High-Pressure Vapor−Liquid Equilibria for CO_2 + Hexanal at (323.15, 353.15, and 383.15) K

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Pressure−composition isotherms are obtained for the system CO_2 + hexanal at (323.15, 353.15, and 383.15) K and pressures between (2.6 and 14.8) MPa. The phase equilibria measurements were carried out with an analytical method. The results were correlated by the Peng−Robinson (PR) equation of state using conventional mixing rules with two temperature-dependent interaction parameters.

Introduction

The production of middle-chain carboxylic acids encounters certain constraints regarding the aldehyde oxidation process as the principal method of commercial importance. The partial oxidation of aldehydes with the oxidation of hexanal to hexanoic acid being an important example is normally carried out at around 330 K in a semibatch process under slow addition of oxygen. The reaction is usually performed in the liquid phase using the salts of copper, manganese, iron, etc. as homogeneous catalysts but can also be feasible without a catalyst.[1,2] The total oxidation has to be avoided, thus determining a rather low space−time yield of this highly exothermal reaction and additional costs of the control system. Therefore, conducting this reaction in supercritical CO_2 in a continuous process and reducing the reaction time by elimination of mass transfer limitations through providing homogeneity of the reactive mixture could exhibit a potential alternative. Besides its cheapness and accessibility, this medium is known for its ability to tune the solubility of particularly nonpolar compounds. This could be obtained by adjusting the pressure and the temperature of the process, thus changing the density of the CO_2.

To identify the advantageous conditions for both, carrying out the reaction in a single phase and separation of the enriched product in the liquid phase, the knowledge of the phase equilibria of the reactive system would be required. Study of phase behavior in supercritical CO_2 is a long established field with a great number of data related to mutual solubilities of hydrocarbons or alcohols and CO_2. The number of publications involving aldehydes is very limited. The only available literature for these systems are the works of Vázquez da Silva.[3,4] The data reported show in the investigated pressure and temperature region only vapor−liquid equilibria coexistence with no liquid−liquid immiscibility.

The intention of this study is to provide experimental data of the phase behavior of the CO_2/hexanal mixture as a subsystem of the multicomponent reactive system for hexanal oxidation in $scCO_2$. For the data correlation, the Peng−Robinson equation of state with the quadratic mixing rule was implemented, and the interaction parameters best fitting the experimental results were evaluated.

Experimental Section

Materials. Carbon dioxide (99.996 % CO_2) was purchased from MESSER, Germany. Hexanal was supplied by MERCK with a certified purity of 99.7 %.

The helium 6.0 used as carrier gas, the synthetic air (80 % nitrogen and 20 % oxygen), and hydrogen 6.0 for the GC analysis were obtained from MESSER, Germany. For the composition analysis of the samples, the gas chromatograph (Hewlett-Packard 5980 A) equipped with TCD and FID detectors and two stainless steel capillary columns with 1 μm of the polyethylene glycol film from J&W Scientific (DB-WAX, 30 m length × 0.53 μm ID) were used.

The temperature program was determined with the ChemStation Software from Agilent company. The oven temperature was initially held at 343.15 K for 0.3 min and then raised to a final temperature of 413.15 K at a rate of 15 $K\cdot min^{-1}$ after each injection. The end temperature of the oven was held for 3 min. The inlet-port temperature was fixed at 473.15 K, and the temperature of the detectors was fixed at 523.15 K. The flow rate of the carrier gas was kept at 8.8 $mL\cdot min^{-1}$.

Apparatus and Procedure. The so-called analytical method was used by drawing and analyzing samples from the static cells. The setup consists of two high-pressure autoclaves with the reaction volume of around 87 mL and four radial and one axial inlet/outlet each. The variable volume static cells, shown in Figure 1, were built by SITEC-Sieber Engineering AG (Maur/Zurich, Switzerland). The maximum allowed operating conditions were 100 MPa and 870 K. A counterbalance piston mounted at the top of each autoclave enabled displacing a volume of 12 mL, thus this value corresponds to the maximum sample volume which can be withdrawn without changing the pressure within the autoclaves. Nitrogen from the cylinder was used to provide force on the piston. The autoclaves were connected to the HAAKE water bath thermostats. The cell blocks were heated by means of four 250 W cartridge heaters located in holes running along the body. The temperature of the cells was measured through the Ni−Cr−Ni thermocouples with an accuracy of 0.1 K. The pressure in the cells was measured with the calibrated pressure transducers (WIKA, type 891.23.510). A relief valve on the CO_2 line was used as the overpressure protection proved for the maximum pressure of 0.7 MPa.

