Vapor−Liquid Equilibria for the Carbon Dioxide + Carvacrol System at Elevated Pressures

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Vapor−liquid equilibria data were measured for the first time for the carbon dioxide + carvacrol system at 313 K from 0.4 to 30.8 MPa and at 323 K from 0.3 to 30.0 MPa. Data were obtained using a circulation-type apparatus at sufficiently high fluid densities and a continuous flow-type apparatus at low fluid densities. The results were correlated by the Peng−Robinson equation of state and by Zudkevitch's modification to the Redlich−Kwong equation of state, using in both cases classical mixing rules with one adjustable parameter.

Introduction

Many herbs of the Labiatae family are rich in essential oils that are of value to the food, alternative medicine, and perfumery industries. In particular, essential oils from the herbs of the genus *Origanum* have a high phenolic content: the major component is carvacrol, which produces the characteristic odor associated with the herb.[1] Herbs of this genus have colonized dry, uncultivated land in the southern Mediterranean and are harvested for the culinary market as oregano. Recently, the insecticidal,[2] antifungal,[3] antimicrobial,[4] and antioxidant[5] properties of carvacrol have been reported by several authors. In addition, Ahn et al.[6] have suggested its use in the vapor phase as a fumigant to protect stored farm products against beetle damage. Pure carvacrol is relatively expensive and, in light of the above, extraction of carvacrol and other components of interest from such herbs could provide a higher financial return from what would otherwise be relatively unproductive land.

Extraction using liquid and supercritical fluids, particularly carbon dioxide, has become an established method for separating components from herbaceous matrixes. To optimize the extraction and fractionation of carvacrol from a herbaceous matrix in this way, accurate information on the phase equilibria is required, not only for the carbon dioxide + carvacrol system, but also for other relevant carbon dioxide systems.

The purpose of this work was to provide comprehensive measurements for the vapor−liquid equilibria of the carbon dioxide + carvacrol system over the entire phase envelope at the temperatures 313 and 323 K. The reliability of the experimental procedure and results was ascertained by first determining vapor−liquid equilibria for the well studied carbon dioxide + limonene system at 318 K and 323 K and comparing the results to existing literature data. The results obtained were correlated by the Peng−Robinson[7] equation of state and Zudkevitch's modification[8] to the Redlich−Kwong equation of state.[9] In both cases, conventional mixing rules with a single adjustable parameter were employed. The structures of both carvacrol and limonene are shown in Figure 1.

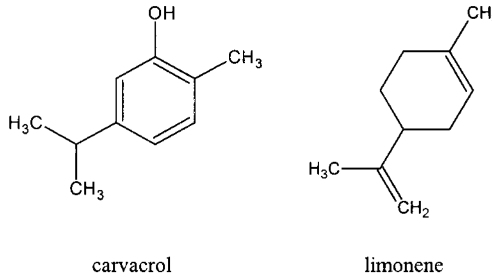

Figure 1. Structures of carvacrol and limonene. Carvacrol: (5-isopropyl-methylphenol) ($C_{10}H_{14}O$, molecular mass 150.22 g mol^{-1}, boiling point 234−236 °C, molar volume at 313 K = 156.17 cm^3 mol^{-1}, molar volume at 323 K = 156.80 cm^3 mol^{-1}). Limonene: (4-isopropenyl-1-methyl-cyclohexene) ($C_{10}H_{16}$, molecular mass 136.24 g mol^{-1}, boiling point 176−177 °C, molar volume at 318 K = 165.79 cm^3 mol^{-1}, molar volume at 323 K = 166.60 cm^3 mol^{-1}).

Experimental Section

Equipment. The circulation apparatus used to determine the high-pressure vapor−liquid equilibria is shown in Figure 2; it was used at sufficiently high fluid densities to allow circulation of the fluid with pump 1. The apparatus was initially set up to determine either liquid or vapor phase results. The carbon dioxide feed entered the cell at the opposite end to the sampling position. This minimized any mixing of fresh makeup carbon dioxide, which was required to maintain the equilibrated pressure during sampling, with the equilibrated mixture being sampled. Because of the corrosive nature of carvacrol, the pump was fitted with PTFE seals (Haskell MCPV-71). The equilibrium cell (2) had an internal volume of 500 cm^3 and was typically charged with (150−200) cm^3 of the liquid of interest. It was maintained at a constant temperature by an insulated air bath, which was controlled to within ±0.1 °C. Liquid carbon dioxide was passed through a chiller, compressed, heated to the desired conditions, and directed to the equilibrium cell. After the cell was full of carbon dioxide, the system was kept for 1 h at a steady state. The air driven circulation pump (1) was then activated, and the vapor phase was passed through the liquid phase until equilibrium was attained. The optimum circulation time was predetermined to be approximately 2 h. After this time, pump 1 was stopped and the liquid phase or vapor phase was sampled. At lower fluid densities, liquid phase measurements were made using a modified version of the

