High-Pressure Equilibrium Data in Systems Containing Supercritical Carbon Dioxide, Limonene, and Citral

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This paper presents experimental equilibrium data for both CO_2 + limonene and CO_2 + citral systems at a constant temperature of 315 K and at pressures varying between (3 and 10) MPa. Experimental data on the ternary system CO_2 + limonene + citral are also presented. The experiments were performed at 315 K and at two different pressure values: (8.4 and 9.0) MPa. The experimental results obtained were correlated by means of the Peng−Robinson equation of state and by applying mixing rules characterized by two different interaction parameters specific to each binary subsystem present in the ternary system. The data obtained show that limonene is characterized by higher solubility in carbon dioxide than citral. It is therefore possible to obtain an enrichment of citral through the extraction of limonene by means of supercritical carbon dioxide starting from a mixture of limonene and citral.

Introduction

As is known, lemon essential oil is a complex mixture of a large number of different components that can be divided into three main classes: terpenic hydrocarbons, oxygenated terpenes, and sesquiterpenes.[1] Despite the relatively small percentage of oxygenated terpenes present in the mixture, the fragrance of the essential oil derives solely from these components. While the terpenic hydrocarbons constitute the main components of the oil in quantitative terms, their basic function is one of physical support. As they can also give rise to oxidation phenomena and hence to degradation reactions that impair the original characteristics of the essential oil, a process of enrichment in oxygenated terpenes could prove useful. Vacuum-distillation processes are applied at present to the essential oil in order to obtain a concentrated residue of oxygenated components. The application of an extraction process with supercritical carbon dioxide to these complex mixtures would be of great interest with a view to preventing thermodegradation of the product. In this connection, two different possibilities have been studied in particular. The first uses carbon dioxide directly to extract the high-value components from the solid matrix.[2] The other consists of a process whereby supercritical carbon dioxide is used to extract selected components from the liquid essential oil in order to obtain a final residue enriched in oxygenated components.[3−5]

The feasibility of this enrichment process has been examined in great depth in the literature[6−9] with respect to the experimental solubility of essential oil components in supercritical carbon dioxide. Due to the complexity of these essential oils, some studies adopt a simplified approach whereby solubility is measured experimentally with reference to a synthetic oil prepared by mixing a restricted number of the components present in the oil. In this synthetic mixture, each component represents its own class of chemical species. Indeed many works propose a drastic schematization of lemon essential oil whereby it is regarded as a simple mixture of only two components representing

the main classes of chemical compounds present, namely terpenes and oxygenated terpenes.[10] This simplified approach was followed also in the present work. Specifically, limonene was chosen to represent terpenes and citral to represent oxygenated compounds. To verify the feasibility of the process for extracting terpenes from natural essential oils, the synthetic system composed of limonene and citral and carbon dioxide was studied. In particular, experimental equilibrium data were obtained on the subsystems CO_2 + limonene and CO_2 + citral as well as the ternary system CO_2 + limonene + citral. Thermodynamic characterization of the CO_2 + limonene + citral system makes it possible to determine the optimal operational conditions at which a supercritical extraction process can be performed to enhance the concentration of citral in the synthetic essential oil. The data obtained could be used subsequently in order to study the same process applied to natural essential oils.

Materials and Methods

D-Limonene (Janssen) characterized by a purity of over 97% and citral (Fluka Chemica) with a purity of 97% were used to perform both binary and ternary equilibrium runs. The carbon dioxide (SOL SUD) used in this study was over 99.9% pure. A cold trap filled with 99.9% pure ethyl alcohol (Carlo Erba) was used to recover both liquid and gas samples.

The samples were analyzed by means of a Hewlett-Packard HPLC apparatus of the HP1050 type equipped with a Spherisorb ODS2 packed column. The packing particles had a mean pore diameter of 5 μm, a specific pore volume of 0.5 mL/g, and a surface area of 220 m²/g. The column can be used in the pH range 2−8 and at pressures of up to 400 bar. The mobile phase used was ethyl alcohol with a flow rate corresponding to a pressure value inside the column equal to 100 bar. The detector used was a Hewlett-Packard refractive index detector HP 1047A, and response peaks were integrated by using a HP 3394A integrator.

