Synthetic methods in phase equilibria: A new apparatus and error analysis of the method

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ABSTRACT

A new apparatus for the study of high-pressure phase equilibria using a synthetic method is described. The apparatus was especially developed for the study of solubilities of gases in condensed phases, at temperatures ranging from 243 K to 353 K and pressures up to 20 MPa. The quality of the equipment was confirmed through several tests, including measurements along the three phase co-existence line for the system ethane + methanol, the study of the solubility of methane in water, and of carbon dioxide in water.

An analysis regarding the application of the synthetic isothermal method in the study of gas solubilities was performed, in order to evaluate the influence of common assumptions and of various experimental aspects on the final solubility results. The analysis revealed that the largest influence on the precision of the solubility results is related to the ratio between the volumes of the two phases in equilibrium. Experiments with small volume of the vapour phase are less susceptible to the influence of other sources of errors, resulting in a higher precision of the final results.

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1. Introduction

The importance of phase equilibria for the design and optimisation of chemical and separation processes has been previously emphasised [1,2], and the importance of reliable and precise experimental phase equilibrium data is unanimously recognised by both the scientific community and by industry [3]. However a high-quality apparatus is not necessarily a guarantee for high-quality results. An understanding of the different methods and of the respective error sources is crucial. Experience and know-how are essential, since experimental problems and mistakes are seldom published. A survey of the European Federation of Chemical Engineering on industrial needs for thermodynamics and transport properties [4] showed that there is a clear need for qualified laboratories with experienced staff to provide experimental measurements.

Experimental methods for the measurement of high pressure phase equilibria can be classified as analytical or synthetic methods, depending on whether the compositions of the equilibrium phases are determined based in the analysis of the phases or a mixture with a precisely known composition is prepared (synthesised) [2,5–8].

While analytical methods are useful for the study of complex multi-component systems, eventually allowing a complete characterisation of all the phases in equilibrium, their application requires apparatus of higher complexity and the development of an analytical method. Also important are the problems normally associated with sampling from high-pressure cells [1,9].

Synthetic methods require simpler (and less expensive) apparatus, useful mainly for the study of binary or pseudo-binary systems. The popularity of these methods has increased over the last decade, as shown in recent reviews [5,6]. From more than 2500 systems reviewed for the period 2005–2008 [5], almost two thirds (63%) were studied using a synthetic method. Methods where the appearance of a new phase is detected are common, for example, in the determination of conditions for hydrate formation. Synthetic isothermal methods, also called "pressure decay" methods, are commonly used in studies of gas solubilities in non-volatile substances, such as polymers [10–12], oils [13], ionic liquids [14–16], or in aqueous solutions [17,18]. In this method, the calculation of the phase equilibria is based on a mass balance. A precisely known amount of gas is added to a previously evacuated cell containing the condensed phase. The pressure in the cell increases with the addition of the gas, decreasing subsequently as the gas dissolves in the condensed phase, eventually reaching an equilibrium value. Based on the volumes and densities of the phases, the solubility of the gas can be calculated. A new addition of gas will lead to a new equilibrium point corresponding to a different global composition.

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The complexity of the mass balance depends on the approximations used, e.g.: the composition of the gas phase can be considered as pure gas if the vapour pressure of the condensed phase is negligible. Alternatively, the gas phase composition can be estimated assuming an ideal gas mixture, or modelled using an equation of state. Another important aspect is the variation of the volume of the phases, especially in the case of high solubilities where the volume of the condensed phase can vary significantly as the gas dissolves into it. The volume of the phases in equilibrium can be observed visually with a view-cell, or be estimated considering an ideal system if the liquid density of the gaseous substance is known. In cases of very low solubility, the volume of the condensed phase can be assumed to remain constant throughout the experiment.

These approximations, as well as other experimental details often not mentioned in the literature (such as the ratio between the volumes of the two phases) can influence the quality of the results. It is therefore relevant to make an analysis of these influences, so that optimal experimental conditions can be selected when performing the measurements and errors can be avoided during calculations.

In this work, a new apparatus using a synthetic isothermal method is presented, together with results obtained in the study of well-known systems, which confirm the quality of the set-up. In addition, the influence of experimental conditions and simplifications on the final results when using the synthetic isothermal method is analysed in detail through selected case-studies.

2. Experimental

2.1. The new apparatus

A new experimental set-up for the measurement of phase equilibria at temperatures ranging from 243 K to 353 K and pressures up to 20 MPa was developed, making use of the synthetic isothermal method. A schematic representation of the apparatus is presented in Fig. 1.

