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Phase Equilibrium Properties of the 1-Phenylethanol−Carbon Dioxide and 2-Octanol−Carbon Dioxide Binary Systems at 303.15 K, 313.15 K, and 323.15 K

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Phase equilibria data for the 1-phenylethanol−CO_2 and 2-octanol−CO_2 systems were measured at 303.15 K, 313.15 K, and 323.15 K and at pressures up to 145 bar. An equilibrium cell with circulating gas phase was used for the measurements. Data were correlated with the Peng−Robinson equation of state. Different methods were tested for calculating the binary interaction parameters k_{ij} and l_{ij} of the quadratic mixing rules.

Introduction

Vapor−liquid equilibrium (VLE) data for the 1-phenylethanol−CO_2 and 2-octanol−CO_2 systems are needed for enzymatic reactions using these substances as substrates. The substrates have to be dissolved in the CO_2 stream which enters the reactor, where the enzyme is located and enzymatic reaction takes place. A knowledge of VLE data is important, because a good solubility of the substances in a wide range of pressure and temperature is desired so that the parameters for the reaction can be varied without encountering a limitation of substrate solubility.

The substances 1-phenyethanol and 2-octanol were measured, because few published data are available. Alwani and Schneider[1] published $p(T)$ isopleths for the CO_2−2-octanol system. For CO_2−1-octanol, phase equilibria measurements were published by Weng and Lee[2] in the temperature range from 40 °C to 75 °C.

Experimental Methods

Apparatus and Procedures. Phase equilibria experiments were performed in an equilibrium cell. The dynamic analytical method was used with circulation of the gas phase. The equilibrium cell (Figure 1) has a volume of 140 mL and is constructed for a maximum operating pressure of 400 bar at maximum temperature of 100 °C. Two sight glasses are installed in the front and back sides of the cell, which give a view into the cell over the whole height so that equilibrium phenomena can be observed. The CO_2-rich phase is withdrawn at the top of the cell, passes through a six-port HPLC valve with a sample loop of 200 μL, and is recycled with a gear pump at the bottom of the cell. For better mixing and therefore faster equilibrium, the gas phase is circulated and a magnetic stirrer is placed in the center on the bottom of the cell. The whole system is placed in a thermostatted water bath and all pipes are thermostated to prevent separation of substances due to temperature gradients. Pressure and temperature in the cell are measured with accuracy of ±0.1 °C and ±0.1 bar.

CO_2-Phase Sampling. During equilibrium time the CO_2-phase passes through the sample loop. Thirty minutes before sampling, the stirrer and circulation of the gas phase are switched off to prevent withdrawing of fine liquid droplets into the sample loop. A sample of the CO_2 phase is taken by switching the six-port HPLC valve and expanding the volume of the sample loop into about 2−3 mL of ethanol situated in a calibrated 5-mL flask, which is placed in ice water in order to collect all of the sample. After expansion, the sample loop is washed with ethanol and cleaned with compressed air to collect the whole sample which separates in the sample loop. The ethanol−sample mixture is filled with ethanol to exactly 5 mL, and this mixture is analyzed by a gas chromatographic method.

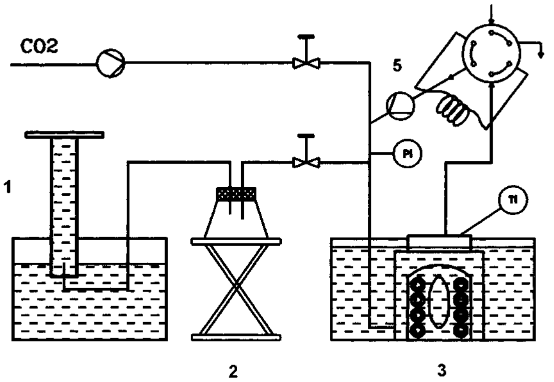

Figure 1. High-pressure equilibrium cell for determining phase behavior: 1, calibrated glass cylinder; 2, liquid-phase sampling; 3, equilibrium cell; 4, six-port HPLC valve with 200 μL sample loop; 5, gear pump.

Liquid-Phase Sampling. For determining the dilute CO_2 in the liquid phase, a sample is withdrawn from the bottom of the equilibrium cell and expanded into a glass vial which is weighed before and after sampling. The volume of the expanded liquid sample is about 1−2 mL so that the amount of dissolved CO_2 in the liquid sample under atmospheric conditions can be neglected. The expanded CO_2 leaves the glass vial at the top and enters a calibrated glass cylinder filled with water of a pH value of about 0.5 to limit solubility of CO_2 in the water. From the measured water volume, the temperature and the pressure of the water bath, and the weight of sample in the glass vial, the amount of solved CO_2 in liquid phase is calculated.