The amount of carbon dioxide removed from the apparatus during the experimental runs was registered by

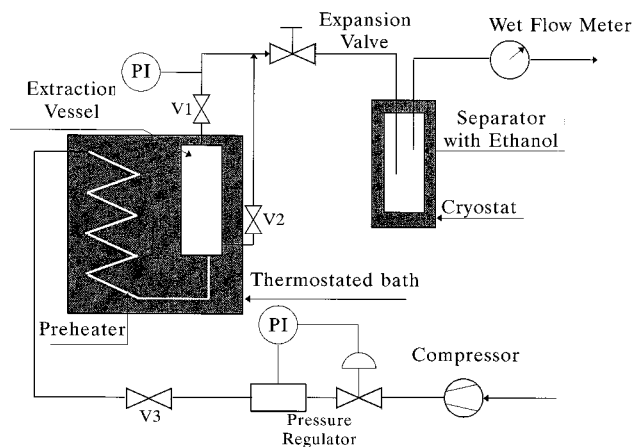* To whom correspondence should be addressed. Fax: 0039 6 44585451. E-mail: gironi@ingchim.ing.uniroma1.it.

Figure 1. Simplified flow sheet of the experimental apparatus.

means of a volumetric wet gas meter with an uncertainty of ±5 mL (at normal conditions).

The experimental apparatus used to perform phase-equilibrium measurements is schematically represented in Figure 1. It consists essentially of a compressor, an equilibrium vessel ($V = 0.2$ L), a preheater to bring the solvent to the desired temperature, a cold trap to recover the solute, and a volumetric meter to measure the quantity of carbon dioxide used in each experimental run. The equilibrium vessel was immersed in a constant-temperature bath, which could be controlled to within ±0.1 K. The equilibrium vessel is equipped with two outlet valves: the first is positioned at the top of the vessel and was used to take samples of the supercritical phase, while the second is set lower down and was used to take samples in the liquid phase. The top of the vessel was equipped with a steel porous septum in order to avoid the mechanic transport of the liquid droplets into the supercritical phase.

All high-pressure tubing was 1 mm i.d., and the distance between the vessel and each expansion valve was equal to about 100 mm: in this way the holdup of tubing was negligible with respect to the holdup of the equilibrium vessel.

The compressor was operated under constant pressure mode to control the system pressure. The pressure could be maintained to an uncertainty of within ±0.2% of the desired value.

The cold trap was filled with ethanol and maintained at 260 K in order to minimize the loss of ethanol and solutes. To avoid possible measurement errors, the liquid in the cold trap was saturated with carbon dioxide before each experiment.

The CO_2 + limonene and CO_2 + citral binary systems were studied at a temperature of 315 K in the pressure range (3−8.6) MPa and (4.7−10.1) MPa, respectively. The CO_2 + limonene + citral ternary system was studied at the same temperature and at (8.4 and 9.0) MPa.

Binary Systems. The experimental procedure consisted of loading a known mass of solute (limonene or citral) into the equilibrium vessel and bringing the system to the desired pressure by introducing compressed carbon dioxide. This procedure was performed with great care as the increase in pressure inside the vessel obviously led to an increase in temperature. The temperature and the pressure inside the vessel were continuously monitored by means of a thermocouple and a gauge with an uncertainty of ±0.1 K and ±0.02 MPa, respectively.

After stable conditions were reached, a sample of the liquid or of the gaseous phase was withdrawn. In fact, at the different values of pressure equilibrium, the experimental runs focused on determining the composition of the liquid phase alone (P, x data) or the vapor phase alone (P, y data).

The liquid-phase samples were taken from the equilibrium vessel through extraction valve 2 and sent to a cold trap so as to separate the solute from the carbon dioxide. After the expansion, traces of solute condensed in the line were recovered by cleaning the line with the ethanol present in the cold trap. While the quantity of carbon dioxide was measured by means of a dry volumetric meter, the quantity of solute trapped was measured through HPLC analysis of an alcohol solution. These data made it possible to determine immediately the mean weight fraction of the liquid phase present in the equilibrium vessel. To obtain a comparable error of measurement during the different runs, the samples were taken in such a way as to obtain a quantity of free carbon dioxide equal to about 200 mL (at normal conditions) after expansion up to atmospheric pressure.

