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High-Pressure Phase Equilibrium of CO_2 + 2-Phenylethanol and CO_2 + 3-Methyl-1-butanol

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Phase equilibrium for CO_2 + 2-phenylethanol and CO_2 + 3-methyl-1-butanol was measured. The two alcohols are both major constituents of wine aroma. The experimental apparatus includes a transparent high-pressure cell made of a sapphire cylinder, which allows full visual observation of the inside. Measurements were performed at temperatures of (313.1 and 323.1) K and at pressures from (8 to 24) MPa for the system CO_2 + 2- phenylethanol and pressures from (5 to 10) MPa for the system CO_2 + 3-methyl-1-butanol. The experimental results were fitted with the Stryjek−Vera modification of the Peng−Robinson cubic equation of state, using the composition-dependent mixing rules of Panagiotopoulos and Reid.

Introduction

Wine aroma is composed mainly of ethanol. However, the distinct characteristic aroma is given by a large number of compounds that are present in small quantities. These are primarily responsible for the aroma and flavor of each different type of wine. Typical compounds present in wine and wine aromas include higher alcohols (e.g., propanol, 3-methyl-1-butanol, 2-phenylethanol, 1-butanol, etc.), terpene alcohols (e.g., linalool, geraniol), esters (e.g., ethyl caprate, ethyl caprylate), phenolic and organic acids, ketones and aldehydes, and lactones.[1,2] All of these compounds are present in wine in small concentrations ranging from (10^{-1} to 10^{-10}) g·kg^{-1}. The two compounds used in this work, 2-phenylethanol and 3-methyl-1-butanol (coupled with the isomer 2-methyl-1-butanol), are usually present in relatively high concentrations compared to the others.[1]

Supercritical and liquid CO_2 extractions of wine and wine must (new wine) aromas have been attempted by several authors.[3−11] Due to the difference in solubility of the aroma compounds, the characteristics of the resulting extracts vary strongly with the extraction conditions. Further applications of these aroma extracts can be found in the food and cosmetic industries.[8−12]

In this work, we studied the vapor−liquid equilibrium in binary mixtures of CO_2 with 2-phenylethanol and with 3-methyl-1-butanol. These compounds were present in large amounts in CO_2 extractions from wine musts.[3] Each of them may represent a different class of compounds of the wine aroma in design methods of fractionation countercurrent columns using supercritical carbon dioxide. Accurate knowledge of fluid phase equilibria of their binary mixtures with CO_2 is essential for this purpose. However, these data are not currently available, except for the recently published results of Vázquez da Silva et al.,[13] at (288.2, 303.2, and 313.2) K, and of Lee at al.[14] at 313.2 K, on the CO_2 + 3-methyl-1-butanol system.

The measurements presented here were performed at two different temperatures, 313.1 and 323.1 K, and pressures from 8 to 25 MPa for the system CO_2 + 2-phenylethanol and from 5 to 10 MPa for the system CO_2 + 3-methyl-1-butanol.

Experimental Section

Materials. Carbon dioxide used in this work was supplied by Air Liquide (0.9995 mole fraction); 2-phenylethanol was obtained from Aldrich (0.99 mole fraction), and 3-methyl-1-butanol was supplied by Merck (0.99 mole fraction). No further purification was attempted.

Apparatus and Procedures. The apparatus used to perform the measurements presented here has previously been described in detail.[15,16] Gourgouillon et al.[17] have also described a similar apparatus.

The equilibrium cell is built around a sapphire cylinder, which allows full visual observation of the phenomena inside the cell. The cell has an internal volume of about 35 cm^3, and it is placed inside an air bath. Stirring of the contents is performed with a magnetic stirrer. Temperature is measured with a platinum-resistance thermometer with an accuracy of 0.2 K and a precision of 0.1 K. Pressure is measured with an accuracy of 0.06 MPa and a precision of 0.05 MPa. The calibration of the temperature and pressure sensors was initially checked by measuring values of the vapor pressure of pure carbon dioxide. At regular intervals during this work, (p,T) measurements at the (visually observed) critical point confirmed the initial calibration.

