1844 *J. Chem. Eng. Data* **2005,** *50,* 1844−1847

Entrainer Effect of Ethanol on High-Pressure Vapor−Liquid Equilibria for Supercritical Carbon Dioxide + Limonene + Linalool System

Yoshio Iwai,* Makoto Ichimoto, Satoshi Takada, Shinichi Okuda, and Yasuhiko Arai

Department of Chemical Engineering, Faculty of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

The high-pressure vapor−liquid equilibria for supercritical CO_2 + citrus oil component (limonene and linalool) + ethanol systems were measured to study an entrainer effect of ethanol. The measured systems were CO_2 + limonene + ethanol at 313.2 K and 6.9 MPa; CO_2 + linalool + ethanol at 313.2 K and 6.9 MPa and at 333.2 K and 10.0 MPa; and CO_2 + limonene + linalool + ethanol at 313.2 K and 6.9 MPa. The experimental apparatus used was based on a circulation-type method for liquid-phase sampling and a flow-type method for vapor-phase sampling. The mole fractions of limonene and linalool in vapor phase are not affected by the addition of ethanol. However, the mole fraction of linalool in the liquid phase decreases with increasing the concentration of ethanol. As a result, the relative volatilities between limonene and linalool increase by factors of 1.2 to 1.5 with the addition of ethanol. The experimental data were correlated by the SRK equation of state with an exponent-type mixing rule. The correlated results are in good agreement with the experimental data.

Introduction

Citrus oil is widely used as a raw material to extract flavors. Steam distillation or solvent extraction is usually applied to refine citrus oil. However, the drawbacks of these processes are low yields, formation of degradation products under high operating temperature, and solvent residue. Therefore, supercritical fluid extraction using CO_2 can be considered as an alternative process for refining citrus oil because of its advantage of low operating temperature and no solvent residue. Limonene is a principal compound of citrus oil. It makes up approximately 90 % (mass) of citrus oil but does not contribute much to the flavor or fragrance of citrus oil. Linalool is one of the most important oxygenated compounds, which makes the characteristic flavor or fragrance of citrus oil. It makes up approximately 1 % (mass) of citrus oil. Limonene is an unsaturated terpene hydrocarbon that is unstable to heat, light, and oxygen. So, it is a common industrial practice to remove limonene and other terpenes to concentrate the oxygenated compounds such as linalool. To apply supercritical fluid extraction using CO_2 to the separation process, the vapor−liquid equilibria for the mixture of CO_2, limonene, and linalool are required. Binary data of the vapor−liquid equilibria for CO_2 + limonene[1−12] and for CO_2 + linalool[6,8,10,13,14] have been reported in the literature. The vapor−liquid equilibria for the CO_2 + limonene + linalool ternary system were measured.[15−17] The relative volatilities show that it is easy to remove limonene from linalool because the values are larger than unity when mixtures are in linalool-rich condition. On the other hand, it is difficult to separate the mixtures in the limonene-rich region because the values are close to unity.[15] Since the solvent power of supercritical CO_2 is relatively poor, it is often necessary to add a small amount of entrainer to improve the solubility and selectivity.[18,19] Ethanol is commonly used as an entrainer for extraction of natural products because the toxicity of ethanol to the human body is low. Badalyan et al.[20] and Chassagnez-Mendez et al.[21] extracted essential oils with supercritical CO_2 and supercritical CO_2 + ethanol to investigate the entrainer effects of ethanol. They reported that the yields increased with addition of ethanol. Vapor−liquid equilibria for citrus oil + ethanol are necessary to understand the entrainer effects. However, the literature data for ternary or quaternary systems containing supercritical CO_2, ethanol, limonene, and linalool are very few. To our knowledge, equilibrium data for CO_2 + limonene + ethanol have been reported only by Drescher et al.[22] at 333 K. In this paper, therefore, the high-pressure vapor−liquid equilibria were measured for CO_2 + limonene + ethanol at 313.2 K and 6.9 MPa, for CO_2 + linalool + ethanol at 313.2 K and 6.9 MPa and at 333.2 K and 10.0 MPa, and for CO_2 + limonene + linalool + ethanol at 313.2 K and 6.9 MPa to study an entrainer effect of ethanol. The relative volatilities between limonene and linalool at 6.9 MPa are higher than those at 10.0 MPa.[15] The entrainer effect of ethanol was mainly measured at 6.9 MPa. The experimental data were correlated by the SRK equation of state[23] with an exponent-type mixing rule[24] using interaction parameters.