Preliminary runs showed that equilibrium conditions were not significantly perturbed during sampling. In other words, it was ascertained that the variation in pressure caused by the extraction of liquid samples was of the same order of magnitude as the uncertainty obtained in the measurement of pressure. Mean values of uncertainty for the solute mass fraction in the liquid phase equal to ±1 × 10^{-3} and to ±3 × 10^{-3} were estimated respectively for the binary systems CO_2 + limonene and CO_2 + citral.

A different procedure was used to sample the gaseous phase, owing to its low solute concentration. It was in fact necessary to remove a large amount of the supercritical phase (from extraction valve 1) in order to obtain a detectable solute concentration in the alcohol cold trap, where separation of the solute from the solvent took place, as in the previous case. To prevent the pressure from dropping during the sampling, which would cause the loss of equilibrium conditions, a stream of pure carbon dioxide was continuously introduced at the bottom of the equilibrium vessel. A very low flow rate of CO_2 was selected (equal to about 100 mL/min after expansion) in order to ensure constant equilibrium conditions between the liquid and the rising supercritical phase in the vessel. Each run ended when the meter indicated a quantity of CO_2 equal to about 10 L. At this point the run was halted, the solute condensed in the line was recovered by cleaning the line with the ethanol present in the trap, and a sample of the alcoholic solution was taken for subsequent HPLC analysis.

The mass fraction of each component in the supercritical phase was then calculated. The uncertainty of the solute mass fraction in the supercritical phase estimated for the binary systems CO_2 + limonene and CO_2 + citral was equal to ±1 × 10^{-4} and ±4 × 10^{-4}, respectively.

Ternary Systems. The experimental procedure adopted to determine the ternary equilibrium data is the same as that used for the binary data. In this case, however, the compositions of both phases were measured at equilibrium in order to determine the tie lines associated with each of the conditions examined.

The different compositions of the supercritical phase were determined through a continuous procedure, as in the case of the binary systems. The constant flow of fresh CO_2 naturally brought about a variation in the composition of the liquid phase, which was, however, very small given the low solubility of the limonene + citral mixture in the supercritical CO_2.

Table 1. Carbon Dioxide (1) + Limonene (2) Equilibrium Mass Fractions at 315 K[a]

P/MPa	w_2	w_1	P/MPa	w_2	w_1
3.05	**0.0006**	**0.9994**	7.68	0.546	0.454
4.07	**0.0012**	**0.9988**	7.92	0.490	0.510
5.08	**0.0018**	**0.9982**	7.98	0.498	0.502
5.18	0.788	0.212	8.04	0.461	0.539
6.10	**0.0025**	**0.9975**	**8.13**	**0.0070**	**0.9923**
6.83	0.693	0.307	8.13	0.424	0.576
6.85	0.649	0.351	8.29	0.446	0.554
6.90	0.650	0.350	**8.39**	**0.0108**	**0.9892**
6.92	0.643	0.357	8.39	0.374	0.626
7.08	0.625	0.375	8.48	0.307	0.693
7.12	**0.0040**	**0.9960**	**8.50**	**0.0180**	**0.9820**
7.37	0.582	0.418	8.50	0.305	0.695
7.59	0.550	0.450			

[a] Bold type refers to supercritical-phase compositions; default type refers to liquid-phase compositions.

Table 2. Carbon Dioxide (1) + Citral (3) Equilibrium Mass Fractions at 315 K[a]

P/MPa	w_3	w_1	P/MPa	w_3	w_1
4.70	**0.0002**	**0.9998**	9.09	0.347	0.653
6.00	**0.0003**	**0.9997**	**9.11**	**0.0086**	**0.9914**
7.00	**0.0005**	**0.9995**	9.21	0.291	0.709
7.35	0.616	0.384	9.29	0.280	0.720
7.65	**0.0008**	**0.9992**	9.44	0.266	0.734
7.80	0.560	0.440	9.56	0.217	0.783
8.00	**0.0013**	**0.9987**	**9.58**	**0.0348**	**0.9652**
8.42	0.468	0.532	9.70	0.200	0.800
8.48	0.457	0.543	9.78	0.180	0.820
8.65	**0.0072**	**0.9928**	9.83	0.134	0.866
8.70	0.415	0.585	9.99	0.089	0.911
8.75	**0.0059**	**0.9941**	10.04	0.073	0.927
9.00	**0.0076**	**0.9924**	10.06	0.058	0.942
9.02	0.370	0.630			

[a] Bold type refers to supercritical-phase compositions; default type refers to liquid-phase compositions.