In each experiment, the time allowed for the phases to reach equilibrium was about 2 h, corresponding to stirring for 1 h and a rest period of another hour. Then, a sample from either the bottom or the top phase was taken through a HPLC valve, into a sample loop (internal volume of 0.5 cm^3). This was followed by an expansion of the loop contents into calibrated large volumes. Measurement of pressure in those volumes before and after the expansion allowed the calculation of the CO_2 quantity in the sample. The expansion volume includes cold traps that ensure precipitation of the other components. Due to the high volatility of 3-methyl-1-butanol, the trap was kept at a temperature of about −20 °C with cooled ethanol. In the next step, a measured amount of ethanol was introduced

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Table 1. Phase Equilibrium Measurements for CO_2 + 2-Phenylethanol at (313.1 and 323.1) K[a]

$T = 313.1$ K			$T = 323.1$ K		
p/MPa	y (CO_2)	x (CO_2)	p/MPa	y (CO_2)	x (CO_2)
8.28	0.9967		8.29		0.431
8.28		0.444	8.36	0.9974	
9.94	0.9899		10.29		0.451
10.24		0.488	10.36	0.9972	
10.24	0.9896		12.60	0.9903	
12.54	0.9829		12.94		0.454
12.62		0.497	14.99		0.453
14.64	0.9820		15.05	0.9858	
14.66		0.495	17.78		0.463
14.74	0.9824		17.85	0.9794	
16.60		0.506	20.67		0.535
17.40	0.9810		20.73	0.9787	
17.39		0.510	22.27	0.9748	
18.78	0.9808		22.67		0.599
20.05		0.533	24.41		0.618
20.05	0.9788				
22.34	0.9780				
22.40		0.559			

[a] x and y are the mole fractions of carbon dioxide in the liquid (phenylethanol-rich) and vapor (CO_2-rich) phases, respectively.

as a solvent, to wash the lines and the glass trap. The resulting solution was analyzed, and the amount of solute in the sample was determined.

Analytical Methods. The amount of 2-phenylethanol in each sample was determined by UV spectroscopy, at 260 nm, of the ethanol solution obtained from the sampling process. In the case of the system CO_2 + 3-methyl-1-butanol, GC capillary chromatography with a FFAP column was used.

Results and Discussion

CO_2 + 2-Phenylethanol. The experimental results for this system are presented in Table 1.

This system was studied at (313.1 and 323.1) K. Each experimental point is the average of at least two, but usually three, runs. The reproducibility (corresponding to a level of confidence of 95%) was ±0.0008 mole fraction for the vapor phase and ±0.01 for the liquid phase. The larger deviation for the liquid phase is probably due to slightly higher pressure drops in the sampling process from the liquid, and also to a generally stronger pressure dependence of equilibrium compositions in the liquid than in the vapor phase.

The experimental (p,x,y) results are represented in Figure 1. The shape of the liquid-phase curves is indicative of a phase diagram type III, in the classification of van Konynenburg and Scott.

In the 2-phenylethanol-rich phase, the solubility of CO_2 at the lower pressures decreases with increasing temperature. This is normal behavior in vapor–liquid equilibrium. However, for pressures higher than 18 MPa, the CO_2 solubility increases with temperature. This is most probably an indication that at 323.1 K, a liquid–liquid upper critical solution point is situated at a pressure not far above the maximum pressure attainable in the apparatus used in this work (25 MPa).

Results for this system were not previously available in the literature; only similar compounds were previously studied. Walther et al.[18] studied the system CO_2 + benzyl alcohol at 313.1 K, and Gamse et al.[19] studied the system CO_2 + 1-phenylethanol, also at 313.1 K. A comparison between the results of this work and those of Walther et al. and Gamse et al. is shown in Figure 2.

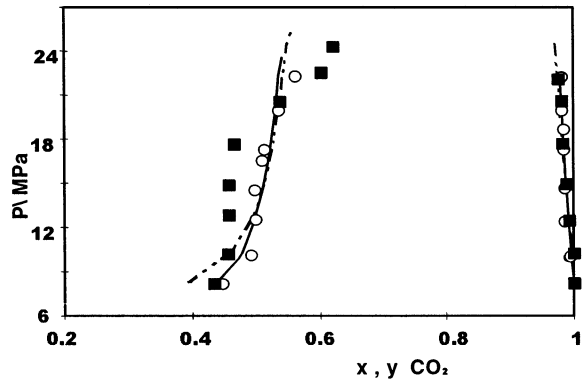

Figure 1. Phase equilibrium pressure–composition diagram for CO_2 + 2-phenylethanol at 313.1 K (○, solid line) and 323.1 K (■, dashed line); the lines represent the results calculated with the Peng–Robinson equation of state.

