# Articles

# High-Pressure Phase Equilibria of Carbon Dioxide + 1-Hexanol at 303.15 and 313.15 K

**Armin Beier, Jegor Kuranov,[†] Karl Stephan, and Hans Hasse\***

Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, D-70550 Stuttgart, Germany

Phase equilibrium data for the system $CO_2$ + 1-hexanol was measured at 303.15 K and 313.15 K. A liquid−liquid immiscibility is observed at 303.15 K that disappears at higher temperatures. The experimental results were correlated with the Redlich-Kwong-Soave EOS applying the Huron-Vidal mixing rules.

## Introduction

High-pressure phase equilibria are of increasing interest due to the development of supercritical fluid technologies. The extension of the database has received much attention in recent years. Reviews can be found in the literature.[1,2] Only small parts of the phase diagram of the system carbon dioxide + 1-hexanol have been investigated so far. The solubility of 1-hexanol in carbon dioxide for several temperatures was measured by Chylinski and Gregorowicz,[3] and liquid−liquid data for the LLV equilibria are available from Lam et al.[4] The present paper reports on experimental studies of the complete phase diagram of the carbon dioxide + 1-hexanol mixture. Data obtained at near- and super-critical temperatures of $CO_2$ are of special interest for process design. Therefore, measurements along the two isotherms at 303.15 K and 313.15 K have been performed.

## Experimental Section

***Materials.*** Carbon dioxide (purity 99.995 vol %) was obtained from Messer Griesheim GmbH. 1-Hexanol (purity higher than 98% as determined by gas chromatography (GC) and analysis of peak areas) was purchased from Merck, Germany, and was further purified by distillation (purity higher than 99.5% by GC).

***Apparatus and Procedures.*** The measurements were carried out in the high-pressure optical cell (volume about 50 cm³, stainless steel) shown in Figure 1. The cell was placed in an air bath to keep the temperature in the cell constant. The temperature was controlled and measured with a calibrated PT100 resistance thermometer placed inside the cell. The accuracy of the temperature measurement is ±0.1 K. The pressure was measured with a pressure transducer. The transducer was calibrated against a high-precision pressure gauge. The uncertainty in the pressure measurements is ±0.15 bar.

1-Hexanol was pumped from a storage vessel into the cell. Next, $CO_2$ was added by a compressor to adjust to the

\* Corresponding author. E-mail: hasse@itt.uni-stuttgart.de.
† Permanent address: Department of Chemistry, St. Petersburg State University, 198504 St. Petersburg, Russia.
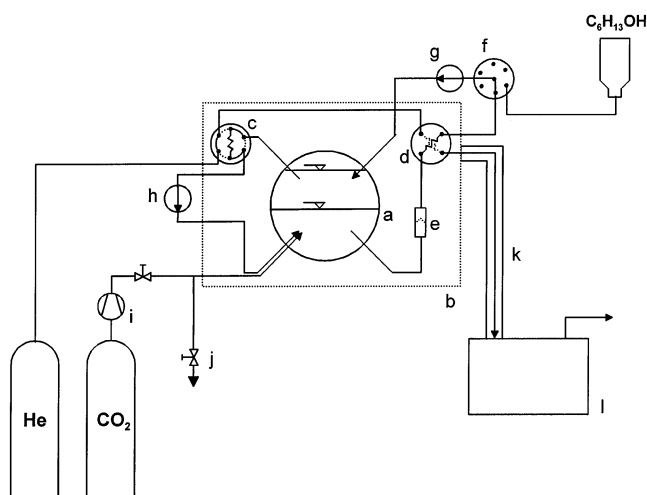


**Figure 1.** Experimental schematic digram: a, high-pressure view-cell; b, thermostate; c and d, sampling valves; e, filter; f, six-way valve for liquid injection; g and h, HPLC pumps for circulation; i, compressor; j, purge valve; k, heated tubing; l, gas chromatograph.

desired pressure. The cell has two external loops in which samples from the light phase and the dense phase are recirculated by high performance liquid chromatography (HPLC) pumps. Stainless steel tubing with an inner diameter of 0.03 in. was used. It was assumed that equilibrium was reached when the system pressure and temperature were constant for at least 2 h. Due to the sampling method used, the pressure was absolutely constant during the measurements at one equilibrium point with a statistical oscillation of ±0.05 bar. The same is true for the temperature values, which were stabilized at ±0.05 K.