A sample of the liquid phase was then taken in the same way as described for the binary systems. The uncertainty of the limonene and citral mass fractions in the supercritical phase estimated for the ternary system CO_2 + limonene + citral was equal to $\pm 2 \times 10^{-4}$ and $\pm 5 \times 10^{-4}$, respectively.

For the ternary system CO_2 + limonene + citral, the mean uncertainty of the limonene and citral mass fractions in the liquid phase was equal to $\pm 1 \times 10^{-3}$ and $\pm 5 \times 10^{-3}$, respectively.

Results and Discussion

Tables 1 and 2 show the experimental results regarding the CO_2 + limonene and CO_2 + citral binary systems, respectively. The equilibrium compositions of the liquid and supercritical phases were measured at 315 K and at the different pressure values shown in the tables.

The experimental data are given in Figures 2 and 3. The equilibrium region extends up to a pressure of about 8.5 MPa for the CO_2 + limonene system and about 10 MPa for the CO_2 + citral system. For comparison purposes, Figure 2 also shows the pressure values at the initial boiling point given in the literature.[11] Unfortunately the comparison is only partial, as the literature data refer to different temperature values from that used in this study.

Tables 3 and 4 show experimental data for the ternary system CO_2 (1) + limonene (2) + citral (3) at 315 K and at 8.4 MPa and at 315 K and at 9.0 MPa.

The ternary equilibrium diagrams are shown in Figures 4 and 5. At 8.4 MPa the system is characterized by a type-
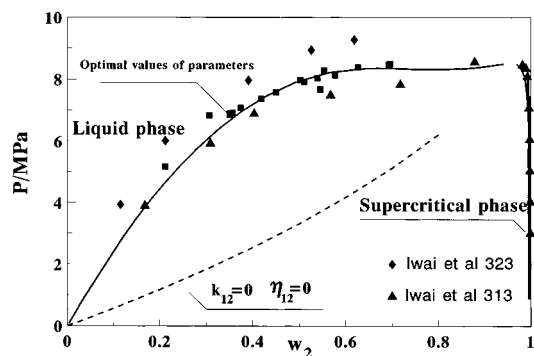
Figure 2. $P-x$, y diagram of the carbon dioxide + limonene system at 315 K.
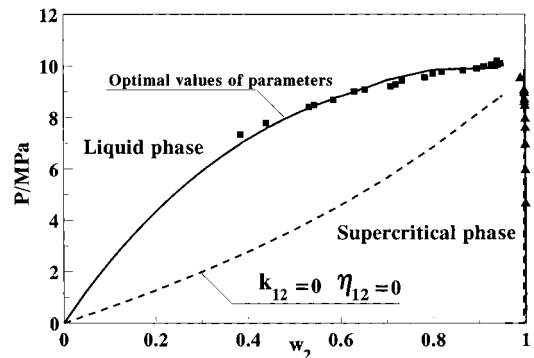
Figure 3. $P-x$, y diagram of the carbon dioxide + citral system at 315 K.

Table 3. Ternary System Carbon Dioxide (1) + Limonene (2) + Citral (3): Tie Lines at 315 K and at 8.4 MPa (Mass Fractions)

liquid phase			supercritical phase		
w_2	w_3	w_1	w_2	w_3	w_1
0.0439	0.3755	0.5806	0.0011	0.0022	0.9967
0.0418	0.3625	0.5957	0.0013	0.0026	0.9961
0.1195	0.2437	0.6368	0.0034	0.0020	0.9945
0.2066	0.1719	0.6215	0.0067	0.0016	0.9917
0.2423	0.1290	0.6287	0.0064	0.0010	0.9926
0.2421	0.1050	0.6529	0.0083	0.0012	0.9905
0.2579	0.0860	0.6561	0.0090	0.0011	0.9899
0.1501	0.2519	0.5980	0.0039	0.0016	0.9945