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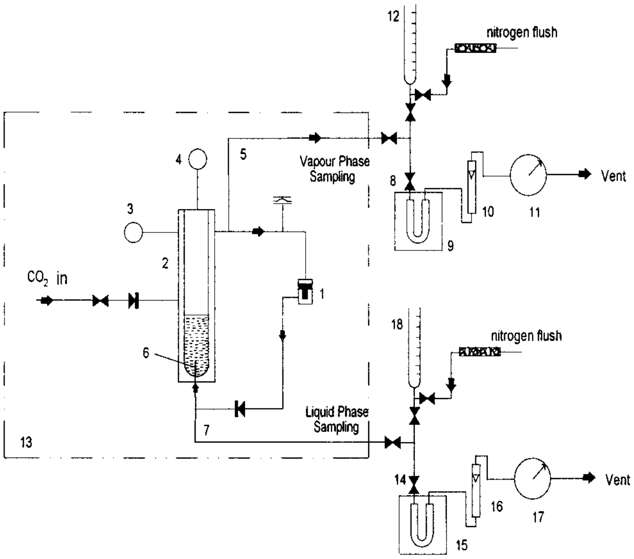

Figure 2. Circulation apparatus used to measure high-pressure VLE: (1) circulation pump; (2) equilibrium cell; (3) pressure transducer; (4) thermocouple; (5) vapor phase sampling line; (6) dip tube; (7) liquid phase sampling line; (8, 14) micrometering expansion valves; (9, 15) baths containing acetone/dry ice slurry; (10, 16) rotameters; (11, 17) wet test meters; (12, 18) solvent wash reservoirs; (13) temperature controlled air bath.

apparatus; this allowed the carbon dioxide stream at the desired conditions to pass continuously through the liquid at a controlled flow rate (~80 cm^3 min^{-1} (at STP) for up to 2.5 h) to saturate the liquid with carbon dioxide.

Sampling Procedure. When taking vapor phase measurements, the micrometering valve (8, Hoke 1315G4Y) was opened and a sample was withdrawn along the sampling line (5) and depressurized to ambient conditions. Any heavy (liquid) component present in the expanded gas stream was trapped in a glass collector maintained at approximately −80 °C in a dry ice/acetone slurry. A volume of up to 16 dm^3 of expanded gas was passed through the wet test meter (11). When taking liquid phase samples, the system was allowed to stand for up to 2 h prior to sample withdrawal. In this time, any undissolved carbon dioxide present in the liquid phase would be transported to the vapor phase. The sample was withdrawn through a dip tube (6) submerged in the liquid, along the liquid phase sampling line (7) and depressurized through a micrometering valve (14, Hoke 1315G4Y) located at the base of the equilibrium cell. (Note: Line 7 was 2 cm in length.) The volume of gas present in the sample was between 0.1 dm^3 and 3 dm^3, depending on the equilibrium conditions. At conditions where the volume of carbon dioxide present in the liquid phase was large (small mass of liquid), and for all vapor phase measurements, a wet test flow totalizer (11, 17) (Alexander Wright 0.25 dm^3/rev) was used to determine the gas volume at STP. At conditions where the volume of gas in the liquid phase was small (large liquid mass), a gas buret filled with calcium chloride confining solution was used. Due to the relatively low vapor pressure of carvacrol (35 Pa at 20 °C)[10] the mass trapped in the glass collector was determined gravimetrically. Limonene has a higher vapor pressure (267 Pa at 20 °C)[11] and was determined by either a gravimetric or a gas chromatographic method. Following sample collection, any carvacrol present in the valve at ambient conditions was usually accounted for by wiping the valve internals with a swab of predetermined mass. The mass of carvacrol typically represented less than 5% of the total mass. The results from this technique were comparable to those attained from washing the valve with acetone and determining the mass by gas chromatographic analysis, but this technique enabled results to be gained more readily. The former swab procedure was applied to a much lesser extent for tests on the limonene + carbon dioxide system, where any residual sample deposited in the valve was largely determined by a valve wash/GC approach. For the gas chromatography, limonene was used as the internal standard for tests with carvacrol, and similarly, a hexadecane internal standard was used for tests on limonene. Injection errors were minimized by correcting the value of the peak area of the internal standard to that of a predetermined set peak area.