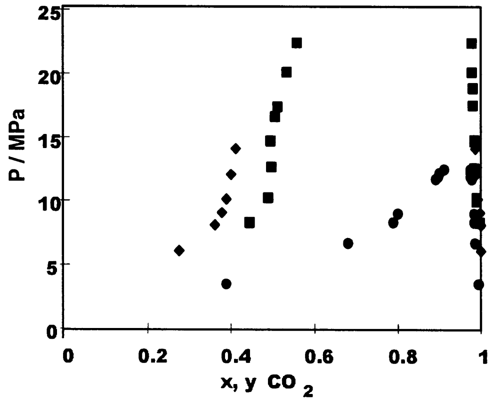

Figure 2. Comparison at 313.1 K between the phase equilibrium results obtained in this work for the system CO_2 + 2-phenylethanol (■) and the systems CO_2 + benzyl alcohol, measured by Walther et al. (◆) (ref 18), and CO_2 + 1-phenylethanol, by Gamse et al. (●) (ref 19).

The liquid-phase data for benzyl alcohol of Walther et al. are parallel to the results obtained in this work. It is plausible that an increase in the number of carbon atoms in the side chain of the phenyl group, as happens from benzyl alcohol to phenylethanol, will lead to an increase of carbon dioxide solubility in the liquid phase. So the two sets of results seem to be in agreement. On the contrary, Gamse et al. obtain a low critical pressure, below 15 MPa, for CO_2 + 1-phenylethanol, which is a surprising result in view of the other two sets of data.

CO_2 + 3-Methyl-1-butanol. The experimental results for this system at (313.1 and 323.1) K are presented in Table 2.

As in the previous case, each experimental point is the average of at least two runs. The reproducibility was ±0.0007 mole fraction for the vapor phase and ±0.009 for the liquid phase. The experimental results at 313.1 K are shown in Figure 3 for the liquid phase and in Figure 4 for the vapor phase.

Critical pressures are low for this system and were determined by visual observation of the characteristic opalescence in the vicinity of the critical point. The results were 8.37 MPa at 313.1 K and 9.94 MPa at 323.1 K. Lee at al.[14] give 8.35 MPa at 313.2 K, in excellent agreement with this work.

Vázquez da Silva et al.[13] and Lee at al.[14] have recently presented vapor–liquid equilibrium results for this system, at 313.2 K. A comparison of the liquid-phase compositions is shown in Figure 3. The three sets of data agree well at

Table 2. Phase Equilibrium Measurements for CO_2 + 3-Methyl-1-butanol at (313.1 and 323.1) K[a]

T = 313.1 K			T = 323.1 K		
p/MPa	y (CO_2)	x (CO_2)	p/MPa	y (CO_2)	x (CO_2)
5.20		0.442	6.70		0.473
5.27	0.9982		6.75	0.9968	
5.69	0.9983		7.90	0.9969	
5.97		0.534	7.95		0.608
6.28	0.9985		8.30	0.9979	
6.48		0.599	8.49		0.665
7.17	0.9984		8.78	0.9977	
7.23		0.638	9.05		0.734
7.63	0.9980		9.06	0.9971	
7.85	0.9976		9.49		0.852
7.88		0.771	9.49	0.9966	
8.02	0.9975				
8.03		0.852			

[a] x and y are the mole fractions of carbon dioxide in the liquid and vapor phases, respectively.

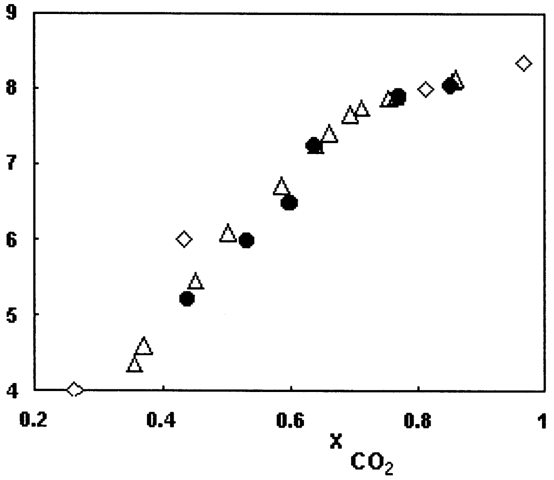

Figure 3. Liquid-phase equilibrium compositions for CO_2 + 3-methyl-1-butanol at 313.1 K (●) and comparison with the results of Vázquez da Silva et al. (△) (ref 13) and Lee et al. (◇) (ref 14).

