

Near infrared spectroscopy applied for high-pressure phase behavior measurements



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ABSTRACT

This work presents a new technique for phase behavior monitoring at high-pressure conditions. The consolidated synthetic method was modified by insertion of a near infrared probe inside the high-pressure variable-volume view cell. A system composed by carbon dioxide and a distilled petroleum fraction was used to validate the proposed methodology. The experiments were performed in the temperature range of 293–333 K, carbon dioxide mass fraction of 0.350–0.900 and pressures up to 20 MPa. The phase transitions pressures visually observed were compared with those detected by the spectrophotometer and good correlations were obtained with global mean deviation of 1.4%. Besides, it was possible to identify the type of vapor–liquid phase transitions (bubble or dew points) and the position at diagram (before or after the critical concentration) for the liquid–liquid equilibrium. The proposed methodology is promptly extended to several others systems.

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1. Introduction

The measurement of experimental data at high pressure conditions is a fundamental step for the understanding the phenomena that occur at high pressures. This information is essential for the design and optimization of high-pressure chemical processes, separation operations [1], and for the efficient modeling and simulation of thermodynamic behavior and phase diagrams at high pressure [2]. Normally, the selection of the experimental technique is based on the system characteristics, such as the chemical nature and physical properties of mixture, range of pressure and temperature, and type of equilibrium data to be investigated.

According to a review series of Dohrn and coworkers [1,3–5], the experimental methods available in the literature for the investigation of high-pressure phase equilibria can be divided in two main classes: analytical methods and synthetic methods. The classification depends on how the compositions of the equilibrium phases are determined (analytically or not) and whether the mixture has been prepared (synthesized) with precisely known composition or not. A detailed description of these methods, advantages, chal-

lenges, measurement principles, and error sources can be found elsewhere [6].

The use of high pressures variable volume view cells, based on synthetic methods, can be considered the simplest method to obtain phase equilibria data at high pressures. Different research groups [7–9], including our own group, have used this methodology in previous works [10,11]. Synthetic methods make use of a mixture whose composition is precisely known. Small high-pressure cells can be used, because no sampling is necessary and the methodology can be applied with or without phase transitions. This method can be applied in cases where phase separation is hard due to similar densities values (close to or even at critical points). For multi-component mixtures, experiments with synthetic methods provide less information than the analytical methods, and are generally used for binary or pseudo-binary systems [1,6].

However, the available methods for high pressure phase equilibria measurements are not sufficiently robust to access all phenomena that can occur when mixtures of different chemical classes are submitted to high pressures conditions. An ideal device should provide information about the number of phases present in the pressurized system, its individual compositions, densities, volume and physical properties, accurately and simultaneously, in a wide range of pressures, temperatures and compositions in a single experimental run. In the class of analytical methods, the use

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of special samplers, which are able to take small samples from the pressurized system, and quickly direct to the column of the chromatograph, has contributed to decrease the problems regarding to equilibrium system perturbation [12,13]. When the analysis is performed in situ (without sampling) different spectroscopic methods as ultraviolet, [14,15] infrared, [14,16,17] fluorescence, [14] Raman, [18–21] and NIR [22–25] have been used. In these cases, the advantage of avoiding the trouble with taking samples is often replaced by the need of time consuming on calibrations and signal evaluation at high pressures [1,5,6].

In the class of synthetic methods, automated high pressure variable volume view cell totally has been proposed for phase behavior measurements of a mixture composed by a synthetic crude oil and carbon dioxide [26]. According to the authors, the experimental apparatus allows a precise control of the system composition, pressurized mixture volume and visual observations of the different phase transitions. The apparatus was validated by reproduction of the literature data, and showed applicability in the temperature range of 298–423 K and at pressures up to 36 MPa.

Following this trend of development and optimization of methods for phase behavior studies at high pressure conditions, in this work is proposed a “hybrid method” where a near infrared probe (analytical method) is coupled to a high-pressure variable-volume view cell. Our goal was merge the advantages of different methods in a single apparatus. This is especially important when the system under investigation presents visually undefined phase transitions (near critical point, for example) or opaque coloration, which limits the use of the most synthetic methods currently available. It was demonstrated that the NIR spectrophotometer can be applied for the identification of phase transition pressures and also to distinguish the phase transition type for a complex system without previous calibration.

2. Experimental

2.1. Materials

Carbon dioxide (White Martins, 99.9%) was used as solvent in all experiments. The solute was composed by a hydrocarbon fraction (HF) obtained by distillation of Brazilian petroleum at 543 K and vacuum pressures of 0.01 MPa. The distilled fraction shows a light yellow color, density at 298 K of 0.8230 g cm^{-3} (determined in a Anton Paar DMA 4500 M digital densimeter), and normal ebullition temperature of 569 K. This system was selected it presents different types of phase transitions as vapor-liquid equilibria (bubble and dew points), liquid-liquid equilibria and vapor-liquid-liquid equilibria. In this sense, the apparatus and methodology was tested for the most common types of high pressure phase transitions found in real process.