Table 4. Ternary System Carbon Dioxide (1) + Limonene (2) + Citral (3): Tie Lines at 315 K and at 9.0 MPa (Mass Fractions)

liquid phase			supercritical phase		
w_2	w_3	w_1	w_2	w_3	w_1
0.0311	0.2492	0.7197	0.0020	0.0065	0.9915
0.0401	0.2402	0.7197	0.0024	0.0060	0.9916
0.0489	0.2210	0.7301	0.0026	0.0051	0.9923
0.0839	0.2129	0.7032	0.0047	0.0053	0.9900
0.0757	0.1966	0.7277	0.0074	0.0054	0.9872
0.0827	0.1753	0.7420	0.0066	0.0049	0.9885
0.1075	0.0839	0.8087	0.0115	0.0042	0.9843
0.1192	0.0646	0.8162	0.0293	0.0170	0.9538
0.1138	0.0457	0.8405	0.0295	0.0117	0.9587

II diagram in that both the CO_2 + limonene and the CO_2 + citral systems show phase equilibrium with carbon dioxide. At 9.0 MPa the system is characterized by type-I behavior in that only the CO_2 + citral system shows a phase-equilibrium condition, while pure limonene forms a single phase with the solvent. In this case, the equilibrium region is very restricted, and a considerably larger enrichment of the liquid phase is therefore obtained by operating at a lower pressure equal to 8.4 MPa.
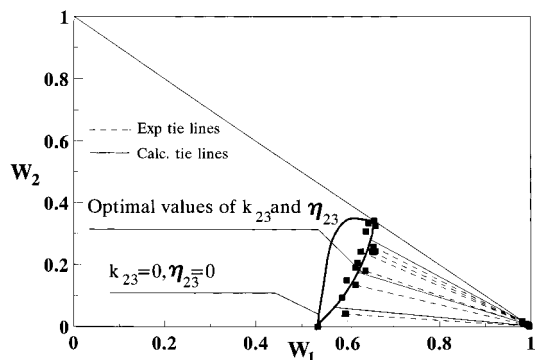
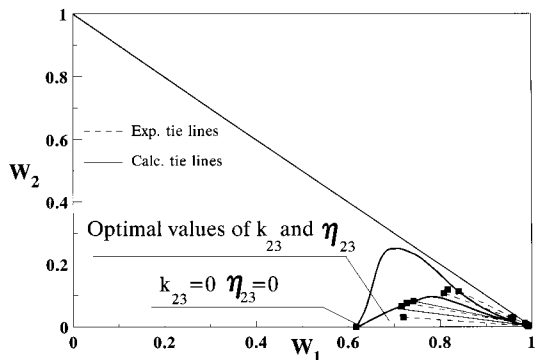**Figure 4.** Phase diagram of the carbon dioxide + limonene + citral ternary system at 315 K and 8.4 MPa.

Figure 5. Phase diagram of the carbon dioxide + limonene + citral ternary system at 315 K and 9.0 MPa.

Correlation

The data obtained in this study were modeled by imposing the isofugacity condition for each component in the liquid and supercritical phases. The fugacity coefficients were calculated by means of the well-known Peng−Robinson equation of state (PR EOS).[12] The usual quadratic mixing rules were used for both mixture covolume and attractive constant:

$$b_m = \sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j b_{ij} \qquad (1)$$

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j a_{ij} \qquad (2)$$

where z_i represent the mole fraction of the liquid or vapor phase and a_{ii} and b_{ii} are pure component parameters defined by Peng−Robinson and can be calculated on the basis of the critical temperatures, critical pressures, and acentric factors of the pure components. In this work the values of these parameters are as reported elsewhere.[10] For $i \neq j$, b_{ij} and a_{ij} were calculated through the arithmetic and geometric mean, respectively, with two binary interaction parameters:

$$b_{ij} = \frac{b_i + b_j}{2}(1 - \eta_{ij}) \qquad (3)$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \qquad (4)$$

Peng−Robinson[12] set $\eta_{ij} = 0$, whereby eq 1 simplifies to $b_m = \sum b_i x_i$. In this work, as suggested by other authors,[13,14] both parameters η_{ij} and k_{ij} were considered, since the components in the mixtures differ considerably in structure

Table 5. Mixture Parameters Calculated by Means of Correlation of Experimental Data

