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Vapor-Liquid Equilibria for Carbon Dioxide + 1-Pentanol

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Vapor-liquid equilibria have been measured for CO_2 + 1-pentanol at 314.6, 325.9, and 337.4 K using a high-pressure flow apparatus. The pressure in the experiments ranged from 5.176 to 11.983 MPa. The results show that the phase behavior of CO_2 + 1-pentanol is similar to the phase behavior observed for CO_2 + ethanol and CO_2 + 1-butanol.

Introduction

This work forms part of a continuing study of CO_2 + alkanols (*1*) of interest in the extraction of biomolecules (*2-4*) with supercritical CO_2 + alkanols, extraction of alkanols from aqueous solutions with carbon dioxide (*5-8*), and the production of alkanols from syngas (*9*). Although much attention has been focused on CO_2 + methanol and CO_2 + ethanol systems, very little attention has been paid to CO_2 + higher alkanol systems. In fact, no previous vapor-liquid equilibrium measurements have been reported in the literature for CO_2 + 1-pentanol with the exception of the critical properties of dilute mixtures measured by Gurdial et al. (*10*).

Experimental Section

The experimental procedure and apparatus have been described in detail previously (*1*), and only brief details are given below. Carbon dioxide from a cylinder and 1-pentanol from a reservoir were mixed and pumped through a series of coils and static mixers placed inside a constant-temperature air bath. Vapor-liquid equilibrium was attained during the pumping process. After equilibration, the phases were separated in a high-pressure stainless steel view cell (similar to a Jerguson level gauge) and each phase was depressurized across a micrometering valve. The pentanol from each phase was condensed and collected in a cold trap, while the carobn dioxide was allowed to pass through a wet test meter. Equilibrium phase compositions were calculated from the weights of the pentanol collected and the volume of carbon dioxide measured by the wet test meters. Small corrections were made for the residual pentanol not condensed and for the carbon dioxide dissolved in the condensed pentanol. Typically, 4-6 liquid samples and 3-5 vapor samples were collected. The reported compositions represent an average of all the samples equilibrated at the desired pressure and temperature. Additionally, to verify that equilibrium conditions had been attained, some experiments at a given temperature and pressure were repeated at different flow rates. No changes in equilibrium compositions with flow rates were detected.

Table I. Experimental Vapor-Liquid Equilibrium Data for CO_2 + 1-Pentanol

P/MPa	T/K	x_{CO_2}	y_{CO_2}
5.178	314.7	0.3368	0.9991
6.157	314.8	0.4135	0.9989
6.902	314.7	0.4850	0.9984
7.598	314.7	0.5657	0.9977
8.074	314.3	0.6714	0.9969
	av: 314.6		
6.164	325.9	0.3367	0.9983
6.943	326.0	0.4044	0.9978
7.667	325.9	0.4612	0.9971
8.274	326.0	0.5077	0.9965
8.977	326.0	0.5695	0.9951
9.660	326.0	0.6433	0.9924
10.342	325.8	0.7516	0.9781
10.556	325.9	0.7944	0.9617
	av: 325.9		
5.585	337.4	0.2834	0.9975
6.943	337.3	0.3583	0.9969
7.639	337.4	0.3976	0.9963
8.294	337.5	0.4346	0.9958
8.956	337.4	0.4767	0.9949
9.660	337.4	0.5220	0.9936
10.418	337.4	0.5772	0.9911
11.052	337.4	0.6300	0.9876
11.983	337.5	0.7185	0.9745
	av: 337.4		

The pressure was measured by a digital Heise pressure gauge (model 710A) which was calibrated against a Budenburg dead weight tester. The pressure measurements were estimated to be accurate within ±0.014 MPa. The temperature was determined by a thermistor inserted into the top side of the view cell. The thermistor was calibrated against a Fluke digital thermometer equipped with a platinum probe (model 2180 A). The temperature measurements were estimated to be accurate within ±0.1 K. Both wet test meters were factory calibrated with a stated accuracy of 0.5%. A Sartorius balance, model 1872, was used to measure the weight of alcohol condensate collected. The weight measurements were reproducible within