Experimental Section

Materials. High-purity CO_2 (more than 99.9 % (volume) purity, Sumitomo Seica Co.) was used as received. (*R*)-(+)-Limonene was supplied by Aldrich Chemical Co., Inc. The density and boiling point of limonene were 840 g·L^{-1} at 25 °C and 175.5−176 °C, respectively, from the catalog of Aldrich. Linalool was supplied by Wako Pure Chemical Industries, Ltd. It was of reagent grade. The density of linalool was 860 g·L^{-1} at 20 °C from the catalog of Wako Chemicals. Ethanol was supplied by Wako Pure Chemical Industries, Ltd. It was of super special grade. The density

---

* Corresponding author. e-mail: iwai@chem-eng.kyushu-u.ac.jp. Phone/Fax: +81 92 642 3496.

10.1021/je050079t CCC: $30.25

Table 1. Experimental Results for Vapor−Liquid Equilibria of Ternary Systems

CO_2 (1) + Limonene (2) + Ethanol (4) at 313.2 K and 6.9 MPa

N_d[a]	x_1[b]	x_2	x_4	S_x[c]	y_1[d]	y_2	y_4	S_y[e]
4	0.6699	0.3206	0.0095	4.3×10^{-3}	0.9973	0.0013	0.0014	7.1×10^{-5}
4	0.7036	0.2718	0.0246	2.6×10^{-3}	0.9953	0.0013	0.0034	7.1×10^{-5}
3	0.6793	0.2882	0.0325	3.3×10^{-3}	0.9944	0.0013	0.0043	1.7×10^{-4}
3	0.7086	0.2575	0.0339	1.9×10^{-3}	0.9941	0.0013	0.0046	0
6	0.6828	0.2639	0.0533	5.1×10^{-3}	0.9932	0.0015	0.0053	7.8×10^{-5}
4	0.7170	0.2192	0.0638	3.3×10^{-3}	0.9927	0.0013	0.0060	6.5×10^{-5}
6	0.7194	0.1851	0.0955	5.0×10^{-2}	0.9919	0.0012	0.0069	1.7×10^{-3}

CO_2 (1) + Linalool (3) + Ethanol (4) at 313.2 K and 6.9 MPa

N_d	x_1	x_3	x_4	S_x	y_1	y_3	y_4	S_y
6	0.6918	0.2670	0.0412	1.3×10^{-2}	0.9980	0.0005	0.0015	2.4×10^{-4}
5	0.6501	0.2665	0.0834	1.5×10^{-2}	0.9967	0.0005	0.0028	2.1×10^{-4}
7	0.5876	0.2720	0.1404	1.9×10^{-2}	0.9962	0.0004	0.0040	1.1×10^{-4}
6	0.6029	0.2382	0.1589	7.8×10^{-3}	0.9945	0.0005	0.0050	5.5×10^{-5}

CO_2 (1) + Linalool (3) + Ethanol (4) at 333.2 K and 10.0 MPa

N_d	x_1	x_3	x_4	S_x	y_1	y_3	y_4	S_y
3	0.7314	0.2353	0.0333	6.8×10^{-3}	0.9939	0.0031	0.0030	6.5×10^{-4}
4	0.7252	0.2100	0.0648	1.4×10^{-2}	0.9909	0.0026	0.0065	5.7×10^{-3}
2	0.7105	0.1980	0.0915	5.6×10^{-3}	0.9890	0.0025	0.0085	7.1×10^{-5}
3	0.6791	0.1735	0.1474	8.1×10^{-2}	0.9850	0.0024	0.0126	5.7×10^{-3}

[a] N_d, number of data points. [b] x_i, mole fraction of component i in liquid phase. [c] $S_x = [(1/(3N_d))\Sigma_n^{N_d} \Sigma_i^3 |x_{i,n} - x_i|^2]^{1/2}$. [d] y_i, mole fraction of component i in vapor phase. [e] $S_y = [(1/(3N_d))\Sigma_n^{N_d} \Sigma_i^3 |y_{i,n} - y_i|^2]^{1/2}$.

