

## Density, dielectric constant and PVT measurements of a gas condensate fluid

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### Abstract

Simultaneous measurements of the volume, dielectric constant and density have been made in both the vapor and liquid phases of a gas condensate fluid. The dielectric constant was measured with a microwave reentrant resonator, the density with a commercial vibrating tube densimeter and the volume with a PVT cell optimised for measurements on gas condensate fluids. Gas chromatography (GC) was used to determine the fluid's composition. Sample fluid in the microwave resonator, densimeter and PVT cell could be thoroughly mixed expediting equilibrium and preserving sample integrity. Measurements were made at approximately 308 and 318 K at 12.4 MPa, conditions representative of the well head. These data will allow the calibration of multiphase flow meters used in the production stream of this fluid. The data are compared with the predictions of a cubic equation of state to ascertain whether simple correlations can provide the accuracy necessary to calibrate multiphase flow meters.

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### 1. Introduction

Multiphase flow and water cut meters are increasingly being used in the production of natural hydrocarbon fluids. These instruments can be placed at the well head, prior to the separation of the gas, condensate/oil and water streams. The fraction and flow of each phase is determined from density, dielectric constant and flow velocity measurements made by a

$\gamma$ -ray densimeter and a microwave measurement system. The microwave measurements determine the multiphase mixture's dielectric constant to estimate the ratio of the phases. Correlations between two microwave measurements separated by a known distance allow the flow velocity to be determined. These instruments are sensitive over a wide range of water cuts, gas void fractions and flow regimes (ROXAR, 2001), and are an economically attractive alternative to the conventional practice of separately metering each stream.

When the separate error contributions of the phase ratio and flow velocity measurements are combined, the accuracy of the flow rate of each phase is about 10% (ROXAR, 2001). This uncer-

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tainty is achieved without any field measurements of the individual phases to calibrate the instrument, largely because of the great difference between the dielectric constants of water and oil or gas. However, as the monitoring of well productivity relies on these multiphase flow measurements, there is significant interest in improving the accuracy of these meters to the level of one percent or better. One method of doing so is to measure the density and dielectric constant of the condensate, gas and produced water phases at well head conditions. However, in early production from a gas condensate well, little or no formation water is produced and measurement of the condensate and gas properties is sufficient for field calibration.

Condensate and gas samples were acquired during exploration testing of a gas condensate reservoir on Australia's North West Shelf. Measurements on these samples then provided the basis for optimising well performance and flow monitoring at production start-up. Three samples were made available for this study. Two were samples from the vapor stream and one from the condensate stream of a test separator. Each sample was taken using a Welker cylinder with a piston driven by a brine hydraulic fluid. The specific objectives of the measurements were to:

1. Measure the composition of the samples.
2. Recombine the samples in the appropriate ratio to simulate the reservoir fluid and measure its dew point at reservoir temperature.
3. Measure the density, dielectric constant and phase volumes at temperatures and pressure conditions representative of the mixed phase production stream at the well head.

The purpose of this article is to describe the experimental system and the procedure employed to make these measurements. One significant innovation of the system is the capability to simultaneously measure the density, dielectric constant and PVT surface of the fluid in a closed system, which ensures sample integrity. The system has the potential for both accurate and precise measurements on important fluids over a broad range of conditions. However, the objective of the measurements reported here was to provide useful, reliable data in a short time frame.

## 2. Experimental overview

Fig. 1 shows a schematic of the experimental system. The centerpiece is a PVT cell designed specifically for measurements of gas condensate fluids. A sample loop containing a circulation pump, a pressure gauge, a vibrating tube densimeter and a microwave resonator is connected to the cell and the entire system is housed in an air bath cabinet. The system's volume is varied via one or other of two volumetric mercury pumps. These volumetric pumps also allow the sample to be translated at constant pressure about the system.

Bottle-opening pressures of the three sample cylinders were determined before the composition of each fluid was measured. The bubble point pressure of the condensate stream sample and the dew point of a vapor stream sample were measured prior to their recombination in the PVT cell. The dew point pressure of the recombined fluid was then determined for the reservoir isotherm.

Four separate measurements of density and dielectric constant were made, all at approximately 12.4 MPa: vapor at 318 K, vapor at 308 K, condensate at 308 K and condensate at 318 K. The sample was prepared at (12.4 MPa, 318 K) in the PVT cell, which was initially isolated from the evacuated external loop. The vapor phase was expanded into the loop and the entire sample repressurised with the volumetric pumps before being thoroughly re-mixed. The density and dielectric constant of the vapor phase at this condition were then measured for about 30 min. Once the first measurement was complete, the temperature of the air bath cabinet was reduced to 308 K and the mixing systems were activated until equilibrium was reached. The mixing systems were switched off while the second vapor phase measurement was made.

