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High-pressure density and vapor–liquid equilibrium for the binary systems carbon dioxide–ethanol, carbon dioxide–acetone and carbon dioxide–dichloromethane

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Abstract

An apparatus for the measurement of vapor–liquid equilibrium (VLE, *P–T–x*) data and density of saturated-liquid and high-pressure liquid phase of compressed gas-organic solvent systems was designed, built and tested. A synthetic method, with recirculation of the liquid phase through a high-pressure densimeter by a magnetic driven centrifugal pump, was used. The thermodynamic equilibrium was reached in a visual cell with variable volume ranging between 30 and 60 cm^3. The compositions of the phases were evaluated by external gravimetric method.

The estimated accuracy of the measured data was ±0.02 K for temperature, ±0.05 MPa for pressure, ±0.005 in mole fraction for liquid compositions and ±0.05 g/L for liquid density. Vapor–liquid equilibrium data and saturated-liquid density were obtained for the following systems: carbon dioxide–ethanol and carbon dioxide–acetone at 291.15, 303.15, 313.15 and 323.15 K and carbon dioxide–dichloromethane at 291.15, 303.15 and 311.15 K. For the latter system, high-pressure liquid density data were measured up to 18 MPa. The experimental data were correlated by both Peng–Robinson and SAFT equation of state. SAFT EOS gives better correlations of vapor–liquid data and accurate predictions of high-pressure density of the liquid phase.

Keywords: Experimental data; Vapor–liquid equilibrium; Density; Carbon dioxide; Ethanol; Acetone; Dichloromethane; SAFT

1. Introduction

Supercritical fluid processes are merging as important alternative to conventional methods in many of fields, such as extraction, particle micronization, material processing, chromatography or crystallization/purification [1]. Equilibrium and volumetric properties of binary mixtures containing organic solvent and supercritical fluids (especially carbon dioxide) play an fundamental role in determining the success of many of these applications. In particular, vapor–liquid equilibria and liquid density are necessary data for properly design gas antisolvent precipitation/recrystallization processes. This technique was successfully applied for production of micro- and nano-particulate powder for pharmaceutical, biomedical, cosmetic, alimentary or electronic application [2–4]. Even if a number of carbon dioxide–organic solvent system are already reported in open literature [5–9] there is still a lacking of experimental equilibrium and density data, especially for dichloromethane, that is one of the most used solvent for production of poly(lactide acid) and poly(lactide glicolide) biodegradable micro-particles [4–10]. In addition, despite density data are important to establish solute precipitation [11] and to determine the swelling and shrinking regime in the mass transfer simulation [12–13] of gas anti-solvent process, density data published for carbon dioxide–organic solvent binary systems are scarce and controversy.

In this work, vapor–liquid equilibrium and saturated-liquid density were measured for two well known systems carbon dioxide–ethanol and carbon dioxide–acetone at 291.15, 303.15, 313.15 and 323.15 K. Vapor–liquid equilibrium and high-pressure liquid density were measured for carbon dioxide–dichloromethane at 291.15, 303.15 and 311.15 K. These temperatures are close to that typically used in gas antisolvent processes [10].

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2. Experimental

Ethanol (purity better than 99.8% mass fraction), acetone (purity better than 99.9% mass fraction) and dichloromethane (purity better than 99.9% mass fraction) were supplied by Sigma–Aldrich (Milano, Italy). 99.998% purity CO_2 was provided by Sapio (Padova, Italy). The organic solvent samples were saturated with CO_2 by fluxing the gas at room temperature and pressure for 1 h. They were used without further purification.

2.1. VLE apparatus

Fig. 1 shows a schematic representation of the VLE apparatus. A vapor–liquid equilibrium (VLE) cell with variable volume (NWA, Lorrach, Germany) was made of stainless steel (corresponding to AISI316) and equipped with two sapphire windows for observing the sample during measurements. O-rings were used to seal the glass windows onto the stainless steel body of the VLE cell. The rear window can be moved by an accurate external hydraulic pressurization systems. The internal VLE cell volume can be varied between 60 and 30 cm^3 with a precision of 0.05 cm^3.

The apparatus is equipped with a recirculation loop for the liquid phase in order to ensure both intensive mixing and measurement of liquid density. Magnetic driven centrifugal pump, appositely designed for this apparatus, ensures a circulation of about 50 cm^3/min of liquid phase and generated 0.050 kPa hydraulic charge. 1/8 in. stainless steel tubes (Nordival, Erbusco, Italy) were used. In order to eliminate stagnant zone and reduce the internal volumes of the recirculation loop special connector was design for the manometer.

Three-way valve (Swagelok, Milan, Italy), located at the bottom of the apparatus, enables the closure of the recirculation loop and to isolate the equilibrium cell during the sample addition to the VLE cell.

The VLE cell and the recirculation loop were fully immersed in a glass thermostatic vessel of about 0.03 m^3 capacity. Mixing is ensured by a submerge centrifugal pump with 40 L/min flow rate. The density was measured by a densimeter (Anton-Paar, Grazz, Austria) placed outside on the thermostat and connected by well insulated 1/8 in. stainless steel tube. The densimeter is equipped with an internal temperature sensor.

The magnetic pump was designed and made by the mechanical laboratory of Department of Chemical Engineering of University of Padova, Italy.

2.2. Measurement and control of temperature, pressure and density

The VLE cell and the recirculation loop was immersed in a thermostatic bath that enabled the temperature to be stabilized within ±0.01 K throughout the measurements. Temperature control was achieved by a PID-controller (Lauda, Genova, Italy) governing a heating element immersed in the thermostatic bath. Temperature was measured by means of a calibrated PT100Ω resistance thermometer connected to a

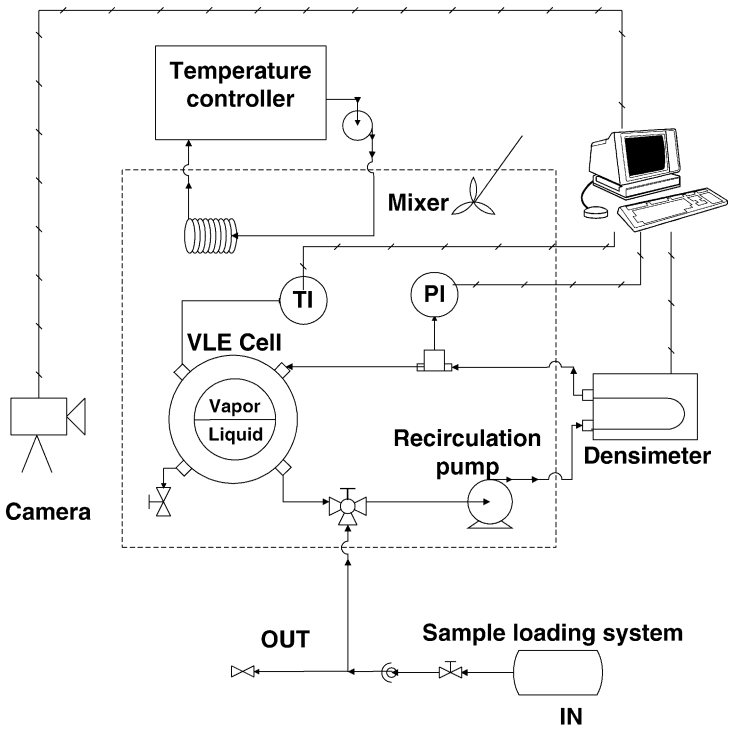

Fig. 1. Schematic diagram of the apparatus. Broken line contains the thermostated apparatus components.