Table 2. Experimental Vapor−Liquid Equilibria and Relative Volatilities for CO_2(1) + Limonene (2) + Linalool (3) + Ethanol (4) System at 313.2 K and 6.9 MPa

N_d	x_1	x_2	x_3	x_4	S_x[a]	y_1	y_2	y_3	y_4	S_y[b]	α_{23}[c]
4	0.7029	0.2494	0.0156	0.0321	1.8×10^{-3}	0.9947	1.2×10^{-3}	6.6×10^{-5}	0.0040	2.8×10^{-4}	1.2
4	0.7074	0.2120	0.0193	0.0613	8.6×10^{-3}	0.9932	1.2×10^{-3}	6.8×10^{-5}	0.0055	6.3×10^{-5}	1.6
4	0.6979	0.1487	0.1203	0.0331	3.7×10^{-3}	0.9964	7.9×10^{-4}	2.1×10^{-4}	0.0026	1.7×10^{-4}	3.0
3	0.6819	0.1335	0.1171	0.0675	4.2×10^{-3}	0.9950	6.8×10^{-4}	1.8×10^{-4}	0.0041	2.7×10^{-4}	3.4
5	0.6659	0.0257	0.2608	0.0476	8.2×10^{-3}	0.9969	1.6×10^{-4}	4.1×10^{-4}	0.0025	1.2×10^{-4}	3.9
5	0.6426	0.0246	0.2432	0.0896	1.1×10^{-2}	0.9955	1.6×10^{-4}	3.9×10^{-4}	0.0040	5.6×10^{-4}	4.1

[a] $S_x = [(1/(4N_d))\Sigma_n^{N_d} \Sigma_i^4 |x_{i,n} - x_i|^2]^{1/2}$. [b] $S_y = [(1/(4N_d))\Sigma_n^{N_d} \Sigma_i^4 |y_{i,n} - y_i|^2]^{1/2}$. [c] α_{23}, relative volatility.

of ethanol was 790 g·L^{-1} at 20 °C from the catalog. The purities of limonene, linalool, and ethanol were more than 99 %, 99 %, and 99.5 %, respectively, by gas chromatographic area analysis. They were used without further purification.

Apparatus and Procedure. A circulation-type method was used to measure the compositions of liquid phase. A detailed description of the apparatus and operating procedure was given previously.[15] CO_2, citrus oil components (limonene and linalool), and ethanol were fed into an equilibrium cell and adjusted at desired temperature and pressure. The temperature and pressure were maintained within ± 0.05 K and ± 0.1 MPa, respectively. After equilibrium condition was achieved, circulation of the liquid phase was started by a magnetic pump and was introduced into a sampling loop. After that, the sampling loop was isolated from the equilibrium cell by switching a six-way valve and then introduced into a cold trap, where CO_2 was separated from citrus oil components and ethanol. The cold trap contained 1-butanol to collect citrus oil components and ethanol. The amount of CO_2 was measured by a dry gas meter. The amounts of citrus oil components and ethanol were determined by gas chromatograph. A flow-type method was used for vapor phase sampling. After equilibrium condition was achieved, about 10 L of CO_2 was fed into the equilibrium cell. Then, vapor phase sample in the cell was introduced into a cold trap through an expansion valve. The amounts of CO_2, citrus oil components, and ethanol were determined by the same procedure for the liquid-phase sample. The standard deviations of concentrations are listed in Tables 1 and 2. The accuracy of mole fractions was estimated within 1 %, 4 %, and 10 % when the mole fractions were from 0.1 to 1.0, from 0.01 to 0.1, and less than 0.01, respectively.

