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Measurement of vapor–liquid–liquid phase equilibrium—Equipment and results

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ABSTRACT

There exists a need for new accurate and reliable experimental data, preferably with full characterization of all the phases present in equilibrium. The need for high-quality experimental phase equilibrium data is the case for the chemical industry in general. All areas deal with processes whose optimization is dependent on phase equilibrium data.

The objective of this work is to provide experimental data for hydrocarbon systems with polar chemicals such as alcohols, glycols and water. A new experimental equipment was designed and constructed for measurement of multi-phase equilibrium in hydrocarbon–water–gas hydrate inhibitor systems, at temperatures ranging from 283 to 353 K and at pressures up to 40 MPa. The core of the equipment is an equilibrium cell, equipped with sapphire windows and connected to an analytical system by capillary samplers.

New vapor–liquid–liquid equilibrium data are reported for methane + *n*-hexane + methanol + water at 296.2 K and pressures of 6 to 10 MPa. The Cubic-Plus-Association (CPA) equation of state is used to model the phase equilibria data measured. A good agreement between predictions and experimental data is observed, supporting the reliability of the new data.

1. Introduction

As the deep water oil and gas exploration is continuously increasing, the complex phase behavior involving petroleum fluids and polar chemicals such as water, methanol or glycols has gained increasing attention. Vast quantities of the so-called "production chemicals" are introduced to the petroleum systems, in order to facilitate production from reservoirs and transport in pipelines. Examples of such chemicals are hydrate inhibitors, such as methanol or glycols, which are injected to the natural gas well stream, in order to prevent the formation of gas hydrates during transportation and further processing. The trend towards long distance multiphase flow pipelines, which are based on the seabed, increases the need for accurate calculations of mixtures containing water, an inhibitor, a gas phase and a condensed phase.

Compounds like methanol or ethylene glycol are good thermodynamic inhibitors, lowering the temperature of hydrate formation for a given pressure. However, a tendency in the use of hydrate inhibitors has gone in the direction of applying considerable safety margins, with an excess of inhibitors being regularly used in the processes, with economic and environmental consequences. This is largely due to the occurrence of problems with the formation of hydrates under conditions in which problem-free operation would be expected, especially in places of peaks of flow such as choke valves.

This increase in production chemicals is not only due to the fact that new fields are brought to production. But also due to the new solutions which have been applied, for instance the use of methanol for multiphase well stream transport from subsea wells. In addition mature fields (e.g. Gullfaks and Statfjord in the North Sea) have increased needs for chemical based treatments like well treatment or water treatment [1].

Despite the overwhelming importance of experimental data, reliable and precise measurements can be difficult to achieve and are often expensive and relatively slow, representing a serious investment, not only concerning the acquisition of equipment or the development of custom-made experimental set-ups, but also regarding human resources. Another serious problem is the existence of experimental data of dubious quality.

It is important to know the distribution of production chemicals in oil, water and gas streams because it is a key to the calculation of the amounts of chemicals required for a specific facility. It is

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Table 1
List of compounds used with mass purity and suppliers.

Chemical name	Supplier	Mass fraction purity
Methane	Linde gas UK	≥0.99
Methanol	Merck KGaA, Germany	≥0.99
n-Hexane	Sigma-Aldrich, Germany	≥0.99

also important information to fulfill the demand from the environmental perspective in order to know the amount of chemicals and hydrocarbons (HC) in a processed water stream for ensuring minimal impact on marine life. Furthermore, it is important for design and operation of separation equipment as well as to report the chemicals and water contents of fuel oil which may be crucial for downstream processing [2,3].

The distribution of the chemicals can either be measured experimentally or predicted using a suitable thermodynamic model. The experimental method is expensive and challenging, partly due to the difficulties involved in measurements of such low solubility data. An evidence for this is the scarcity of such experimental data in the literature.

This work sets out to provide a modest yet solid contribution to bridging the gaps in experimental data, not only by measuring new data, but by developing new experimental equipment for the study of phase equilibrium through the use of different methods.

Parallel to the experimental work, the Cubic Plus Association (CPA) equation of state (EoS) proposed by Kontogeorgis et al. [4], which has been shown previously to be a suitable model for such mixtures [5], was used in the modeling of mixtures containing hydrocarbons, water and thermodynamic hydrate inhibitors. Such systems, containing associating compounds, are challenging from a theoretical point of view since the components form hydrogen bonds and often exhibit an unusual thermodynamic behavior.

2. Experimental

The experimental work has been carried out at Center for Energy Recourses Engineering (CERE) at the Department of Chemical and Biochemical Engineering of The Technical University of Denmark, where an analytical isothermal cell was used. The experimental set-up was designed for measurement of multi-phase equilibrium in hydrocarbon–water–gas hydrate inhibitor systems, at temperatures ranging from 283 to 353 K and at pressures up to 40 MPa.

