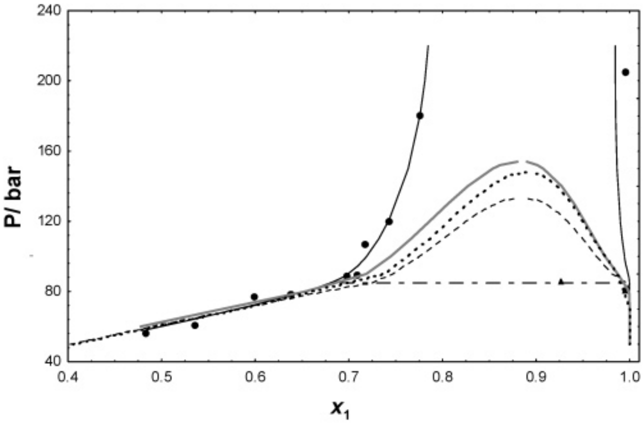

Figure 4. $P-x-y$ plot for CO_2 + fennel extract at 313.1 K: ●, LL or LV; ▲, L-L-V; — and - -, model using the pseudo-component of this work. Calculated phase equilibrium using the pseudo-components (– –, FE_1; —, FE_2; and ····, FE_3), which thermophysical properties were calculated based on the compositions of fennel extracts given by Damjanovic et al.[23] The binary interaction parameters obtained in the present work (Table 3) were used.

Conclusions

Fennel extract obtained by SFE is a mixture formed by fenchone and anethole (terpenoids) and fatty acids. The system CO_2 + fennel extract exhibited LV, LL, and LLV phase transitions. Despite the strong nonideality of the system, the PR EOS was capable of describing the experimental data. The use of the stability test and the optimized set of binary interaction parameters allowed calculating a small LV phase envelope. The results showed that the coupling of a good strategy to fit the experimental data with the phase stability test allowed studying complex phase behavior with a simple model such as PR EOS.

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