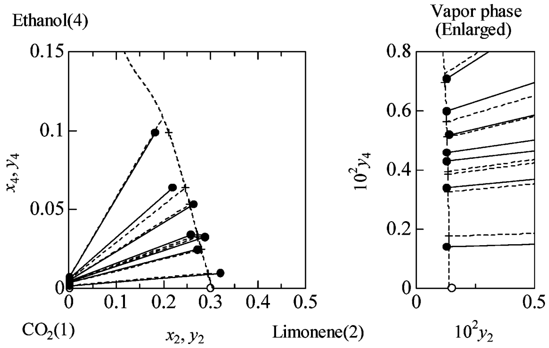

Figure 1. Vapor−liquid equilibria for CO_2 (1) + limonene (2) + ethanol (4) system at 313.2 K and 6.9 MPa: ●−●, this work; ○, binary data;[5] + - - +, calculated results.

Results and Discussion

The experimental results are shown in Table 1 and Figures 1 to 3 for the ternary systems. The results were obtained as an averaged value of several measurements at each condition. As shown in Figures 1 to 3, the mole fractions of linalool and limonene in vapor phase for the ternary systems are almost the same as those for CO_2 + linalool and CO_2 + limonene binary systems, respectively.

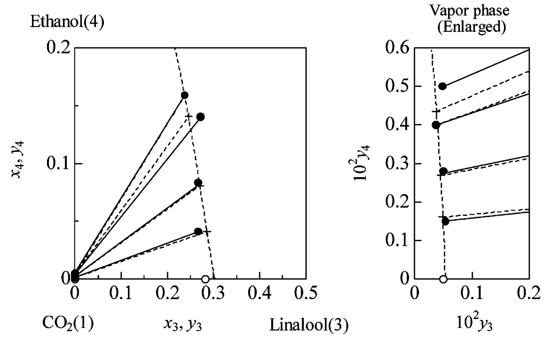

Figure 2. Vapor−liquid equilibria for CO_2 (1) + linalool (3) + ethanol (4) system at 313.2 K and 6.9 MPa: ●−●, this work; ○, binary data;[13] + - - +, calculated results.

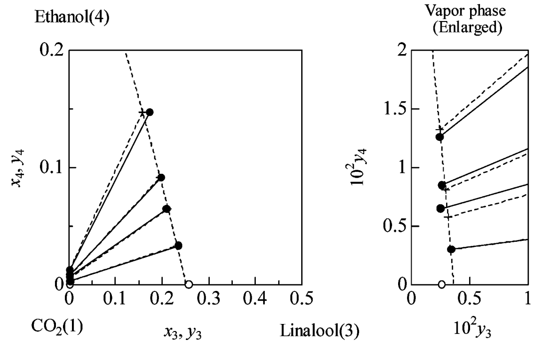

Figure 3. Vapor−liquid equilibria for CO_2 (1) + linalool (3) + ethanol (4) system at 333.2 K and 10.0 MPa: ●−●, this work; ○, binary data;[13] + - - +, calculated results.

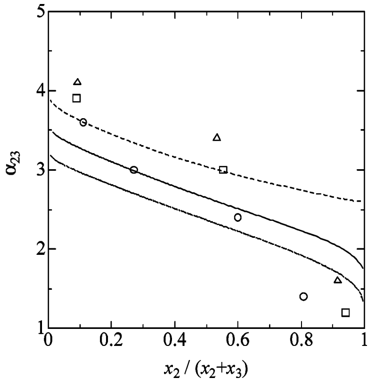

Figure 4. Relative volatilities between limonene (2) and linalool (3) in CO_2 (1) + limonene (2) + linalool (3) + ethanol (4) system at 313.2 K and 6.9 MPa: □, △, this work; ○, ternary data;[15] -·-·-, —, ----, calculated results at x_4 = 0.00, 0.03, 0.06.