Table 1. Vapor−Liquid Equilibria for CO$_2$ (1) + Limonene (2)

$T = 318$ K				$T = 323$ K			
P/MPa	x_1	P/MPa	y_1	P/MPa	x_1	P/MPa	y_1
0.30	0.0281	8.00	0.9979	0.41	0.0343	7.32	0.9991
0.47	0.0434	8.22	0.9981	0.59	0.0479	8.14	0.9986
0.50	0.0476	8.68	0.9942	1.03	0.0739	8.63	0.9977
0.67	0.0579	8.75	0.9932	1.65	0.1215	8.79	0.9968
0.88	0.0762	8.79	0.9928	2.38	0.1722	9.46	0.9885
1.29	0.1128	8.93	0.9899	3.90	0.2773	10.05	0.9744
4.69	0.4005	8.96	0.9900	6.95	0.5398		
6.90	0.6254	9.04	0.9878	8.55	0.7179		
8.03	0.7559	9.10	0.9804	8.80	0.7398		
8.45	0.8206			9.54	0.8528		
8.68	0.8693			9.68	0.8829		
8.78	0.9089						
8.95	0.9345						
9.00	0.9445						

Materials. Limonene [5989-27-5] was supplied from Fluka and carvacrol [499-75-2] from Aldrich U.K., and both were used without further purification. The purities of limonene and carvacrol were determined by GC peak area analysis and were found to be 98% and 99%, respectively. Liquid carbon dioxide, CP grade, was obtained from BOC and had a given purity of 99.995%.

Results and Discussion

Vapor−liquid equilibria data for the CO$_2$ + limonene system were measured at 318 K and 323 K to ascertain the reliability of the apparatus and methodology employed. The experimental results are shown in Table 1 and are expressed in mole fraction of CO$_2$ in the vapor (y_1) and liquid (x_1) phases. Values of x_1 listed in the table are the average of several measurements at each pressure. The worst probable error of each individual result did not exceed 0.0043 mole fraction of CO$_2$. The probable error of the mean of the liquid data results was no greater than ±0.0025 mole fraction. Figures 3 and 4 show that the experimental values are in good agreement with that of other workers, with a maximum absolute average deviation of no greater than 4.5% over the whole range.

Vapor−liquid equilibria were determined at 313 K and 323 K for the carbon dioxide + carvacrol system. The experimental data are shown in Table 2. The liquid measurements were repeated several times, and the values of x_1 listed in the table are the mean of the values obtained. The error in x_1 did not exceed 0.0095 mole fraction of CO$_2$, and the probable error of the mean was no greater than ±0.0048.

Correlation of Data

The vapor−liquid equilibrium can be calculated at a defined temperature from the fundamental equation

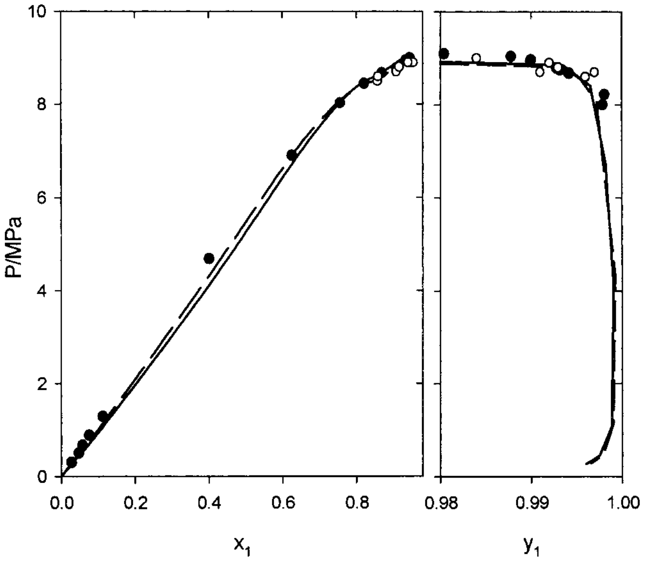

Figure 3. Vapor−liquid equilibria for CO_2 (1) + limonene (2) at 318 K: ●, this work; ○, Matos et al.;[16] —, Peng−Robinson equation of state; − − −, Zudkevitch's modification to the R−K equation.