CO_2-Density Calculation. The density of pure CO_2 as a function of pressure and temperature was calculated with

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Table 1. Isothermal Vapor–Liquid Equilibrium Data for the Carbon Dioxide (1)–1-Phenylethanol (2) System

P^{exp}/bar	X_1	Y_1	P^{exp}/bar	X_1	Y_1
		$T = 303.15$ K			
48	0.6240	0.9843	80	0.8650	0.9754
56	0.7050	0.9827	85	0.8795	0.9727
59	0.7400	0.9816	89	0.8900	0.9708
		$T = 313.15$ K			
35	0.3890	0.9937	117	0.8920	0.9766
67	0.6800	0.9871	119	0.8960	0.9762
83	0.7890	0.9840	122	0.8990	0.9756
90	0.8000	0.9830	125	0.9110	0.9748
		$T = 323.15$ K			
40	0.3600	0.9970	79	0.6631	0.9926
46	0.4290	0.9971	120	0.8030	0.9858
48	0.4490	0.9965	132	0.8431	0.9830
50	0.4870	0.9962	137	0.8546	0.9806
74	0.6290	0.9932	145	0.8952	0.9773
75	0.6302	0.9936			

Table 2. Isothermal Vapor–Liquid Equilibrium Data for the Carbon Dioxide (1)–2-Octanol (2)–System

P^{exp}/bar	X_1	Y_1	P^{exp}/bar	X_1	Y_1
		$T = 303.15$ K			
30	0.4172	0.9984	55	0.723	0.9975
44	0.6047	0.9985	62	0.8246	0.9961
48	0.6411	0.9984	63	0.8425	0.9965
51	0.654	0.9981	65	0.901	0.9962
		$T = 313.15$ K			
44	0.517	0.9964	66	0.7305	0.9943
52	0.578	0.9954	71	0.774	0.9941
53	0.588	0.9944	76	0.837	0.9938
56	0.6553	0.9944	78	0.815	0.9928
64	0.6629	0.9938	80	0.9035	0.9936
65	0.6661	0.9948	81	0.9099	0.9936
		$T = 323.15$ K			
22	0.255	0.9957	81	0.76	0.9892
46	0.4929	0.994	88	0.7876	0.9879
62	0.6156	0.9921	89	0.8226	0.9867
71	0.671	0.991	91	0.825	0.9866
72	0.645	0.9905			

the Bender[3,4] equation. The amount of CO_2 in the sample loop for vapor-phase sampling and in the calibrated glass cylinder for liquid-phase sampling could be calculated with a knowledge of density calculated with this equation.

Gas Chromatographic Method. The ethanol mixture from the CO_2-phase sampling process is analyzed in a gas chromatograph (HP 5890 series II) with a flame ionization detector (GC-FID) using a capillary column (type DB-5, 25 m × 0.32 mm × 0.58 μm). The injector temperature is held constant at 250 °C, and detector temperature is at 350 °C. The oven temperature is kept constant for 1 min at 100 °C, increased by 25 $°C\cdot min^{-1}$ up to 150 °C, and then is held constant for another 2 min. A calibration with different amounts of 1-phenylethanol and 2-octanol in ethanol was done to determine the calibration line and retention times of the substances.

Materials. 1-Phenylethanol (purity >98%), 2-octanol (purity >97%), and ethanol (purity >99.8%) were supplied by Merck. The carbon dioxide with a purity >99.94% and a dew point lower than −60 °C was purchased from Linde (Graz) and stored in a tank with a capacity of 3200 L.

Results

Table 3. Critical Parameters T_C and P_C and Acentric Factor ω of the Pure Substances

	MW/g mol^{-1}	T_C/K	P_C/bar	ω
CO_2	44.01	304.21	73.795	0.2250
1-phenylethanol	122.17	686.03	40.93	0.7806
2-octanol	130.23	613.66	27.53	0.7506

Table 4. Optimized k_{ij} and l_{ij} Values of the Carbon Dioxide (1)–1-Phenylethanol (2) and Carbon Dioxide (1)–2-Octanol (3) Systems

method	k_{12}	l_{12}	k_{13}	l_{13}
1	−0.0169		0.0398	
2	−0.0172	0.0038	0.0430	0.0070

Table 5. ΔP/% Values in the Predicted Bubble Point Pressure and Mean Deviation ΔY between Experimental and Calculated Vapor Composition for the Carbon Dioxide (1)–1-Phenyethanol (2) System

	method1		method 2	
temp/K	ΔP/%	ΔY	ΔP/%	ΔY
303.15	5.91	0.0166	5.00	0.0164
313.15	1.75	0.0077	2.39	0.0078
323.15	3.69	0.0054	3.47	0.0055
av	3.60	0.0088	3.49	0.0088

In Table 1 we have given our original, unsmoothed data for the CO_2–1-phenylethanol system and in Table 2 for the CO_2–2-octanol system at 303.15 K, 313.15 K, and 323.15 K. These data have been correlated by using the Peng–Robinson equation of state[5]

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{1}$$

where P is the pressure, R is the gas constant, T is the temperature, and V is the molecular volume. Different methods for calculating the parameter b and the temperature-dependent function a were used to correlate the data with the van der Waals one-fluid mixing rules.

