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Compressed liquid densities and excess molar volumes for (CO_2 + 1-pentanol) binary system at temperatures from 313 to 363 K and pressures up to 25 MPa

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Abstract

Measurements of compressed liquid densities for 1-pentanol and for {CO_2 (1) + 1-pentanol (2)} system were carried out at temperatures from 313 K to 363 K and pressures up to 25 MPa. Densities were measured for binary mixtures at 10 different compositions, $x_1 = 0.0816$, 0.1347, 0.3624, 0.4651, 0.6054, 0.7274, 0.8067, 0.8573, 0.9216, and 0.9757. A vibrating tube densimeter was used to perform density measurements using two reference calibration fluids. The uncertainty is estimated to be better than $\pm 0.2\ kg \cdot m^{-3}$ for the experimental density measurements. For each mixture and for 1-pentanol, the experimental densities were correlated using an explicit volume equation of six parameters and an 11-parameter equation of state (EoS). Excess molar volumes were determined for the (CO_2 + 1-pentanol) system using 1-pentanol densities calculated from the 11-parameter EoS and CO_2 densities calculated from a multiparameter reference EoS.

Keywords: BWRS EoS; Carbon dioxide; Correlation; Density; Excess molar volumes; 1-Pentanol; Vibrating tube densimeter

1. Introduction

New phase equilibrium and volumetric properties of pure compounds and mixtures at high pressure are important for the design, simulation, and optimization of processes related to supercritical fluid extraction. (Carbon dioxide + alcohols) mixtures represent (supercritical + cosolvent) systems which are used in supercritical fluid technology. This work deals with the measurement of the volumetric properties of the binary system (CO_2 + 1-pentanol). A literature review has identified a gap in volumetric properties data for binary systems containing CO_2 and alcohols. In early works [1–3], the volumetric properties of of (CO2 + ethanol), 1-propanol, 2-propanol, and 1-hexanol were measured. However, density data were not found for the system (CO_2 + 1-pentanol). However, phase equilibria data for this system have been reported in the literature. Silva-Oliver *et al.* [4] have reported (vapor + liquid) equilibria for the system (CO_2 + 1-pentanol) at temperatures from 333.08 K to 426.86 K. Raessi *et al.* [5] measured critical endpoints for this system and they found that this system shows type IV fluid phase behavior. Staby and Mollerrup [6] reported results at temperatures from 283.2 K to 373.2 K. Jennings *et al.* [7] measured the (vapor + liquid) equilibria for (carbon dioxide + 1-pentanol) at temperatures from 314.6 K to 337.4 K. Lam *et al.* [8] reported liquid–liquid–vapor locus endpoints at low temperatures. Gurdial *et al.* [9] measured critical points for this system.

This work is a continuation of a project, whose main goal is performing systematic studies of (p,v,T) and phase

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equilibria for binary mixtures containing CO_2 and alcohols (from ethanol to decanol) in order to select the best operating conditions for industrial supercritical applications.

An apparatus based on the vibrating tube densimeter is used to study the (p,v,T) behavior of pure compound and binary mixtures [1–3]. The capability of this apparatus has previously been tested by measuring the density of diverse pure compounds and mixtures [10–12].

2. Experimental

2.1. Materials

1-Pentanol ($C_5H_{12}O$, $M = 88.15\ g \cdot mol^{-1}$, CAS-RN: 71-41-0) is from Aldrich (USA) with a stated purity better than 99 mol%. Carbon dioxide (CO_2, $M = 44.01\ g \cdot mol^{-1}$, CAS-RN: 124-38-9) is supplied by Infra Air Products (México) with a certified purity of 99.995 mol%. Reference fluids for the calibration of the densimeter are water (H_2O, $M = 18.02\ g \cdot mol^{-1}$, CAS-RN: 7732-18-5) and nitrogen (N_2, $M = 28.01\ g \cdot mol^{-1}$, CAS-RN: 7727-37-9). Water (HPLC grade, >99.95 mol%) is from Aldrich (USA), and nitrogen (chromatographic grade, 99.995 vol%) is from Infra Air Products (México).