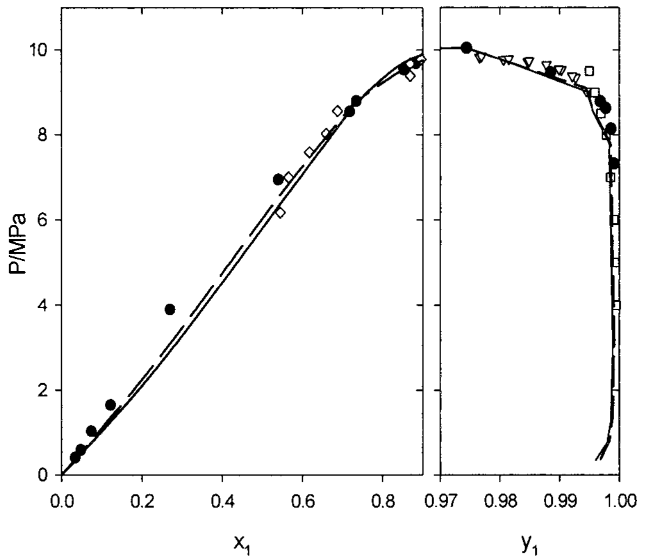

Figure 4. Vapor−liquid equilibria for CO_2 (1) + limonene (2) at 323 K: ●, this work; ◇, Bertucco et al.;[17] □, Di Giacomo et al.;[18] ▽, Marteau et al.;[19] —, Peng−Robinson equation of state; − − −, Zudkevitch modification to the R−K equation.

$$\phi_i^{\mathrm{L}} P y_i = \phi_i^{\mathrm{V}} P x_i \tag{1}$$

where ϕ is the fugacity coefficient of component i, P is the equilibrium pressure, and x and y are the mole fractions of component i in the respective liquid (L) or vapor (V) phase. Two separate cubic equations of state were used to determine ϕ_i; the Peng−Robinson (P−R) equation of state and Zudkevitch's modification to the Redlich−Kwong (R−K) equation of state. The P−R EOS is expressed as

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{2}$$

and the R−K EOS as

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5} V(V + b)} \tag{3}$$

Table 2. Vapor−Liquid Equilibria for CO_2 (1) + Carvacrol (2)

$T = 313$ K				$T = 323$ K			
P/MPa	x_1	P/MPa	y_1	P/MPa	x_1	P/MPa	y_1
0.40	0.0233	7.70	0.9971	0.26	0.0144	8.75	0.9966
0.64	0.0370	7.74	0.9957	0.36	0.0196	10.73	0.9927
1.09	0.0627	7.75	0.9972	0.45	0.0256	12.99	0.9783
1.30	0.0741	8.49	0.9935	0.64	0.0355	15.34	0.9670
3.60	0.1997	8.57	0.9922	2.14	0.1146	17.99	0.9590
6.19	0.3969	8.66	0.9934	4.80	0.2610	18.03	0.9553
7.03	0.4564	9.64	0.9885	9.00	0.4843	19.99	0.9433
7.30	0.4832	10.48	0.9825	11.30	0.5572	20.85	0.9388
8.98	0.5580	11.07	0.9806	13.25	0.5746	20.95	0.9403
10.71	0.5819	11.30	0.9814	15.35	0.5938	22.65	0.9219
12.93	0.6103	12.05	0.9770	15.90	0.6080	22.94	0.9324
14.52	0.6179	13.60	0.9725	17.44	0.6139	24.87	0.9028
16.57	0.6389	14.09	0.9690	20.67	0.6319	26.52	0.8952
18.10	0.6571	17.34	0.9593	21.13	0.6409	27.35	0.8842
20.20	0.6660	20.39	0.9478	23.55	0.6543	27.82	0.8865
20.88	0.6724	20.57	0.9518	24.85	0.6655	28.57	0.8505
23.01	0.6849	20.70	0.9519	25.61	0.6706	29.23	0.8218
25.21	0.6996	22.65	0.9427	26.76	0.6640	30.05	0.8331
27.05	0.7205	23.26	0.9415	28.89	0.6846		
28.14	0.7342	23.77	0.9381	30.04	0.7120		
28.83	0.7400	25.82	0.9263				
29.43	0.7539	25.90	0.9285				
30.32	0.7908	26.02	0.9229				
30.84	0.8313	26.12	0.9228				
		27.78	0.9089				
		28.40	0.9118				
		29.02	0.8953				
		29.51	0.8935				
		29.64	0.8890				
		30.43	0.8838				
		30.85	0.8804				