Samples for the gas chromatographic analysis of the equilibrium phases were withdrawn from the loops through two sampling valves (volume of 5 $\mu$L for the gas phase and 1 $\mu$L for the liquid phase). The tubing between the sampling valves and the gas chromatograph were heated in order to avoid condensation of the heavy components. Each sample
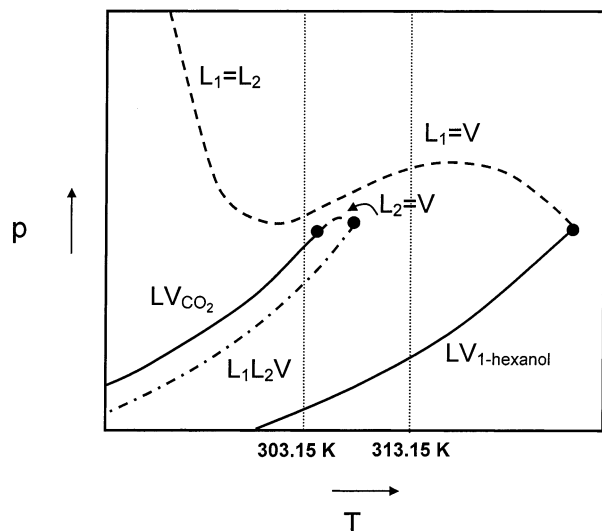
**Figure 2.** $p,T$-projection of the phase diagram for the $CO_2$ + 1-hexanol system: - - -, critical locus; - · -, three-phase line.

**Table 1. Vapor−Liquid Equilibria, Liquid−Liquid Equilibria, and Critical Points of Carbon Dioxide + 1-Hexanol at 303.15 and 313.15 K**

| | $T = 303.15$ K | | | $T = 313.15$ K | |
|---|---|---|---|---|---|
| $P$/bar | phase | $x_{CO_2}$/ (mol·mol$^{-1}$) | $P$/bar | phase | $x_{CO_2}$/ (mol·mol$^{-1}$) |
| 7.7 | $L_1$ | 0.051 | 5.3 | $L_1$ | 0.028 |
| 13.5 | $L_1$ | 0.101 | 10.0 | $L_1$ | 0.065 |
| 21.1 | $L_1$ | 0.142 | 22.2 | $L_1$ | 0.142 |
| 25.8 | $L_1$ | 0.195 | 30.1 | $L_1$ | 0.188 |
| 30.3 | $L_1$ | 0.241 | 42.5 | $L_1$ | 0.276 |
| 42.2 | $L_1$ | 0.339 | 49.8 | $L_1$ | 0.335 |
| 50.2 | $L_1$ | 0.396 | 59.8 | $L_1$ | 0.419 |
| 60.3 | $L_1$ | 0.517 | 64.2 | $L_1$ | 0.446 |
| 65.2 | $L_1$ | 0.579 | 69.0 | $L_1$ | 0.474 |
| 65.5 | $L_1$ | 0.594 | 76.0 | $L_1$ | 0.546 |
| 71.3 | $L_1$ | 0.720 | 81.6 | $L_1$ | 0.607 |
| 71.4 | $L_1$ | 0.719 | 85.9 | $L_1$ | 0.661 |
| 71.4 | $L_1$ | 0.723 | 92.7 | $L_1$ | 0.719 |
| 75.9 | $L_1$ | 0.745 | 97.2 | $L_1$ | 0.765 |
| 77.4 | $L_1$ | 0.753 | 5.4 | V | 0.986 |
| 71.3 | $L_2$ | 0.970 | 10.1 | V | 0.995 |
| 75.2 | $L_2$ | 0.915 | 81.4 | V | 0.989 |
| 77.0 | $L_2$ | 0.885 | 85.9 | V | 0.985 |
| 5.8 | V | 0.984 | 92.5 | V | 0.946 |
| 9.9 | V | 0.994 | 98.2 | $L_1 = V$ | 0.872 |
| 15.4 | V | 0.995 | | | |
| 79.6 | $L_1 = L_2$ | 0.820 | | | |

was analyzed at least five times. The relative error of the analysis is about 4%. Critical points were determined by visual observation of the critical opalescence. For more details see ref 5.