CO_2 + limonene	CO_2 + citral	limonene + citral
$k_{12} = 0.1127$	$k_{13} = 0.0570$	$k_{23} = -0.1500$
$\eta_{12} = 0.0100$	$\eta_{13} = 0.0040$	$\eta_{23} = -0.0975$

and molecular size. Therefore, the fugacity coefficient was evaluated according to the following equation:

$$\ln \overline{\varphi}_i = \frac{B'_i}{B}(Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_j x_j a_{ij}}{a_m} - \frac{B'_i}{B}\right)\ln\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \qquad (5)$$

where Z is the compressibility factor of the mixture. A, B, and B'_i are given by the expressions:

$$A = \frac{Pa_m}{R^2 T^2} \qquad (6)$$

$$B = \frac{b_m P}{RT} \qquad (7)$$

$$B'_i = 2\frac{P}{RT}\sum_j x_j b_{ij} - B \qquad (8)$$

where T is the temperature, P the pressure, and R the gas-law constant.

If $\eta_{ij} = 0$, $B'_i = b_i P/RT$ and the above equation is equal to that reported by Peng−Robinson.[12]

The values of η_{ij} and k_{ij} were determined by fitting the experimental data in accordance with the procedure outlined below.

The interaction parameters for the carbon dioxide (1) + limonene (2) system were obtained from the fitting of binary $P-x-y$ data at 315 K reported in this work. For this system, the optimal interaction parameters were determined from flash calculations by minimization of the following objective function:

$$\Phi = \sum_{m=1}^{ml} \frac{|x_{2,m}^{exp} - x_{2,m}^{calc}|}{x_{2,m}^{exp}} + \sum_{m=1}^{mv} \frac{|y_{2,m}^{exp} - y_{2,m}^{calc}|}{y_{2,m}^{exp}} \qquad (9)$$

where ml and mv are the number of liquid and vapor data points, respectively, for each binary system whereas $x_{2,m}$ and $y_{2,m}$ are the weight fractions of solute in the liquid and vapor phases, respectively.

The values of the binary parameters obtained from optimization are given in Table 5.

The same procedure was utilized for the correlation of the data for the carbon dioxide (1) + citral (3) system. The optimal values of k_{13} and η_{13} are given in Table 5.

A different procedure was used to determine the interaction parameters for limonene and citral, owing to the lack of high-pressure equilibrium data for the binary system limonene + citral. In particular, these parameters were obtained from the fitting of equilibrium data for the ternary system carbon dioxide (1) + limonene (2) + citral (3) at 315 K and at (8.4 and 9.0) MPa. To this end, a different

objective function was defined:

$$\Omega = \sum_{t=1}^{nt}\left(\sum_{k=2}^{3}\frac{|x_{k,t}^{\ exp} - x_{k,t}^{\ calc}|}{x_{k,t}^{\ exp}} + \sum_{k=2}^{3}\frac{|y_{k,t}^{\ exp} - y_{k,t}^{\ calc}|}{y_{k,t}^{\ exp}}\right) \quad (10)$$

where the first summation is extended to all the tie lines at (8.4 and 9.0) MPa ($nt = 17$), whereas the inner summations are extended to the two solutes in the liquid and supercritical phases. The values of the binary parameters (k_{23} and η_{23}) obtained by optimization of ternary data are shown in Table 5.

Figures 2 and 3 show the calculated VLE data for the CO_2 + limonene and CO_2 + citral binary systems. From the figures it is evident that the fitting of experimental data is very good for the first system whereas the model overestimates the equilibrium pressures near the critical point for the second system.

The figures also show the calculated curves obtained by making the values of the binary interaction parameters equal to zero (dotted curves). It is evident that, in this case, the agreement between experimental and calculated values is only qualitative.

Calculated ternary phase diagrams at 8.4 and 9.0 MPa are given in Figures 4 and 5 together with experimental data. For the sake of simplicity the figures show only some of the experimental tie lines (dotted lines). The same figures also show binodal calculated curves at each pressure value with reference to the following conditions: (a) considering the values of the parameters k_{23} and η_{23} equal to zero and (b) using the values of the parameters k_{23} and η_{23} obtained by means of the correlating method reported above.

The figures also show some tie lines (continuous lines) obtained with optimal values of the parameters k_{23} and η_{23}.

The figure clearly shows the significant influence of the parameters relative to the limonene + citral binary system on the trend of calculated equilibrium data. In particular, the equilibrium region is clearly overestimated if the above parameters are set equal to zero, whereas the agreement is quite satisfactory if the values of the parameters obtained from the fitting are utilized.

