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Experimental phase behavior study of a five-component model gas condensate

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ABSTRACT

In this work, the bubble points and dew points of a multicomponent mixture of methane, butane, heptane, decane and tetradecane as a model mixture representative of a gas condensate, have been measured experimentally. Ten samples with approximately the same composition were prepared and their bubble-point and/or their dew-point pressures were measured at several temperatures. The phase-behavior measurements were carried out in the temperature range of 240–410 K, and at pressures up to 21.6 MPa. The temperature and pressure ranges of the critical point for this system was measured and the cricondenbar and cricondentherm of the phase envelope were determined. The Peng–Robinson equation of state (PR EOS) was used for modeling of the phase behavior of this system. The PR EOS was able to successfully determine the bubble- and dew-points of this model gas condensate. Using the PR EOS, the retrograde region and liquid drop out characteristic of this model gas condensate were determined.

1. Introduction

Concerning phase behavior, gas-condensate reservoir fluids are one of the most interesting hydrocarbon mixtures. Because of the positions of the critical points on their phase boundaries and their reservoir conditions of pressure and temperature, liquid can be condensed from these gas mixtures due to their retrograde behavior with decreasing pressure upon depletion of the reservoir. If the phase behavior of such reservoirs is not accurately studied prior to their depletion, and gas production continues from these types of reservoirs without any precautions for condensation prevention, then some hydrocarbons may be condensed in the reservoirs. This liquid condensate contains mostly the heavy fraction of the gas mixture, which is the most valuable part of the fluid. By gravity and phase segregation, the condensed liquid can migrate to other parts of the reservoir or get trapped in capillary pores and lose its equilibrium with the gas phase. This means that the condensed liquid may never be recovered.

In order to avoid the condensation and loss of valuable hydrocarbons, it is possible to separate the heavy components of the gas at well-head and recycle the lighter fraction of the gas by injecting it back into the reservoir. In this way, the reservoir pressure is either maintained nearly constant or else decreased at a very slow rate. In addition, by separating the heavier part of the reservoir fluid and recycling the lean gas to the reservoir, the composition of the reservoir fluid gradually changes to a lighter gas, and after a while, the reservoir fluid may behave as wet gas reservoir fluid instead of gas condensate [1].

The above-mentioned discussions show the importance of accurate knowledge of the phase behavior of hydrocarbon reservoir fluids, in particular, gas-condensate-reservoir fluids because of the retrograde condensation phenomenon.

By performing phase equilibrium measurements on simple mixtures, it is possible to come to a good understanding of the phase behavior of real reservoir fluids. Pure normal alkanes and normal alkane mixtures are among the most common representative systems studied by a number of researchers [2–9]. Dohrn and coworkers presented good review on this topic through three extensive review-papers [10–12].

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In this work the phase behavior of a model gas condensate, consisting of five hydrocarbon constituents, has been studied by measuring the bubble-point and dew-point pressures of a certain composition at different temperatures. This five-component hydrocarbon mixture consists of methane, butane, heptane, decane, and tetradecane. This study is the continuation of our previous work [13] on the phase behavior of gas-condensate mixtures, in which a three-component gas mixture, consisting of methane, butane, and decane was studied.

In order to model the experimental phase behavior, the PR EOS was used to determine the phase envelope of this five-component model gas condensate.

2. Experimental

2.1. Chemicals

Methane and butane were purchased from Air Products (Waddinxveen, the Netherlands) with a specified purity of ≥99.995 vol%, and ≥99.95 vol%, respectively.

Heptane was supplied by Merck (Darmstadt, Germany) with a specified purity of >99%. Both decane and tetradecane were supplied by Janssen Chimica (Geel, Belgium) and both had a specified purity of >99%. The purities of heptane, decane, and tetradecane were checked by gas chromatography, which showed no significant impurities. Therefore, all the materials were used without further purification.

2.2. Apparatus

In this work, two different apparati were used for phase equilibrium measurements. The sapphire-windowed autoclave apparatus is suitable for high-pressure measurements, and is extensively described in detail by de Loos et al. [14]. For low-pressure phase equilibrium measurements the Cailletet equipment is more appropriate. This equipment was also described in detail earlier by Raeissi and Peters [15] and Peters et al. [16]. However, the experimental procedure is in principle the same for both types of equipments as the both operate according to the synthetic method [17], in which pressure is varied at constant temperature for a sample with fixed and known overall composition, until it changes from two phases into one phase (the disappearance of the last bubble of vapor in the case of bubble points, or the last drop of liquid in the case of dew points).