The autoclaves were evacuated before loading the components. First, hexanal was injected into the cells using the

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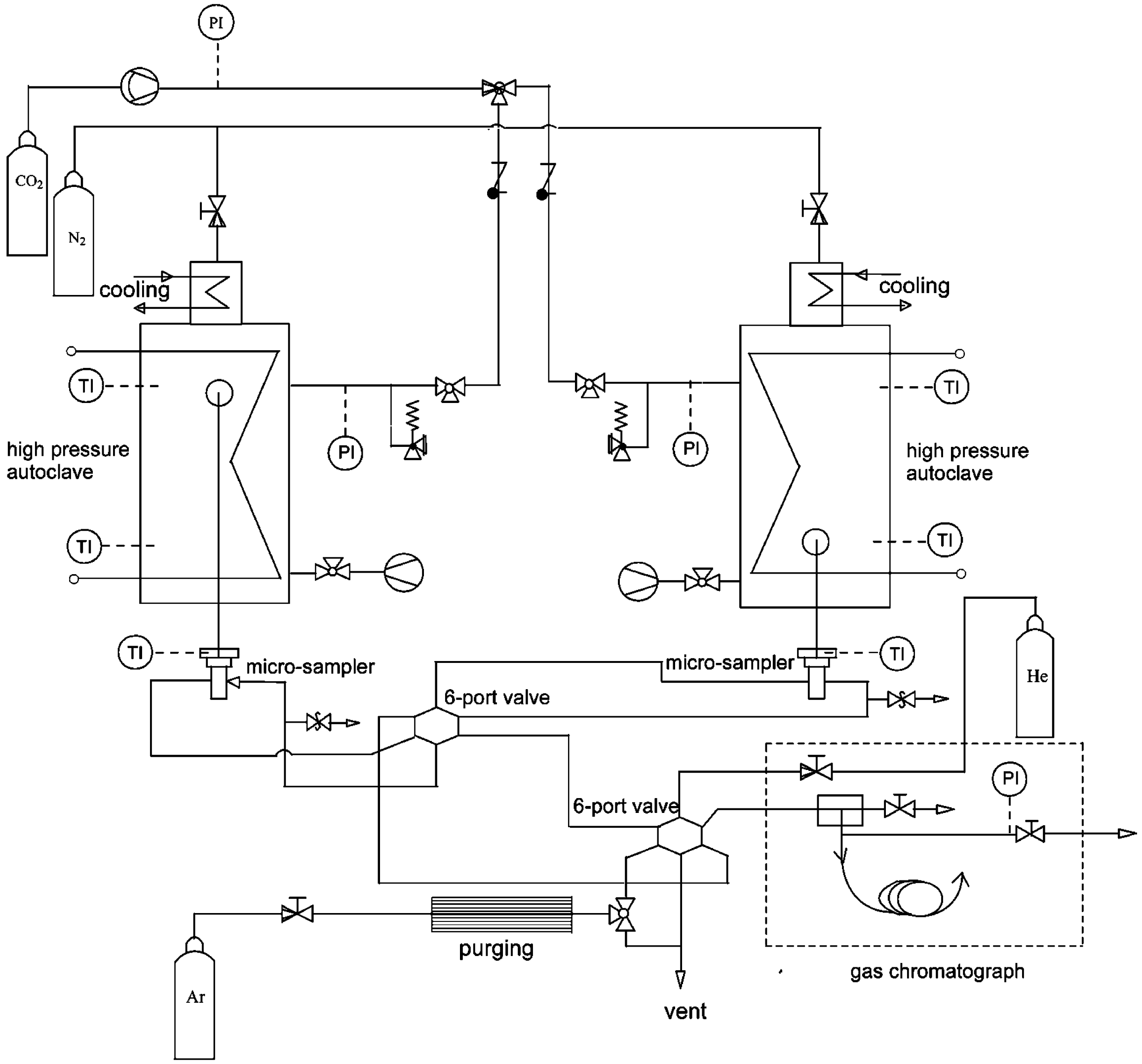

Figure 1. Experimental setup for phase equilibria measurements.

Hamilton syringe, and then carbon dioxide was compressed through the diaphragm-type SITEC compressor (maximum discharge pressure, 100 MPa) and pressed in the cells via the high-pressure needle valves (SITEC).