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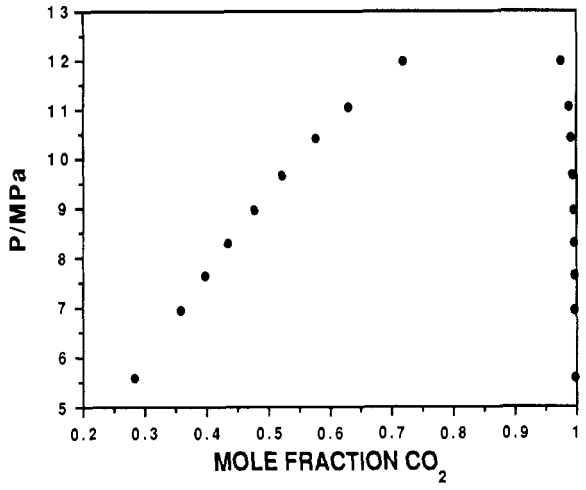

Figure 1. Vapor–liquid equilibria for CO_2 + 1-pentanol at 337.4 K.

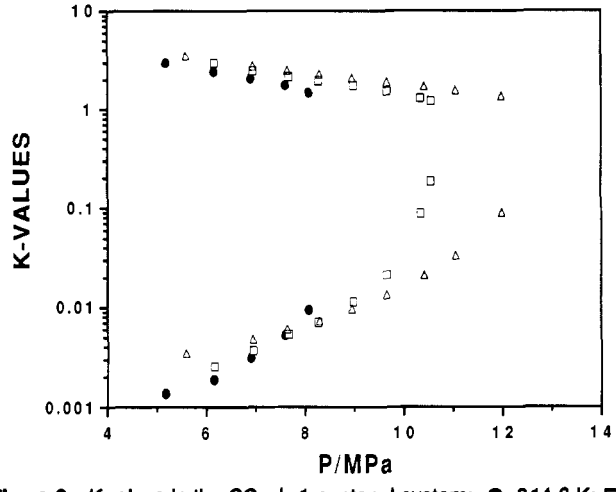

Figure 2. K values in the CO_2 + 1-pentanol system: ●, 314.6 K; □, 325.9 K; △, 337.4 K.

±0.0001 g, and the accuracy of the weight measurements was estimated to be within ±0.0010 g.

The pressure and temperature were recorded throughout the experiment to determine how "equilibrium conditions" were being maintained. The pressure fluctuations were generally less than ±0.024 MPa during an experiment. On the other hand, the temperature generally increased slightly from the first to the last sample, although this change was less than 0.3 K. The reported temperature is an average of the maximum and minimum temperatures recorded during the sampling period.

The reproducibility of the liquid-phase compositions was usually within ±0.001 mole fraction, and that of the vapor-phase compositions within ±0.0002 mole fraction. The liquid-phase compositions were estimated to be accurate within ±0.003, and the vapor-phase compositions within ±0.0006. These estimates are based on the accuracy and the precision of the instruments used in measuring the compositions, the reproducibility of the measurements, and comparisons with measurements of other investigators made in our earlier work (*1*).

Source and Purity of the Materials. Coleman grade carbon dioxide of minimum purity 99.99% was obtained from Matheson Gas Products. 1-Pentanol was obtained from Aldrich Chemicals and had a stated purity of 99+%. All substances were used without further purification.

Results

Vapor–liquid equilibrium data for CO_2 + 1-pentanol at 314.6, 325.9, and 337.4 K are presented in Table I. The data at 337.4 K are shown in Figure 1. The data exhibit phase behavior which is similar to that found for CO_2 + ethanol and CO_2 + 1-butanol systems in our earlier work. K values (y_i/x_i) for all three isotherms are shown in Figure 2.

Registry No. CO_2, 124-38-9; 1-pentanol, 71-41-0.

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