2.2. Proposed phase equilibrium apparatus and procedure

The experimental apparatus is schematically depicted in Fig. 1. Near infrared spectroscopy (NIR) was employed for the phase transitions identification in the pressurized system. The apparatus consisted of a high-pressure variable-volume view cell with internal volume of 28 cm^3 , equipped with frontal and lateral sapphire windows to visualize the system under pressure. A piston inside the cell was used to control the system pressure with the help of the syringe pump (Teledyne ISCO, 260D). Pressure and temperature monitoring were performed with a pressure transducer (Novus, TP HUBA 691, with a precision better than 0.005 MPa) and a J type thermocouple (Salcas, with a precision better than 0.5 K), respectively. A magnetic bar inside the cell provides intense stirring, allowing homogeneity to the investigated mixture. The cell was embedded

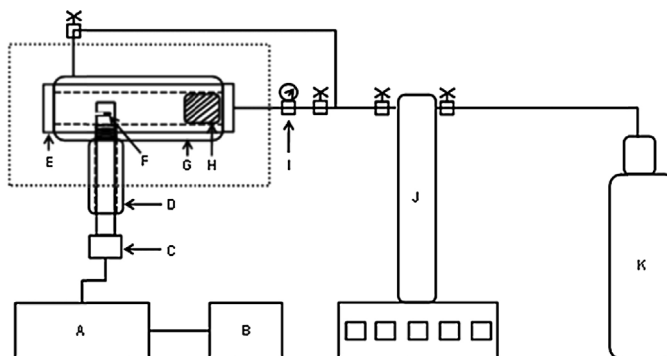


Fig. 1. Schematic of the experimental apparatus: A) NIR spectrophotometer; B) Personal computer; C) NIR probe; D) NIR probe support; E) Sapphire window; F) Optical pathlength; G) High-pressure variable-volume view cell; H) Movable piston; I) Pressure transducer; J) Syringe pump and K) CO₂ cylinder.

into an aluminum block with internal paths connected to a circulation water bath (Julabo, ED) for temperature control.

A near infrared probe for transreflectance measurements with 1.0 mm of optical pathlength (Solvias) was connected to the cell. The optical pathlength was positioned inside the cell, allowing the monitoring of the phase transition phenomena in-situ. The pressure and temperature operation when the NIR probe was connected to the high-pressure cell was limited to 20 MPa and 473 K, respectively, in function of the characteristics of the near probe. The NIR probe could be positioned in any direction, horizontal or vertical, but for convenience the horizontal position was more indicated. Independent of the cell position, NIR probe was fixed perpendicularly to the cell, as depicted in Fig. 1. The experimental apparatus was tested against pressure and temperature gradients (by checking pressure and temperature in both sides of the piston). The system was continuously stirred during the depressurization, lowering any composition gradients into the cell. Thus, the NIR spectra collected inside the cell may represent the fully system.

NIR spectra were collected with an in-line FT-NIR spectrophotometer (ABB Bomem model FTLA-2000-160D), configured to scan the spectral region ranging from $10,000$ to 4000 cm^{-1} (1000 to 2500 nm) with a resolution of 4 cm^{-1} in absorbance mode, according to previously described [27].

2.3. Experimental procedure

The general experimental procedure was similar to those widely reported in the literature for phase equilibrium measurements using the static synthetic method [28–32], with the addition of NIR spectra recording during the depressurization of the system. Firstly, precise quantities of solute (hydrocarbon fraction) was weighed on a precision scale balance (Shimadzu, AX 200, $\pm 0.0001 \text{ g}$) and added into the high-pressure cell. In the sequence, an amount CO₂ was loaded into the equilibrium cell by means of the syringe pump, enabling an accuracy of $\pm 0.005 \text{ g}$ in carbon dioxide loadings. When a specific global composition is attained, the cell charge is continuously agitated by a magnetic stirrer and a Teflon-coated stirring bar. Then, the temperature control system is programmed to the desired temperature ($\pm 0.5 \text{ K}$), and the pressure system was increased until the visualization of a one-phase system in the cell. At this point, the system is kept at least 20 min to allow stabilization. NIR spectra were captured regularly to check alterations in the baseline and/or in the peaks intensity. If no alterations are detected in the spectra, the pressure is slowly decreased (typically at a rate of 0.10 – $0.30 \text{ MPa min}^{-1}$). NIR spectra were captured for each 0.10 MPa during the depressurization until the formation of a new phase. This procedure was repeated at least three times for

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