Samples were withdrawn via a pneumatic sampler system. The sampler (ROLSI) was connected to the cell through the coated RESTEK tubing (Silcosteel, 1/16 in. OD × 0.030 in. ID). A six-port Swagelok valve enabled the switching between the samplers. Another six-port Swagelok valve was used for switching between the carrier gas constantly flowing through the sampler line and argon used to purge the tubing. Because the equilibrium measurements were carried out in separate autoclaves for gas and liquid phases, the capillaries had different lengths enabling the sample to be withdrawn from the upper gas phase from one of the autoclaves and the lower liquid phase from the other. The temperature set in both autoclaves was identical as was the injected amount of the aldehyde ((12 to 15) mL) to provide the same equilibrium conditions. The end pressure values, however, changed to some extent due to the solution process, so the end value taken for the calculation was not necessarily identical for both autoclaves. This fact did not affect the equilibrium within each autoclave because in the binary system it only depends on the temperature as long as the volume and the pressure are determined and the mutual saturation of both phases is assured through a sufficient amount of the solute. As a consequence, the pressure had to not be held identical in both cells to obtain the solubility curves of each phase investigated.

To reassure that the sample was withdrawn from the predetermined phase (gas or liquid) of the corresponding autoclave, the ends of the capillaries were placed in the way enabling observation in the window of the cell. In the opposite end of the capillary, a fine titanium needle was placed sealing the capillary and providing the constancy of pressure inside the cell under the counterpressure of the compressed air ((0.2 to 0.6) MPa) while taking the sample.

The moment of reaching equilibrium was determined as the moment when the relative peak areas of the spectra showed constant values, which normally occurred after 8 h after loading the cells. The samples were directly transferred to the gas chromatograph and quantitatively analyzed. With one run lasting 15 min, 15 to 25 samples were taken and averaged for one data point. The composition was measured based on the external standard calibration method. The uncertainty of the measured mole fraction was estimated to be 3 %. The reproducibility of the gas chromatograph within one data series was (1 to 2) %.

Results

The experimentally measured phase compositions for the CO_2 + hexanal system at (323.15, 353.15, and 383.15) K are summarized in Table 1 and shown in Figure 2.

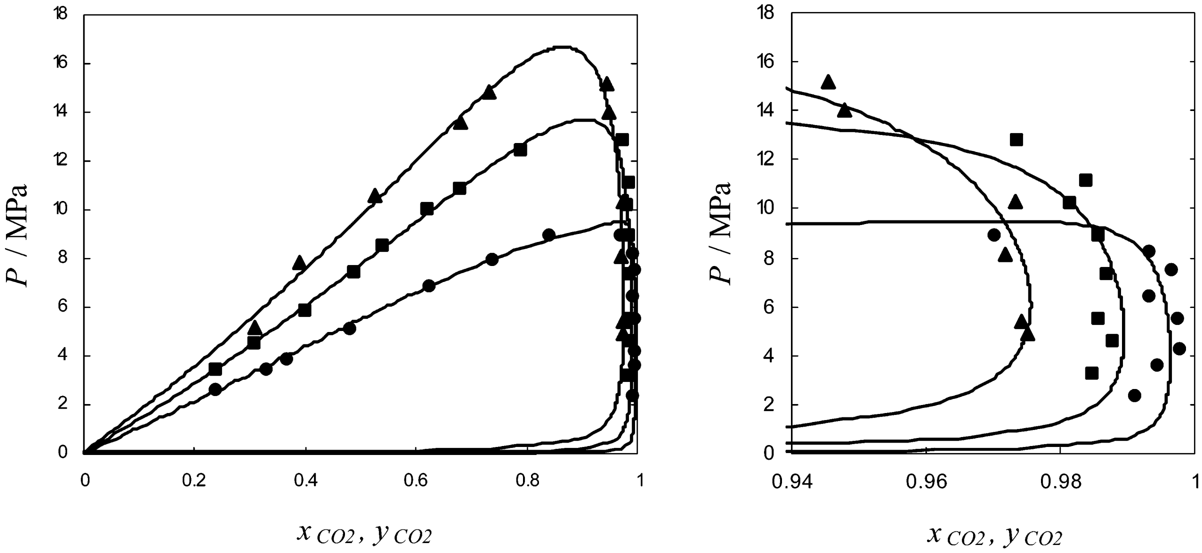

Figure 2. Vapor−liquid equilibrium diagram (P, x_{CO_2}, y_{CO_2}) for the system CO_2 + hexanal. Comparison of the experimental data (●, 323.15 K; ■, 353.15 K; ▲, 383.15 K) with calculations (—) obtained with the PR-EOS.