The pre-mixed liquid hydrocarbon mixture consisting of heptane, decane and tetradecane with known mass fractions was injected into a one-side-open capillary glass tube. The amount of the liquid was determined by weighing. The liquid mixture was then degassed carefully under vacuum by repetitive freezing and melting of the liquid. A known amount of methane and butane was then dosed volumetrically with a special dosing system. The open end of the glass tube was submerged into mercury and therefore a mixture with a fixed and known composition was trapped inside the capillary tube which acts as the equilibrium cell. The mercury served as both the sealing fluid for the sample and as the pressure transmitting fluid to the equilibrium cell.

In the case of the Cailletet-equipment, only the open end of the glass tube was placed in an autoclave. The closed end of the tube was surrounded by thermostat fluid (controlled by a LAUDA RCS 20 thermostatic bath) and a Pt-100 resistance thermometer was placed as close as possible to the top of the glass tube. In the case of the autoclave equipment, the glass tube was placed in an autoclave and surrounded by the pressurized thermostat fluid. The autoclave was placed in a thermostat-fluid bath. A Pt-100 resistance thermometer was placed inside a well in the autoclave housing, so that it was close to the glass tube. The thermostat fluid used was ethanol for lower temperatures (up to 40 °C) and silicon oil for higher temperatures. The Pt-100 was connected to a resistance bridge (ASL F16) for which the achieved accuracy of the temperature measurement is ±0.01 K. The pressure was kept constant and measured with a dead weight gauge (Budenberg "High Range"). The accuracy of the pressure measurements was better than 0.05% of the reading.

The procedure to determine bubble points and dew points was as follows. The temperature was maintained constant and the pressure was increased in small steps (less than 0.05 bar near the bubble point). The bubble point was considered as the average pressure at which a gaseous phase was still visible and the next pressure step at which the gas phase just disappeared. For dew points, a transition was observed from a turbid phase to a clear phase in a pressure step less than 0.05 bar. In this way, the bubble points and dew points could be determined with an accuracy of better than ±0.05 bar in the Cailletet equipment and up to an accuracy of about ±0.1 bar at about 100 °C in the windowed autoclave.

2.3. Calculations

Equations of state are usually used for calculating the phase behavior of reservoir fluids. References [18–22] are just a few of such papers. In this work, the PR EOS [23] was applied to determine the phase behavior of the studied synthetic model gas condensate containing methane, butane, heptane, decane, and tetradecane. The PR EOS can usually determine the phase behavior of hydrocarbon mixtures adequately, especially when these mixtures are not very close to their critical points. The original mixing rules of the PR EOS (a quadratic mixing rule for its attractive term and a linear mixing rule for its repulsive term) was used in order to calculate the phase behavior of the system of methane + butane + heptane + decane + tetradecane. The binary interaction parameters between hydrocarbons which is presented by Danesh [1] were used for the predictions. Readers are referred to Ref. [23] for further details of this EOS. For predicting the retrograde region of the system, a series of flash calculations was performed at each specified temperature between the critical temperature and the cricondentherm of the system in order to find the pressures that produce the maximum liquid dropouts at selected temperatures.

3. Results and discussions

Ten samples with approximately the same compositions were prepared in order to study the phase behavior of a particular hydrocarbon mixture as a model gas condensate. The reason that all the samples had almost the same composition, was that a complete phase envelope of a gas condensate mixture can be measured. Table 1 shows the compositions of the selected samples whose bubble points and/or dew points were measured. The Cailletet apparatus was used for the phase behavior measurements of Samples 1–6 and the autoclave apparatus was used for the measurements of Samples 7–10. To compare the accuracy and reproducibility of the data using two different apparati, a certain range of pressures and temperatures were measured using both equipment, i.e., there was an overlap range of measurements among two apparati.

Tables 2–11 which are provided as supplementary data, report the bubble points and dew points of the samples, measured by either the Cailletet or autoclave apparatus. Fig. 1 is a plot of the pressure–temperature data of Samples 1–10, which actually shows the phase envelope of the selected five-component model gas condensate. In the measurements of bubble points and dew points of Sample 1, the temperature range of the critical temperature was determined to be between 273.15 K and 276.65 K. The