Conclusions

The binary equilibrium data for both carbon dioxide + limonene and carbon dioxide + citral presented in the present work were successfully fitted using the PR EOS. The equation was modified by introducing two interaction parameters, one for each binary subsystem. It was established that the equation fails if these parameters are set equal to zero.

The ternary system CO_2 + limonene + citral was also studied at the temperature 315 K. The results show that at 8.4 MPa and at 9.0 MPa the system exhibits a ternary type-II and type-I equilibrium phase, respectively. The interaction parameters obtained from the correlation of binary data were used to predict ternary equilibrium data by means of the PR EOS. The prediction was carried out by setting the interaction parameters of the limonene + citral system equal to zero. Unfortunately the agreement between the calculated and experimental data was not satisfactory, and it was therefore necessary to perform a fitting of ternary experimental data in order to evaluate the parameters for the limonene + citral system.

The results obtained clearly show that supercritical carbon dioxide extracts limonene preferentially, while citral is concentrated in the refined phase.

Literature Cited

(1) Chamblee, T. S.; Clark, B. C., Jr.; Brewster, G. B.; Radford, T.; Iacobucci, G. A. Quantitative Analysis of the Volatile Constituents of Lemon Peel Oil. Effect of Silica Gel Chromatography on the Composition of Its Hydrocarbon and Oxygenated Fractions. *J. Agric. Food Chem.* **1991**, *39*, 162−169.

(2) Reverchon, E. Supercritical Desorption of Limonene and Linalool from Silica Gel: Experiments and Modeling. *Chem. Eng. Sci.* **1997**, *52*, 1019−1027.

(3) Reverchon, E. Supercritical Fluid Extraction and Fractionation of Essential Oils and Related Products. *J. Supercrit. Fluids* **1997**, *10*, 1−37.

(4) Reverchon, E.; Marciano, A.; Poletto, M. Fractionation of a Peel Oil Key Mixture by Supercritical CO_2 in a Continuous Tower. *Ind. Eng. Chem.* **1997**, *36*, 4940−4948.

(5) Sato, M.; Goto, M.; Kodama, A.; Hirose, T. New Fractionation Process for Citrus Oil by Pressure Swing Adsorption in Supercritical Carbon Dioxide. *Chem. Eng. Sci.* **1998**, *53*, 4095−4105.

(6) Mathias, P. M.; Copeman, T. W.; Prausnitz, J. M. Phase equilibria for supercritical extraction of lemon flavors and palm oils with carbon dioxide. *Fluid Phase Equilib.* **1986**, *29*, 545−554.

(7) Pavlicek, J.; Richter, M. High-Pressure Vapour-liquid Equilibrium in the Carbon Dioxide−α-Pinene System. *Fluid Phase Equilib.* **1993**, *90*, 125−133.

(8) Richter, M.; Sovovà, H. The Solubility of Two Monoterpenes in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1993**, *85*, 285−300.

(9) Stahl, E.; Gerard, D. Solubility Behaviour and Fractionation of Essential Oils in Dense Carbon Dioxide. *Perfum. Flavor.* **1985**, *10*, 29−37.

(10) Di Giacomo, G.; Brandani, V.; Del Re, G.; Mucciante, V. Solubility of Essential Oil Components in Compressed Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1989**, *52*, 405−411.

(11) Iwai, Y.; Morotomi, T.; Sakamoto, K.; Koga, Y.; Arai, Y. High-pressure vapor-liquid equilibria for carbon dioxide + limonene. *J. Chem. Eng. Data* **1996**, *41*, 951−952.

(12) Peng, D.-Y.; Robinson, D. B. A New Two Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(13) Occhiogrosso, R. N.; Igel, J. T.; McHugh, M. A. Phase Behaviour of Carbon Dioxide-Aromatic Hydrocarbon Mixtures. *Fluid Phase Equilib.* **1986**, *26*, 165−179.

(14) Tan, C.-S.; Yarn, S.-J.; Hsu, J.-H. Vapor Liquid Equilibria for the Systems Carbon Dioxide−Ethylbenzene and Carbon Dioxide−Styrene. *J. Chem. Eng. Data* **1991**, *36*, 23−25.