In order to remove any residual moisture, 1-pentanol was stored over 3 Å molecular sieves. The purity of 1-pentanol samples was tested using a gas chromatograph (HP 5890 Series II) fitted with a flame ionization detector (FID) and a packed column. The verified purity of 1-pentanol was better than 99.1 mol%. Water and 1-pentanol were degassed under vacuum and vigorously stirred before they were used.

2.2. Apparatus and procedures

The experimental apparatus has been described previously [1–3,10–12]. A diagram of the experimental apparatus is shown in figure 1. It is based on a vibrating tube densimeter (VTD). An Anton Paar DMA 512P VTD was used to determine the density. The full range in temperature is 263.15 K to 423.15 K and in pressure it is 0 MPa to 70 MPa. The VTD (Hastelloy C-276 U-tube) containing a sample of approximately 1 cm^3 is filled by means of a sapphire tube cell (ST), which allows measurements up to 25 MPa. The density values of the fluid under study are obtained from the periods of oscillation of the vibrating tube and this was calibrated using water and nitrogen as reference fluids [1–3]. Pressure measurements are made inside the sapphire tube cell using a pressure transducer (PT) (Sedeme 250, France). The pressure transducer was thermoregulated at a specific temperature value and is calibrated periodically. Three platinum probes (PTP*i*) (Specitec, France) located in the top and bottom of the cell and inserted in the VTD are used for temperature measurements. The VTD is thermoregulated using a circulation liquid bath (LB) with water as the thermal fluid.

The experimental procedure used here has been previously described by Galicia-Luna *et al.* [13] and Zúñiga-Mor-

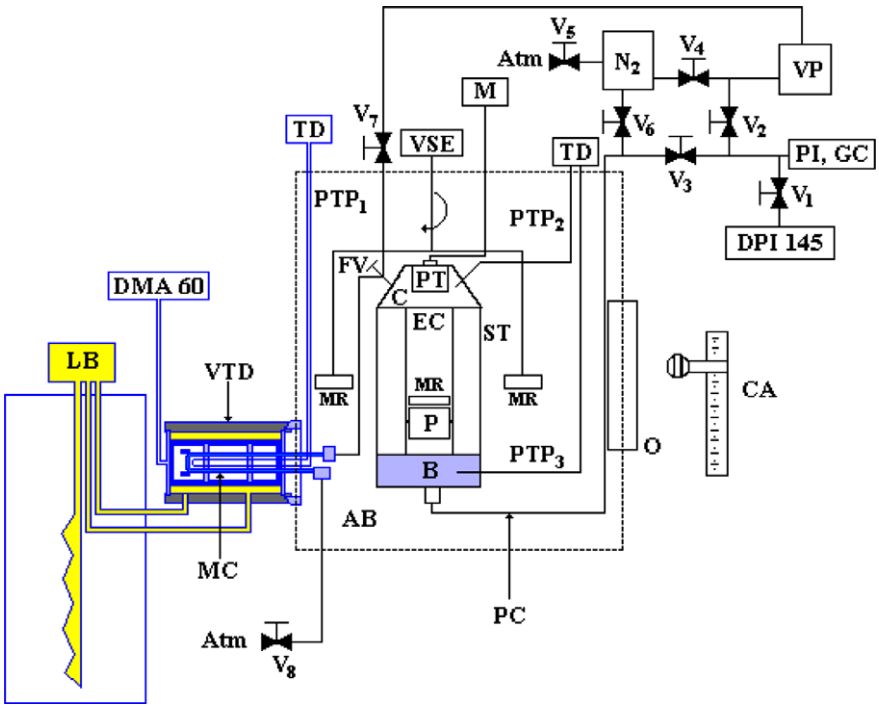

FIGURE 1. Schematic flow diagram of the experimental apparatus: AB air bath, CA cathetometer, DMA 60 period meter, DPI 145 digital indicator of pressure, EC sapphire tube equilibrium cell, GC gas compressor, PI Isco pump, LB liquid bath, VTD vibrating tube densitometer, MC measurement cell, MR magnetic rod, PT pressure transducer, M multimeter, PTP*i* platinum probe *i*, TD digital indicator of temperature F250, V*i* shut-off valve *i*, VSE variable speed engine, VP vacuum pump, FV feeding valve, P piston, ST, sapphire tube, B cylindrical support, C cap, PC pressurization circuit, O window.