Table 3. Determined Densities

substance	T/K	ρ/(kg·m^{-3})	$10^4 V_m$/(m^3·mol^{-1})
limonene	318	821.75 ± 0.008	1.6579
	323	817.78 ± 0.002	1.6660
carvacrol	313	961.92 ± 0.095	1.5617
	323	958.10 ± 0.010	1.5680

Table 4. Pure Component *a* and *b* from Zudkevitch's Method

substance	T/K	a/(Pa·(m^6·mol^{-2})·K$^{0.5}$)	$10^4 b$/(m^3·mol^{-1})
limonene	318	118.8835	1.453 21
	323	119.3183	1.455 48
carvacrol	313	148.8856	1.417 66
	323	149.9110	1.414 94

Table 5. Critical Constants and Acentric Factors

substance	T_c/K	P_c/MPa	ω
CO_2	304.21	7.38	0.225
limonene	658.97	2.75	0.318
carvacrol	720.42	3.34	0.583

Zudkevitch's modification enables improved values of a and b to be calculated as functions of temperature from the vapor pressure ($P°$) and saturated liquid volume (V_m) of the heavy component. $P°$ and V_m were used to generate new values of a and b at the temperatures studied by simultaneously solving eq 3 and the expression for the fugacity coefficient for the saturated liquid phase given in eq 4, where $P = P°$ and $V = V_m$.

$$\phi_2^{\mathrm{L}} = \frac{PV}{RT} - 1 + \ln\left(\frac{RT}{P(V - b)}\right) - \frac{a}{RTbT^{0.5}} \ln\left(\frac{V + b}{V}\right) \tag{4}$$

This step was then repeated for the saturated vapor phase. If $\phi_2^{\mathrm{L}} \neq \phi_2^{\mathrm{V}}$ to a designated tolerance (i.e. < 0.00001), then a new value of b was found by trial and error and a new

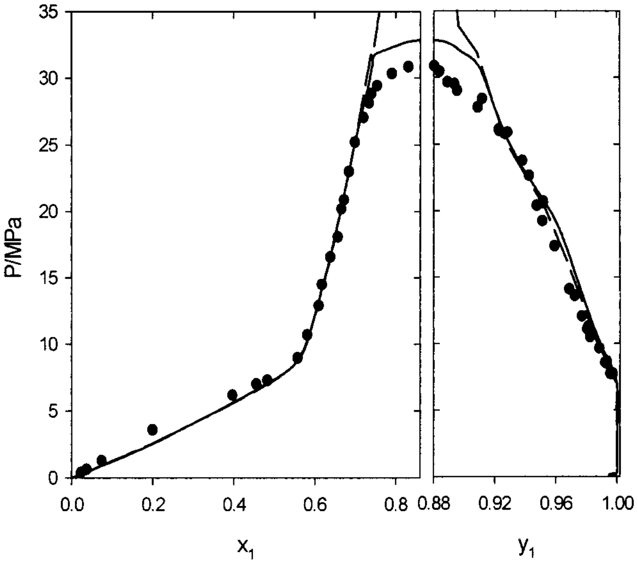

Figure 5. Vapor−liquid equilibria for CO_2 (1) + carvacrol (2) at 313 K: ●, this work; —, Peng−Robinson equation of state; − − −, Zudkevitch modification to the R−K equation.