This means that ethanol is not effective as an entrainer on solubility of limonene and linalool in supercritical CO_2 at the experimental conditions. The reduction rates of mole fraction for limonene in liquid phase by addition of ethanol are higher than those for linalool as shown in Figures 1 to 3.

The experimental results are listed in Table 2 for the quaternary system. The relative volatility between limonene (2) and linalool (3), α_{23}, is defined by the equation:

$$\alpha_{23} = (y_2/x_2)/(y_3/x_3) \tag{1}$$

The experimental results for α_{23} are shown in Table 2 and Figure 4. The relative volatilities for quaternary system are 1.2 to 1.5 times higher than those of the ternary system. This means that ethanol is effective as an entrainer on separation of limonene and linalool by supercritical CO_2.

Table 3. Physical Properties

substance	T_C[a]/K	p_C[b]/MPa	ω[c]	g[d]
CO_2	304.1[28]	7.37[28]	0.225[28]	1.000
limonene	649.1[25]	2.72[25]	0.374[27]	1.006[29]
linalool	630.5[26]	2.42[26]	0.748[27]	0.964[29]
ethanol	513.9[28]	6.15[28]	0.649[28]	0.992[30]

[a] T_C, critical temperature. [b] p_C, critical pressure. [c] ω, acentric factor. [d] g, constant in eq 4.

Correlation

The following thermodynamic relations were used to calculate the vapor−liquid equilibria at given condition:

$$f_i^V = f_i^L \quad f_i^V = \phi_i^V p y_i \quad f_i^L = \phi_i^L p x_i \tag{2}$$

where f is the fugacity; ϕ is the fugacity coefficient; p is the pressure; and y_i and x_i are the mole fractions of component i in vapor and liquid phases, respectively. Superscripts V and L mean vapor and liquid phases, respectively. To calculate the fugacity coefficient (ϕ_i), the SRK equation of state[23] was used:

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{3}$$

$$a = 0.42747\alpha \frac{R^2 T_C^{\,2}}{p_C} g \tag{4}$$

$$b = 0.08664 \frac{RT_C}{p_C} \tag{5}$$

$$\alpha = \left[1 + m\left\{1 - \left(\frac{T}{T_C}\right)^{0.5}\right\}\right]^2 \tag{6}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{7}$$

where v is the molar volume, R is the gas constant, T is the temperature, a is the energy parameter, b is the size parameter, g is the constant, and ω is the acentric factor. The constant g was introduced to give a good representation of the saturated vapor pressures of pure components. Subscript C means the critical properties. The properties of pure components are shown in Table 3. Those of limonene and linalool were estimated by the Wilson and Jasperson method,[25] the Lydersen method,[26] and the Edmister method[27] because no published experimental data were available. The values for CO_2 and ethanol were cited from the literature.[28] An exponent-type mixing rule[24] was applied to the energy parameter a by

$$a = \sum_i \sum_j x_i^{\beta_{ij}} x_j^{\beta_{ji}} a_{ij}, \quad a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{8}$$

where k_{ij} is the interaction parameters between components i and j. Introducing an exponential parameter β_{ij} may express the contact probability of molecule i with molecule j. The conventional mixing rule was applied to the size parameter b. The mixing rule is given as follows:

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad b_{ij} = (1 - l_{ij})\frac{(b_i + b_j)}{2} \tag{9}$$

where l_{ij} is the interaction parameter between components i and j. The fugacity coefficient can be derived by using eqs 3 to 9. The interaction parameters k_{ij}, l_{ij} and β_{ij} are treated as fitting parameters. The parameter estimation

Table 4. Interaction Parameters

i	j	k_{ij}	l_{ij}	β_{ji}	S^a	ref
CO_2	limonene	0.076	−0.041	1.004	0.032	5
CO_2	linalool	0.085	−0.017	0.993	0.015	13
CO_2	ethanol	0.048	−0.039	1.018	0.073	31
limonene	linalool	0.015	0.008	1.006	0.546	15
limonene	ethanol	0.161	0.218	1.058	0.140	this work
linalool	ethanol	0.033	0.100	1.030	0.388	this work