## Results and Discussion

The experimental data on the phase equilibria of carbon dioxide + 1-hexanol at 303.15 and 313.15 K are summarized in Table 1. As also confirmed by the measurements of Scheidgen,[6] the phase behavior of the mixture of carbon dioxide and 1-hexanol can be attributed to type III according to the classification of van Konynenburg and Scott.[7] This type is characterized by an miscibility gap and two critical lines (Figure 2), one of which connects the gas−liquid critical point of the more volatile component (carbon dioxide) with the critical end point of the liquid−liquid−gas line. The temperatures at which the experiments in the present work were carried out are slightly below the critical temperature of carbon dioxide and above the critical
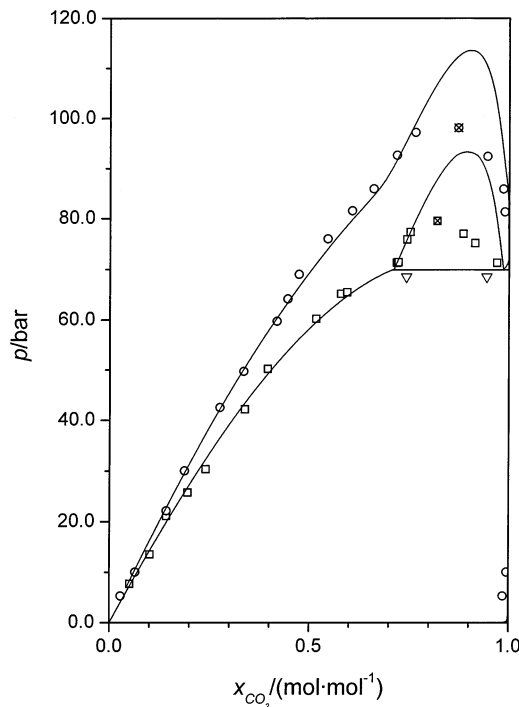


**Figure 3.** Phase equilibria in the system carbon dioxide + 1-hexanol at 303.15 and 313.15 K: □, 303.15 K (this work); ▽, 303.15 K;[4] ○, 313.15 K (this work); −, Redlich−Kwong−Soave EOS.

**Table 2. EOS Parameters of the Pure Substances Used for Calculation**

| | $T_c{}^a$/K | $m^b$ | $n^b$ | $b$/(L·mol$^{-1}$) |
|---|---|---|---|---|
| carbon dioxide | 304.2 | 0.5809 | 0.2727 | 0.0297 |
| 1-hexanol | 611.0 | 0.4880 | 0.8004 | 0.1087 |

$^a$ Critical temperature. $^b$ See ref 6.

**Table 3. Symmetric Parameter $\alpha_{ij}$ of the Huron and Vidal Mixing Rule**

| | carbon dioxide | 1-hexanol |
|---|---|---|
| carbon dioxide | | 1.035 |
| 1-hexanol | 1.035 | |

**Table 4. Asymmetric Parameter $C_{ij}$/(kJ·mol$^{-1}$) of the Huron−Vidal Mixing Rule**

| | carbon dioxide | 1-hexanol |
|---|---|---|
| carbon dioxide | | 4.045 |
| 1-hexanol | 2.060 | |

end point of the three-phase curve, respectively, as is shown in Figure 2.

Experimental results were correlated by means of the Redlich−Kwong−Soave equation of state with the energy parameter calculated using the method of Sandarusi et al.[8] The mixing rules of Huron and Vidal were used in their original form based on the NRTL model for the $G^E$ term.[9] This model has three parameters for each pure component which are fitted to the vapor pressure curve and three binary parameters which were determined from the experimental data of the present work. Tables 2−4 summarize the model parameters used for the calculations.

Figure 3 demonstrates the comparison between correlated and experimental results at 303.15 K and 313.15 K in the pressure−composition plane. At 303.15 K, a three-phase LLV equilibrium exists at 71.5 bar, as shown by the straight line. This equilibrium was found experimentally

and is confirmed by the model. The experimental results also show a reasonable agreement with the data from Lam et al.[4]

With rising temperature the small region of the LV equilibrium disappears and so does the three-phase equilibrium. The model predicts a temperature of about 308.25 K for the critical end point, whereas Lam et al.[4] give an experimental value of 312.93 K. In any case, the 313.15 K isotherm thus represents states above this point.

The experimental and calculated isotherms show a very good qualitative, as well as quantitative, agreement, except for in the critical region. The simple model used here is successful in modeling qualitatively the complicated topology of the phase behavior of the system under study.

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