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High-pressure phase equilibria for the binary system carbon dioxide + benzyl alcohol

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ABSTRACT

The phase equilibria of the carbon dioxide + benzyl alcohol system were measured at 298.15, 306.35 and 313.15 K, under pressures from 1.03 to 16.15 MPa. An upper critical end point (UCEP) of the binary system was identified at 307.45 K and 7.77 MPa and three-phase equilibria were observed along the liquid–liquid–vapor (LLV) equilibrium line between 279.75 and 307.45 K. The experimental data were correlated well by the Peng–Robinson equation of state with two binary parameters. According to the experimental results, the phase behavior of the carbon dioxide + benzyl alcohol system appears to belong to Type-III according to the classification of van Konynenburg and Scott.

1. Introduction

Aromatic aldehydes are versatile intermediates for the production of pharmaceuticals, plastic additives, and perfumes, so the oxidation of an aromatic alcohol into its corresponding aldehyde is an important transformation [1,2]. However, a major drawback of such oxidation reactions is their lack of selectivity owing to the easy over-oxidation of aldehydes into carboxylic acids since aldehydes are more readily amenable to oxidation than aromatic alcohols.

In recent years, supercritical carbon dioxide, recognized as an environmentally benign solvent, has attracted much attention in oxidation of aromatic alcohols into aromatic aldehydes [3–10], for its advantages as reaction media, such as increasing mass transfer rates, simplifying post product-separation process, and tuning product selectivity by changing pressure. As the oxidation of benzyl alcohol was performed in supercritical carbon dioxide, the selectivity of benzaldehyde was improved greatly [11–13].

When supercritical carbon dioxide is employed as solvent in chemical reactions and separations that are conducted at high pressures and high temperatures, it is very important to understand the phase behavior for the significant influence on reaction rate, selectivity, mass transfer properties, etc. [14–16]. However, data on the phase behavior of carbon dioxide + benzyl alcohol system are limited in the literature. Vapor–liquid equilibrium phase compositions were measured for the binary system of benzyl alcohol with carbon dioxide at temperatures from 333.15 to 453.15 K and pressures up to 19 MPa by Chen and Lee [17], and at two temperatures of 308.2 K and 318.2 K and pressures up to 20 MPa by Chen et al. [18]. The phase behavior of carbon dioxide + benzyl alcohol system were also reported by Walther and Maurer at temperatures from 313 to 393 K and pressures up to 20 MPa [19]. Three-phase equilibrium data of carbon dioxide + benzyl alcohol system has not been reported in the literature. Furthermore, according to the six basic types of binary system classified by van Konynenburg and Scott [20], it has not been reported which phase type of carbon dioxide + benzyl alcohol system belongs to. Therefore, in order to verify the type of the binary system, in this work we have determined the phase behavior of carbon dioxide + benzyl alcohol binary system at high pressures up to 16.15 MPa and temperatures up to 313.15 K, including the three-phase equilibrium of the binary system. The Peng–Robinson equation of state (PR EoS) [21] was selected to correlate the measured phase behavior data of the carbon dioxide + benzyl alcohol binary mixtures.

2. Experimental

2.1. Materials

Carbon dioxide with a purity of 99.995% was supplied by the Beijing Haipu Company. Benzyl alcohol and ethyl alcohol were analytical grade purchased from Beijing Chemical Reagent Plant. Their purities were more than 99% and 99.8%, respectively. The purity of benzyl alcohol was confirmed by gas chromatograph, which

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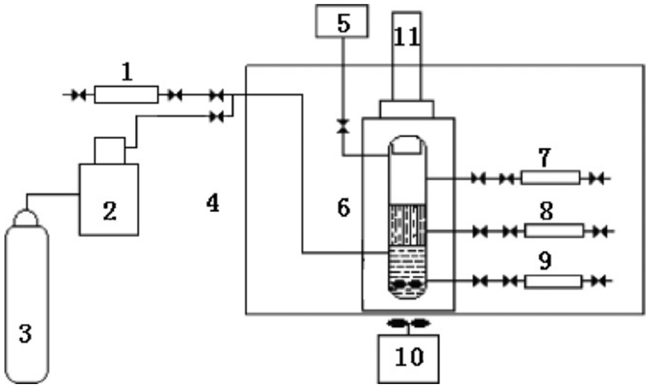

Fig. 1. Schematic diagram of the apparatus. 1, carbon dioxide bomb; 2, computer-controlled metering syringe pump; 3, carbon dioxide cylinder; 4, constant temperature water bath; 5, pressure gauge; 6, high pressure variable-volume view cell; 7–9, sampling tubes; 10, magnetic stirrer, and 11, piston.

showed that the purity was 99.6%; and its water content was 0.21% by a Karl Fischer analysis.