[a] $S = 1/(N_d)\sum_1^{N_d}\{\sum_{i=1}^{N_{co}}|x_{i,\exp} - x_{i,\mathrm{calc}}|/x_{i,\exp} + \sum_{i=1}^{N_{co}}|y_{i,\exp} - y_{i,\mathrm{calc}}|/y_{i,\exp}\}$. $k_{ij} = k_{ji}$. $l_{ij} = l_{ji}$. $\beta_{ii} = \beta_{jj} = \beta_{ij} = 1$.

was performed at each temperature by minimizing the following objective function F_{obj}:

$$F_{\mathrm{obj}} = \frac{1}{N_d}\sum_1^{N_d}\left\{\sum_{i=1}^{N_{co}}\frac{|x_{i,\exp} - x_{i,\mathrm{calc}}|}{x_{i,\exp}} + \sum_{i=1}^{N_{co}}\frac{|y_{i,\exp} - y_{i,\mathrm{calc}}|}{y_{i,\exp}}\right\} \quad (10)$$

where N_d is the number of data; N_{co} is the number of compounds; and the subscripts calc and exp mean the calculated and experimental results, respectively. The values for the parameters are listed in Table 4. The correlated results are shown in Figures 1 to 4. The correlated results are in good agreement with the experimental results.

Conclusion

High-pressure vapor−liquid equilibria for supercritical CO_2 + citrus oil component (limonene and linalool) + ethanol systems were measured to study the entrainer effect of ethanol. The mole fractions of limonene and linalool in vapor phase are not affected by the addition of ethanol. Ethanol is not effective as an entrainer on solubility of limonene and linalool in supercritical CO_2 at the experimental conditions. The reduction rates for mole fraction of limonene in liquid phase by the addition of ethanol are higher than those of linalool. The relative volatilities between limonene and linalool increase by factors of 1.2 to 1.5 with the addition of ethanol. Ethanol is effective as an entrainer on separation of limonene and linalool in supercritical CO_2. The experimental data were correlated by the SRK equation of state with an exponent-type mixing rule. The correlated results are in good agreement with the experimental data.

Literature Cited

(1) 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.

(2) Matos, H. A.; Gomes de Azevedo, E. Phase equilibria of natural flavours and supercritical solvents. *Fluid Phase Equilib.* **1989**, *52*, 357−364.

(3) Brandani, V.; Del Re, G.; Di Giacomo, G.; Mucciante, V. Phase equilibria for essential oil components and supercritical carbon dioxide. *Fluid Phase Equilib*. **1990**, *59*, 135−145.

(4) Marteau, P.; Obriot, J.; Tufer, R. Experimental determination of vapor−liquid equilibria of CO_2 + limonene and CO_2 + citral mixtures. *J. Supercrit. Fluids* **1995**, *8*, 20−24.

(5) 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.

(6) Suzuki, J.; Nagahama, K. Measurement and correlation of solubility of limonene and linalool in high-pressure carbon dioxide. *Kagaku Kogaku Ronbunsyu* **1996**, *22*, 195−200.

(7) Akgun, M.; Akgun, N. A.; Dincer, S. Phase behaviour of essential oil components in supercritical carbon dioxide. *J. Supercrit. Fluids* **1999**, *15*, 117−125.

(8) Chang, C. M. J.; Chen, C. C. High-pressure densities and *P*−*T*−*x*−*y* diagrams for carbon dioxide + linalool and carbon dioxide + limonene. *Fluid Phase Equilib.* **1999**, *163*, 119−126.

(9) Kim, K. H.; Hong, J. Equilibrium solubilities of spearmint oil components in supercritical carbon dioxide. *Fluid Phase Equilib.* **1999**, *164*, 107−115.

(10) Berna, A.; Chafer, A.; Monton, J. B. Solubilities of essential oil components of orange in supercritical carbon dioxide. *J. Chem. Eng. Data* **2000**, *45*, 724−727.

(11) Gamse, T.; Marr, R. High-pressure phase equilibria of the binary systems carvone−carbon dioxide and limonene−carbon dioxide at 30, 40, 50 °C. *Fluid Phase Equilib.* **2000**, *171*, 165−174.