Method 1. For parameter a a quadratic mixing rate was used, and for b a linear mixing rule was used.

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$

$$b = \sum_i x_i b_i \tag{3}$$

$$a_{ij} = (a_{ii} a_{jj})^{0,5}(1 - k_{ij}) \tag{4}$$

Method 2. Parameter a was calculated with eqs 2 and 4, but parameter b was calculated with a quadratic mixing rule

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{5}$$

where

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2}\right)(1 - l_{ij}) \tag{6}$$

Table 3 gives the critical data T_C and P_C and the acentric factor ω of the pure components used with the Peng–Robinson equation of state. The values of the interaction parameters k_{ij} and l_{ij} were optimized by minimizing the ΔP/% values in the predicted bubble point pressure by using the experimental temperature, pressures, and liquid-phase compositions.

$$\Delta P/\% = \frac{100}{n} \sum_{i=1}^{n} \frac{|P_i^{exp} - P_i^{calc}|}{P_i^{exp}} \tag{7}$$

Table 6. ΔP/% Values in the Predicted Bubble Point Pressure and Mean Deviation ΔY between Experimental and Calculated Vapor Composition for the Carbon Dioxide (1)−2-Octanol (2) System

	method 1		method 2	
temp/K	ΔP/%	ΔY	ΔP/%	ΔY
303.15	1.64	0.0024	1.62	0.0024
313.15	2.85	0.0051	2.99	0.0051
323.15	3.46	0.0084	3.22	0.0084
av	2.71	0.0054	2.68	0.0054

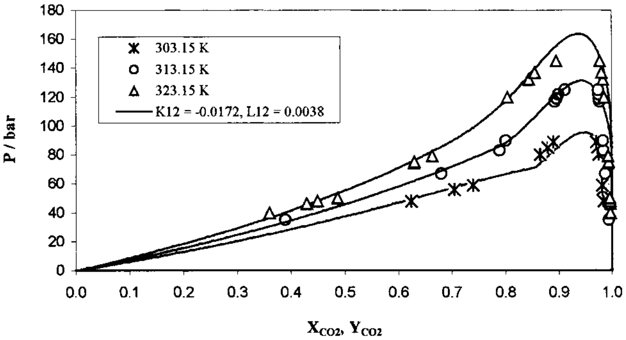

Figure 2. Pressure−composition diagram including experimental data and calculated with method 2 for the CO_2 (1)−1-phenylethanol (2) system at 303.15 K, 313.15 K, and 323.15 K.

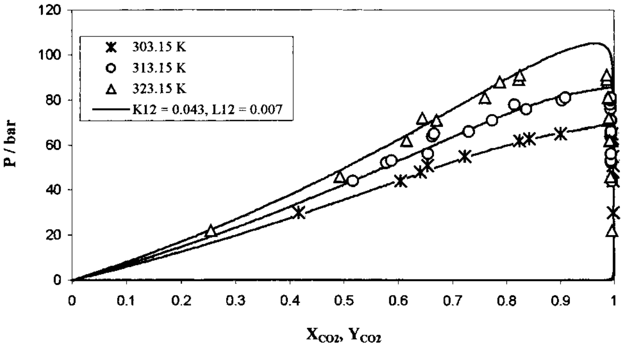

Figure 3. Pressure−composition diagram including experimental data and calculated with method 2 for the CO_2 (1)−2-octanol (2) system at 303.15 K, 313.15 K, and 323.15 K.

All calculations were done with the program OHGFOR developed by Professor Evelyne Neau of the Laboratoire de Chimie Physique, Marseille, France.

Optimized values of the interaction parameters k_{12} and l_{12} for the different methods are given in Table 4. The ΔP/% values and the mean deviation between experimental and calculated vapor composition Δy for the different calculation methods as well for each temperature and also for the average of the three calculated temperatures are given in Tables 5 and 6. From the ΔP/% values, it is obvious that both methods result in the same accuracy and thus the quadratic mixing rule for parameter *b* brings no benefit.

The Peng−Robinson equation of state provided a fairly good representation of the VLE data for these systems as shown in the pressure composition diagrams, Figures 2 and 3, which depict both the experimental data and the calculated results of method 2.

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Glossary

a,*b*	parameters in Peng−Robinson equation of state
k_{ij}, l_{ij}	binary interaction parameters
P	pressure
T	temperature
x	mole fraction CO_2 in the liquid phase
y	mole fraction CO_2 in the vapor phase

Greek Letters

Δ	difference between experimental and calculated value
ω	acentric factor

Subscripts

C	critical
1	CO_2
2	1-phenylethanol or 2-octanol

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