Table 1. Experimental Equilibrium Data for the System CO_2 (1) + Hexanal (2) at (323.15, 353.15, and 383.15) K

P/MPa	x_{CO_2}	P/MPa	y_{CO_2}	P/MPa	x_{CO_2}	P/MPa	y_{CO_2}	P/MPa	x_{CO_2}	P/MPa	y_{CO_2}
	T = 323.15 K				T = 353.15 K				T = 383.15 K		
2.6	0.2406	2.3	0.9913	3.4	0.2387	3.2	0.9849	5.2	0.3098	4.9	0.9751
3.4	0.3298	3.6	0.9945	4.5	0.3106	4.6	0.9879	7.8	0.3912	5.4	0.9741
3.8	0.3675	4.2	0.9979	5.8	0.3992	5.5	0.9857	10.6	0.5258	8.1	0.9718
5.1	0.4798	5.5	0.9976	7.4	0.4880	7.3	0.9870	13.6	0.6798	10.3	0.9732
6.8	0.6251	6.4	0.9932	8.5	0.5413	8.9	0.9859	14.8	0.7316	14.0	0.9480
7.9	0.7388	7.5	0.9968	10.0	0.6217	10.2	0.9814			15.2	0.9456
8.9	0.8410	8.2	0.9933	10.8	0.6789	11.1	0.9840				
		8.9	0.9702	12.4	0.7915	12.8	0.9735				

Table 2. Critical Pressure P_c, Critical Temperature T_c, and Acentric Factor ω of the Components

component	T_c/K	P_c/bar	ω
carbon dioxide	304.12[a]	73.74[a]	0.225[a]
hexanal	592.8[b]	34.6[b]	0.3778[c]

[a] Ref 6. [b] Ref 7. [c] Calculated with the Lee Kesler method.[8]

The data were modeled with the Peng−Robinson equation of state (PR-EOS)[5] using the quadratic mixing rule with two interaction parameters k_{ij} and l_{ij} as given below

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

where

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{2}$$

$$b = \sum_i \sum_j z_i z_j b_{ij} \tag{3}$$

and

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{4}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{5}$$

The critical properties (T_c, P_c) and acentric factor (ω) of CO_2 and hexanal used to calculate the parameters for the PR-EOS are given in Table 2.

Table 3. PR-EOS Binary Interaction Parameters, k_{ij} and l_{ij}, and Corresponding Values of the Relative Root-Mean-Square Deviation (RRMSD) for the System CO_2 + Hexanal at Measured Temperatures

T/K	k_{ij}	l_{ij}	RRMSD
323.15	0.0740	−0.0060	$2.7 \cdot 10^{-1}$
353.15	0.0715	−0.0049	$1.3 \cdot 10^{-1}$
383.15	0.0660	−0.0026	$1.2 \cdot 10^{-1}$

The parameters of the equation were obtained by minimizing the following objective function (OF)

$$\mathrm{OF} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\xi_i^{\mathrm{exptl}} - \xi_i^{\mathrm{calcd}}}{\xi_i^{\mathrm{exptl}}}\right)^2} \tag{6}$$

where n is the number of experimental points and ξ^{exptl} and ξ^{calcd} are the experimental and the calculated mole fraction of CO_2 in each phase, respectively. The interaction parameters best fitted to the experimental data and the corresponding values of the objective function for all temperatures measured are summarized in Table 3.

Conclusions

High-pressure phase behavior data are obtained at (323.15, 353.15, and 383.15) K and for pressure ranges of (2.6 to 14.8) MPa. In the temperature and pressure ranges measured, this system showed an immiscibility region with no occurrence of a second liquid phase. The phase behavior of the binary experimental data was correlated with the PR equation of state. The fitted binary temperature-dependent parameters for each isotherm are reported, and the correlation between the experimental ant theoretical results is presented.

Note Added after ASAP Publication. This paper was published ASAP on August 14, 2007. An author name was corrected. The revised paper was reposted on August 17, 2007. Erroneous data appeared in Table 1 due to production error. The revised paper was reposted on August 29, 2007.

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