(12) Sovova, H.; Stateva, R. P.; Galushko, A. A. Essential oils from seeds: solubility of limonene in supercritical CO_2 and how it is affected by fatty oil. *J. Supercrit. Fluids* **2001**, *20*, 113−129.

(13) Iwai, Y.; Hosotani, N.; Morotomi, T.; Koga, Y.; Arai, Y. High-pressure vapor−liquid equilibria for carbon dioxide + linalool. *J. Chem. Eng. Data* **1994**, *39*, 900−902.

(14) Raeissi, S.; Peters, C. J. Bubble-point pressures of the binary system carbon dioxide + linalool. *J. Supercrit. Fluids* **2001**, *20*, 221−228.

(15) Morotomi, T.; Iwai, Y.; Yamaguchi, H.; Arai, Y. High-pressure vapor−liquid equilibria for carbon dioxide + limonene + linalool. *J. Chem. Eng. Data* **1999**, *44*, 1370−1372.

(16) Chafer, A.; Berna, A.; Monton, J. B.; Mulet, A. High-pressure solubility data of the system limonene + linalool + CO_2. *J. Chem. Eng. Data* **2001**, *46*, 1145−1148.

(17) Fonseca, J.; Simoes, P. C.; Nunes da Ponte, M. An apparatus for high-pressure VLE measurements using a static mixer. results for (CO_2 + limonene + citral) and (CO_2 + limonene + linalool). *J. Supercrit. Fluids* **2003**, *25*, 7−17.

(18) Catchpole, O. J.; Grey, J. B.; Noermark, K. A. Solubility of fish oil components in supercritical CO_2 and CO_2 + ethanol mixtures. *J. Chem. Eng. Data* **1998,** *43*, 1091−1095.

(19) Walsh, J. M.; Ikonomou, G. D.; Donohue, M. D. Supercritical phase behavior: the entrainer effect. *Fluid Phase Equilib.* **1987**, *33*, 295−314.

(20) Badalyan, A. G.; Wilkinson, G. T.; Chun, B. S. Extraction of Australian ginger root with carbon dioxide and ethanol entrainer. *J. Supercrit. Fluids* **1998**, *13*, 319−324.

(21) Chassagnez-Mendez, A. L.; Machado, N. T.; Araujo, M. E. Supercritical CO_2 extraction of curcumins and essential oil from the rhizomes of turmeric (*Curcuma longa* L.). *Ind. Eng. Chem. Res.* **2000**, *39*, 4729−4733.

(22) Drescher, M.; Seidel, O.; Geana, D. High-pressure vapor−liquid equilibria in ternary system orange peel oil (limonene) + ethanol + carbon dioxide. *J. Supercrit. Fluids* **2002**, *23*, 103−111.

(23) Soave, G. Equilibrium constants from a modified Redlich−Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(24) Higashi, H.; Furuya, T.; Ishidao, T.; Iwai, Y.; Arai, Y.; Takeuchi, K. An exponent-type mixing rule for energy parameters. *J. Chem. Eng. Jpn.* **1994**, *27*, 667−669.

(25) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001; p 2.9.

(26) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; p 12.

(27) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; p 20.

(28) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001; p A.6.

(29) Espinosa Diaz, M. A.; Guetachew, P.; Landy, J. J.; Voilley, A. Experimental and estimated saturated vapour pressures of aroma compounds. *Fluid Phase Equilib.* **1999**, *157*, 257−270.

(30) Stull, D. R. Vapor pressure of pure substances. organic and inorganic compounds. *Ind. Eng. Chem.* **1947**, *39*, 517−540.

(31) Jennings, D. W.; Lee, R. J.; Teja, A. S. Vapor−liquid equilibria in the carbon dioxide + ethanol and carbon dioxide + 1-butanol systems. *J. Chem. Eng. Data* **1991,** *36*, 303−307.

Received for review February 28, 2005. Accepted September 3, 2005.

JE050079T