The central part of the apparatus is a high-pressure view-cell, originally built by Top Industrie, France, with an internal volume around 570 cm^3 and equipped with two parallel sapphire windows. The cell was originally used in an apparatus based on an analytical method using a moveable needle to sample from different phases, as described by Laursen [19]. Viton O-rings guarantee the sealing between the lid and the body of the cell, and between the body of the cell and the sapphire windows. The airtightness of the original cell was improved by redesigning and building a new lid for the cell, with fewer connections, and by substituting the existing stirring motor by a magnetic system. A scale was added to one of the sapphire windows, which after calibration, allows the determination of the volume occupied by each of the phases.

The cell is placed inside a temperature chamber WTB Binder MK 720 (BINDER GmbH, Germany), suitable for applications in the temperature range from 233 K to 423 K. According to preliminary tests, the temperature stability of the cell is better than 0.01 K.

The temperature of the cell is monitored with a precision of 0.01 K through two platinum resistance thermometers Pt100 (class 1/10 DIN) calibrated in accordance with the International Temperature Scale ITS-90 at the triple point of water. These thermometers are positioned at opposite sides of the cell, in cavities inside its thick wall, and are connected to a computer for monitoring and recording of the experimental conditions through a data acquisition system Agilent 34970A (Agilent Technologies Inc., USA). The pressure inside the cell is monitored by a digital temperature compensated pressure transmitter Keller 33X (KELLER AG, Switzerland), for measurements up to 20 MPa with an accuracy of 0.1% FS (0.02 MPa). The zero of the sensor was adjusted against a Crouzet quartz mano 2100,

Table 1
List of compounds used in this work and respective values of mass fraction purity.

Chemical name	Source	Mass fraction purity
Ethane	AGA Gas AB, Sweden	0.9995
Carbon dioxide	Linde AG, Germany	0.99995
Methane	Linde Gas UK Ltd, UK	0.999995
Methanol	Merck KGaA, Germany	0.998

calibrated by Buhl & Bønsøe A/S, a company accredited by DANAK, The Danish Accreditation and Metrology Fund.

In order to ensure that the system reaches equilibrium rapidly, a commercial magnetic stirrer is placed under the cell. The stirrer was adapted so that it can be controlled remotely from outside the temperature chamber. A video camera already used in the apparatus described by Laursen [19] is conveniently placed in front of one of the sapphire windows and connected to a video monitor, for observation of the interior of the cell with the aid of an external cold light source Schott KL 200 LED (Schott AG, Germany) connected to an optical fibre.

2.2. Chemicals

In order to confirm the quality of the results provided by the new apparatus, different tests were performed. A first series of tests focused on the quality of the temperature and pressure measurements. The vapour–liquid equilibrium line for carbon dioxide was studied and the results compared with literature. Measurements were also performed along the three-phase coexisting line for the binary system methanol + ethane.

The performance of the apparatus and of the experimental method in the study of gas solubilities was verified through the study of the solubility of methane in water and of carbon dioxide in water.

A list of the compounds used in this work is given in Table 1, together with the respective values of their mass fraction purity. All compounds were used as received, without further purification. Milli-Q deionised water was used in the solubility studies.

3. Results

In order to test the quality of the temperature and pressure measurements, the vapour–liquid equilibrium line of pure carbon dioxide was studied at temperatures between 258 K and 300 K. A total of 17 equilibrium points were measured, and the results compared with the reference equation recommended by the DIPPR database [20]. This reference equation is based on experimental data with an estimated error estimated to be less than 1%. The deviations of the results obtained in this work relatively to the reference equation were below 0.8% for all the experimental points.

Equilibrium measurements were also performed along the three phase (vapour–liquid–liquid) co-existence line for the system ethane + methanol, at temperatures between 263 K and 300 K and pressures between 1.8 MPa and 4.3 MPa. The results, given in Table 2, were compared with the available literature [21–26] as presented in Fig. 2, where the reference line was calculated from the values of Zeck and Knapp [26]. The results obtained in this work are in excellent agreement with most of the literature, namely with the values of Brunner [21], Ishihara et al. [22], and the values of Zeck and Knapp [26]. The deviations from the reference for all the points are below 0.5%.

In order to evaluate the performance of the apparatus and of the experimental method in the study of gas solubilities, the solubilities of methane and of carbon dioxide in water were determined at different temperatures.