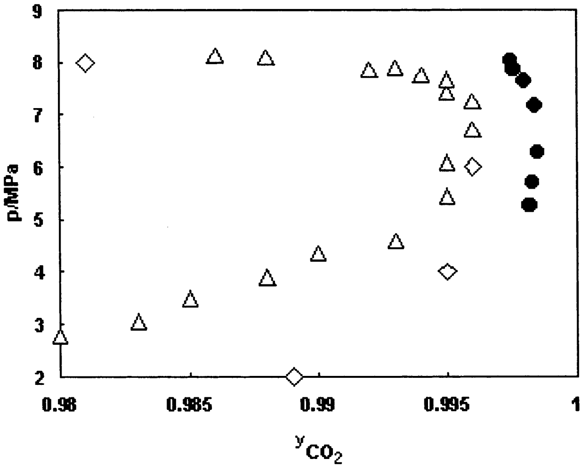

Figure 4. Vapor-phase equilibrium compositions for CO_2 + 3-methyl-1-butanol at 313.1 K (●) and comparison with the results of Vázquez da Silva et al. (△) (ref 13) and Lee et al. (◇) (ref 14).

the highest pressures, but on the low-pressure side, Lee et al. give lower solubilities of carbon dioxide in the liquid. For the vapor phase, Vázquez da Silva et al. obtained solubilities of 3-methyl-1-butanol in carbon dioxide that are 2−3 times higher than the solubilities presented in this work. The compositions given by Lee et al. differ again from those of Vásquez da Silva et al. at lower pressures but are in better agreement on the high-pressure side.

Table 3. Parameters k_{12} and k_{21} of the Panagiotopoulos−Reid Mixing Rules[a] **Obtained for the Stryjek−Vera Modification of the Peng−Robinson Equation of State**[b]

	k_{12}	k_{21}		k_{12}	k_{21}
CO_2 + 2-Phenylethanol			CO_2 + 3-Methyl-1-butanol		
T = 313.1 K	0.185	0.183	T = 313.1 K	0.046	0.102
T = 323.1 K	0.201	0.211	T = 323.1 K	0.019	0.130

[a] Reference 23. [b] Reference 22.

Table 4. Pure-Component Data Used in the Fitting of the Experimental Results[a]

compound	T_c/K	P_c/MPa	ω
carbon dioxide	304.21	7.382	0.225
2-phenylethanol	730.15	4.750	0.502
3-methyl-1-butanol	579.40	3.911	0.607

[a] T_c and P_c are the critical temperature and pressure, respectively; ω is the acentric factor.

Comparison can be made with the results for the vapor phase of mixtures of CO_2 with other pentanols, at the same temperature: Those of Staby et al.[20] for CO_2 + 1-pentanol, of Lee et al.[14] for 3-methyl-2-butanol, and of Lee et al.[21] for CO_2 + 2-pentanol. While the data of Staby et al. lie very close to the vapor-phase compositions of this work, those of Lee et al. are consistent for the three alcohols they have studied and are in general good agreement with Vázquez da Silva et al. above 5 MPa.

This type of discrepancy is common in the literature. Due to the small solubilities in the carbon dioxide rich vapor phase, any small systematic error in the calculation of the solute quantities introduces large uncertainties in the composition. These may be amplified by perturbations to equilibrium conditions produced by the sampling procedures adopted in each case.

Correlation of the Experimental Results. The experimental results were fitted by the Stryjek−Vera modification of the Peng−Robinson equation of state,[22] using the mixing rules of Panagiotopoulos and Reid.[23] The Stryjek−Vera additional parameter m_1 was taken as 0.0429 for carbon dioxide. This parameter is not given by those authors for 2-phenylethanol and 3-methyl-1-butanol, and the published data on their thermodynamic properties that would allow their calculation are very scarce. In this work, m_1 for those two substances was taken as an additional variable parameter to be obtained by the fitting to the binary mixture properties. The fitting procedure was performed for different values of m_1. Mean square deviations between experimental and calculated compositions varied slowly with this parameter. The lowest values were found for the following m_1 values: for 2-phenylethanol, −1.67 at 313.1 K and −2.05 at 323.1 K; for 3-methyl-1-butanol, −0.34 at 313.1 K and −0.89 at 323.1 K.

The values of the binary interaction parameters k_{12} and k_{21} are given in Table 3. The pure-component data used in the fitting are given in Table 4. They were taken from Angus et al.[24] for carbon dioxide. For 2-phenylethanol and 3-methyl-1-butanol, they were estimated using methods described in the book of Reid et al.[25]

For the CO_2 + 2-phenylethanol system, the results are shown in Figure 2. The standard deviation of the equation of state fit to the experimental results is 0.012 mole fraction for the 2-phenylethanol-rich phase at 313.1 K and 0.049 at 323.1 K, and the standard deviation is 0.009 at the two temperatures for the CO_2-rich phase. In the case of the system CO_2 + 3-methyl-1-butanol, the standard deviation is 0.011 for the liquid phase and 0.004 for the vapor phase, at both temperatures.

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