2.2. Apparatus and procedure

The schematic diagram of the apparatus is shown in Fig. 1. It consisted of a high pressure variable-volume view cell, a carbon dioxide cylinder, a constant temperature water bath, a pressure gauge, a computer-controlled metering syringe pump, a carbon dioxide bomb, two liquid sampling tubes, a vapor sampling tube, and a magnetic stirrer. The volume of the view cell could be changed from 23 to 50 cm^3 by moving the piston. The constant-temperature water bath was controlled by a temperature controller (A2, Beijing Changliu Scientific Instrument Company) and the temperature was controlled by a Pt resistance thermometer within ±0.1 K. The temperature was monitored by precision mercury thermometers that had a maximum uncertainty of ±0.05 K. The pressure gauge consisted of a pressure transducer and an indicator (Beijing Tianchen Instrument Company). Its uncertainty was ±0.025 MPa in the pressure range of 0–20 MPa, which was calibrated with a Heise standard pressure gauge before used.

The procedures were similar to those previously reported [22–25]. In a typical experiment, air in the view cell was removed by pure carbon dioxide through vacuum treatment, and then an amount of benzyl alcohol was charged into the view cell before it was sealed with the piston. During the charging process, a small amount of air may enter into the view cell. To remove the small amount of air in the view cell, carbon dioxide was introduced into the cell up to 0.4 MPa, and then the carbon dioxide was slowly released to atmospheric pressure, which process was repeated 3 times. Then, carbon dioxide was charged into the cell from a carbon dioxide pump or a carbon dioxide bomb to a desired amount. The view cell was then placed in the water bath, which was set at the desired temperature and the system was stirred. Equilibrium was reached when the system pressure and temperature were constant for an hour. After thermal equilibration, the phase behavior (1 phase, 2 phases, or 3 phases) could be observed clearly through the sapphire windows. To measure the concentration of each phase, then sampling from each phase was carried out. The valve of the sampling tube for sampling the bottom liquid phase was opened slowly to collect some samples. At the same time, the piston on the view cell was moved up or down to keep pressure of the system constant. The valve was closed after the sampling tube was filled with sample. Using the similar procedure, middle phase (if present) and top phase samples were collected, respectively. Then the sampling tubes were removed for composition analysis.

Table 1
Pure component parameters and binary parameters used in PR EoS and corresponding value of AARD for carbon dioxide + benzyl alcohol system.

Components	T_c (K)	P_c (MPa)	ω	k_{12}	l_{12}	AARD (%)
Carbon dioxide	304.2	7.38	0.225	0.25	0.16	6.5
Benzyl alcohol	681.7[a]	4.47[a]	0.653[a]			

[a] Calculated using the method reported by Joback and Reid [27].

The composition of a liquid sample was analyzed by gravimetric method. For the middle and top phase sample, the benzyl alcohol left in a sampling tube was washed into a desired volumetric flask using ethyl alcohol. Then the amount of benzyl alcohol in the sample was determined using UV–vis method as reported in the literature [26]. At the critical point, very strong opalescence was observed and the meniscus appeared at half-volume after a slight pressure reduction.

The uncertainty of the bubble point pressure, critical pressure, and dew point pressure is better than ±0.05 MPa, and that of the bubble point temperature, critical temperature, and dew point temperature is better than ±0.1 K. The reproducibility of the UV–vis analysis within one data series is 0.5–1.5%. The uncertainty of the measured mole fraction is estimated to be 3.4%.

3. Correlation

The PR EoS [21] with van der Waals mixing rules was used to calculate the vapor–liquid equilibrium data, which is expressed as

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

$$a = 0.457235\frac{R^2T_c^2}{P_c}\alpha \tag{2}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{3}$$

$$\alpha = \left[1+m\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{4}$$

$$m = 0.37464 + 1.54266\omega - 0.26922\omega^2 \tag{5}$$

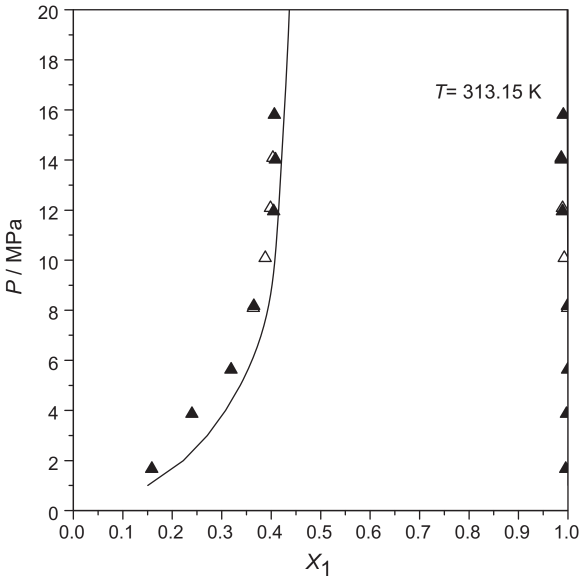

Fig. 2. Correlated and experimental phase transition pressure for the system carbon dioxide (1) + benzyl alcohol (2) at 313.15 K, experimental data (▲), literature data (△), and calculated results by PR EoS (lines).