Purities and suppliers of chemicals are presented in Table 1. No further purifications were made.

2.1. The experimental equipment

The main part of the equipment is the high-pressure equilibrium cell, specially designed for this application. The cell is fitted with sapphire windows in each end, which allow for viewing of all phases and any phenomena appearing during experiments. The temperature, measured by platinum resistance thermometers, is monitored and recorded over time through a computer. The equilibrium cell is situated in a liquid bath (water or glycol dependent on temperature range), where the temperature is regulated by external liquid circulation thermostat, enabling temperature to be held constant within 0.5 K. The body of the cell is presented as a schematic in Fig. 1.

The cell is in stainless steel, which is fitted with sapphire windows in each end. The inner diameter of the cell is 25 mm. The sapphire windows have a thickness of 30 mm and it was dimensioned according to the properties of the material provided by the supplier, to cope with pressures of 30 MPa for extended periods of time, but also to pass the safety tests imposed by the internal rules at the department, according to which, the cell had to be tested for a pressure of approximately 140% of the maximum operating pressure (28 MPa). The synthetic sapphire single crystal (Al_2O_3, 99.9%) was acquired from Encole LLC, USA, with a polishing better than 0.1 μm Ra (the average radius of the irregularities or cavities in the surface is inferior 0.1 μm).

An important part of the equilibrium cell, is the possibility of proper stirring of the mixture. The stirring should be powerful enough, so that all phases (vapor–liquid–liquid) get mixed properly and chemical equilibrium is achieved. The stirring is done using powerful magnets from Supermagnete, Germany. A winged axis is placed within the cell, situated in a small sapphire bearing in the center of each sapphire window, which can be seen in Figs. 1 and 2. The axis is powered by a magnetic belt, which is fitted on the outside of the cell, similar fitted with high powered magnets. The principal idea is that the magnetic belt turns the axis within the cell, without any direct contact, since the magnets are powerful enough, to work through the thick stainless steel cell. Drawings showing the schematic representation of the cell are presented in Fig. 2.

The equilibrium cell is fitted with two automatic electromagnetic capillary ROLSI^{TM} samplers [6,7], a product developed by the CENERG-TEP laboratory of the ENSMP (École Nationale Supérieure des Mines de Paris), with patents registered to Armines (PCT patent 2004/090508, PCT patent 2000/011462, EPO patent EP 1105722) and commercialized by Transvalor, France.

Developed specifically for the purpose of phase equilibria studies, the ROLSI^{TM} samplers have been established as a reference worldwide, being currently used in many universities as well as in industry. In many research groups they are considered as a reference for phase equilibrium and petroleum related studies [8–15]. These sampler-injectors are electromagnetic valves that allow samples to be taken from each of the phases without disturbing the phases in equilibrium, and vaporizing the liquid ones directly to the carrier gas stream of a gas chromatograph, without any manipulation of the samples.

The gas chromatograph used for the experimental set-up is a PR2100 GC System (Alpha Mos, France). The GC is equipped with a RTX1 capillary column (This can be changed to Packed column Shincarbon ST 80/100 or Column RTX-WAX, dependent on the experimental needs). It is important to notice, that optimizing the gas chromatograph with regards to components (Column type), pressure and temperature should be considered for every new type of system investigated. Changing the column of a GC can increase the accuracy of phase equilibrium data by orders of magnitude. The GC is fitted with a thermal conductivity detector (TCD) coupled in series with a flame ionization detector (FID). For acquiring and analyzing data from the GC, the software Winilab (Supplied by Alpha Mos, France) is used. Both the ROLSI^{TM} samplers and the GC carrier gas line can be heated up to 523 K, for immediate vaporization of the samples. Besides promoting the immediate vaporization of the samples, the heating has also the purpose of avoiding, or at least minimizing, the possible adsorption of the analytes in the carrier gas line, which would constitute a serious source of errors in the analysis, especially when dealing with samples containing very low amounts of certain compounds.

The gas chromatograph detectors were calibrated using chromatographic syringes with maximum mole numbers uncertainties of 5% in the TCD and 3% in the FID.

The temperature of the cell is monitored with a resolution of 0.05 K and a precision of 0.1 K, through a platinum resistance thermometer Pt100 class 1/10 DIN, acquired from Dostmann Electronic GmbH, Germany, placed vertically over at the top of the cell. The thermometer, with a diameter of 1.5 mm, is inserted in a special cavity with thermal paste, in order to improve the thermal contact. The temperature sensor was calibrated according to the International Temperature Scale ITS-90, at the triple point of water, through the careful measurement of their electrical