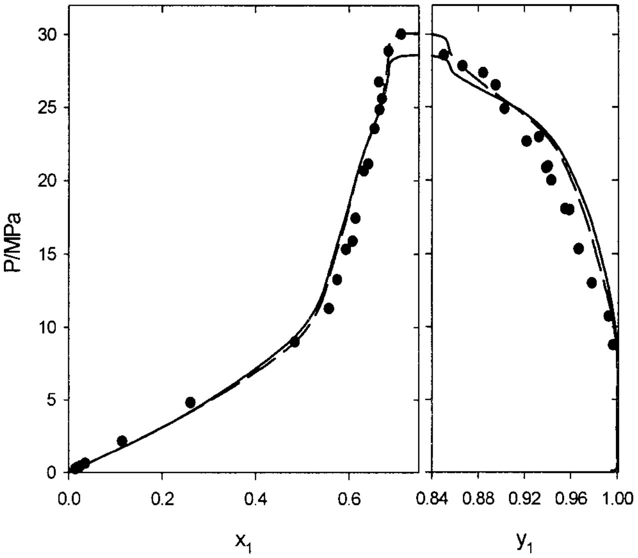

Figure 6. Vapor−liquid equilibria for CO_2 (1) + carvacrol (2) at 323 K: ●, this work; —, Peng−Robinson equation of state; − − −, Zudkevitch modification to the R−K equation.

Table 6. Binary Interaction Parameters for CO_2 (1) + Heavy Component (2)

heavy component	T/K	Peng−Robinson		Zudkevitch's modification to R−K	
		k_{ij}	π_1	k_{ij}	π_1
limonene (2)	318	0.0825	0.0531	0.0950	0.0204
	323	0.1038	0.0588	0.1095	0.0441
carvacrol (2)	313	0.0898	0.0471	0.0914	0.0762
	323	0.1002	0.0635	0.1005	0.0570

value of a was calculated. When $\phi_2^L = \phi_2^V$, the correct values of a and b had been found.

Using this method, the need to estimate critical parameters for more unusual liquid components (which usually decompose before the critical condition is attained) is removed. At the temperature conditions studied, liquid volume data were unavailable in the literature for both carvacrol and limonene and were experimentally determined by a density bottle technique. The results obtained are shown in Table 3. The subsequent values of a and b for both carvacrol and limonene calculated by Zudkevitch's approach that were used in eq 3 are shown in Table 4. The additional pure component parameters required to calculate the vapor−liquid equilibria are shown in Table 5. Critical parameters for limonene and carvacrol, required for use with the P−R equation of state, were estimated by the group contribution method of Lydersen[12] and their respective acentric factors, ω, by the Lee−Kesler approach.[12] Pure component data for carbon dioxide were obtained from the literature.[12,13]

Random mixing of the components was assumed, and the classical mixing rules for the constants a and b were employed:

$$a_m = \sum_i\sum_j y_i y_j a_{ij}, \quad a_{ij} = (1 - k_{ij})a_i^{0.5}a_j^{0.5} \tag{5}$$

$$b_m = \sum_i y_i b_i \tag{6}$$

where a_m includes the cross parameter k_{ij} to account for interactions between unlike molecules. The fugacity coefficients were thermodynamically derived from eq 2 or 3 (P−R or R−K) and from eqs 5 and 6 (see for example *Molecular Thermodynamics of Fluid-Phase Equilibria*),[14] and the vapor−liquid equilibrium (VLE) was calculated for the entire phase envelope using the bubble point approach. The cross parameter k_{ij} was treated as a fitting parameter to the experimental data at each isotherm and was adjusted using the Golden Section method to minimize the objective function, π_1:

$$\pi_1 = \frac{1}{2n}\sum^{n}\left(\frac{|P^{calc} - P^{exp}|}{P^{exp}} + \left|y_2^{calc} - y_2^{exp}\right|\right) \tag{7}$$

where P^{calc} is the calculated pressure, P^{exp} is the experimentally determined bubble pressure, y_2 is the mole fraction of carvacrol in the vapor phase, and n is the number of data points. Lee et al.[15] have successfully used π_1 in the prediction of vapor−liquid data for the carbon dioxide + dimethoxybenzene, + 2-methoxyphenol, and + p-cresol systems. The results obtained from the modeling are shown in Figures 3−6 for both the carbon dioxide + limonene and carbon dioxide + carvacrol systems. In each figure, the curve drawn between the experimental data points was that predicted by the relevant equation of state detailed in the legend. Overall, the data correlated well with both equations of state, although an improved fit, particularly for the carbon dioxide + limonene system, was obtained from Zudkevitch's modification to the R−K equation. Prediction of vapor−liquid equilibria for the carbon dioxide + carvacrol system in the vicinity of the critical mixture point was less satisfactory. The behavior reflects the limitations of cubic equations of state within this region, especially when the VLE is predicted over a wide pressure range. The calculated interaction parameters are listed in Table 6.

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