Volumetric pump 1 was used to transport some of the condensate phase from the PVT cell to the microwave resonator and densimeter at constant pressure. Once the first condensate measurement was completed, the liquid was returned to the cell before the temperature of the air bath cabinet was changed back to 318 K. The second condensate measurement was then made, once equilibrium had been established.

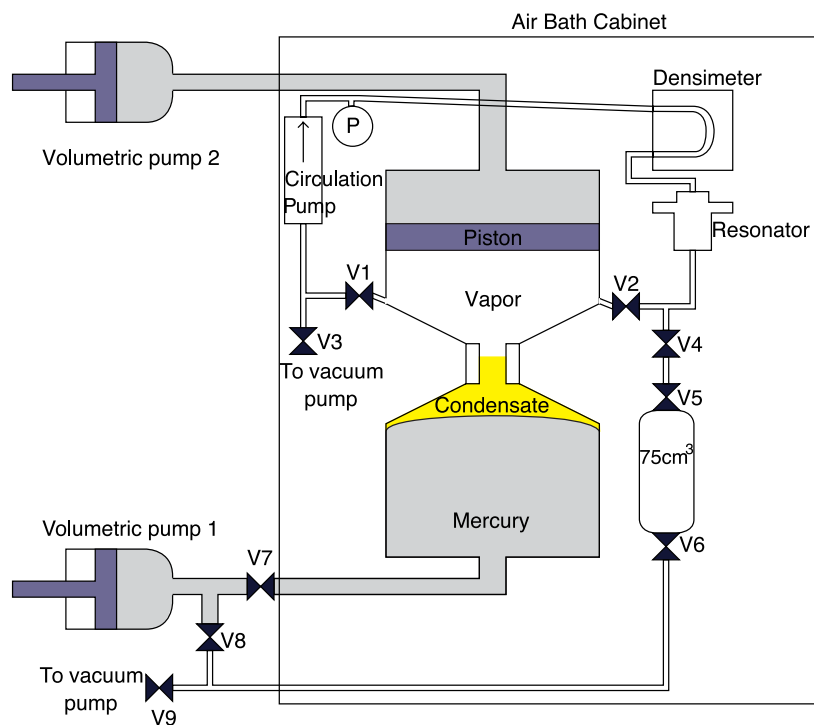


Fig. 1. Schematic of experimental system.

The measurements were performed in this order because the circulation pump allowed the vapor in the external loop to be mixed with the vapor in the PVT cell whereas condensate measurements resulted in a small volume ( $\approx 7 \text{ cm}^3$ ) of condensate being isolated in the external loop. By following the above sequence, only the final condensate measurement could be affected, to a small degree, by inadequate mixing.

### 3. Experimental system

The PVT cell is of variable cross-section; a 6.00-mm ID sapphire cylinder, located in the center of the cell connects two stainless steel high-pressure vessels. These vessels have cylindrical bores of ID 120.04 mm that taper down to 6.00 mm to mate with the sapphire. The PVT cell has a maximum sample volume of approximately  $4600 \text{ cm}^3$ . The portion of the sample in the upper stainless steel pressure cylinder is bounded by a piston that is driven by one of the volumetric pumps. The other pump drives a free

mercury surface into the lower stainless steel pressure cylinder; this surface forms the lower boundary of the sample. The free mercury surface can be driven through the sapphire window region and into the top stainless steel pressure cylinder. The total sample volume can be calculated from the volume of mercury displaced by each of the pumps. By slaving the pumps together (in anti-phase), the sample can be translated at constant volume. This allows the condensate and mercury menisci to be sequentially positioned and viewed in the sapphire window. The liquid volume is determined as the difference in volumetric pump readings at each meniscus position. The resolution of the liquid volume measurements is better than  $0.01 \text{ cm}^3$ . The PVT cell also contains an internal mixing system to hasten phase equilibrium. Further detail can be found in [Edwards \(1987\)](#).

At the lowest level that the upper piston can reach, the PVT cell has two valved outlet ports; these outlets are angled to facilitate sampling of the vapor phase from one and the condensate phase from the other. The external loop is connected between these two

ports. The intake of a circulating pump, described in May et al. (2001), is connected to the vapor sample port (V1) of the PVT cell and this defines the direction of flow through the loop. With the circulating pump operating, fluid can be pumped at about  $1 \text{ cm}^3 \text{ s}^{-1}$  through the loop and back into the PVT cell via the condensate sample port (V2). The external loop can be isolated by closing V1 and V2 and evacuated through valves V3 and/or V4.

The pressure gauge in the external loop is a diaphragm strain gauge-type. Three other gauges of similar type, intrinsic to the PVT cell, measure the pressure of each of the mercury pumps and the pressure of the sample in the center of the cell. All pressure gauges were calibrated against a gas operated piston gauge and are accurate to  $(0.1\% \pm 0.01 \text{ MPa})$ . Temperatures within the cell and air bath cabinet are measured with several factory calibrated platinum resistance thermometers (PRT) and have an estimated uncertainty of 0.3 K. The uniformity of the cell temperature is about 0.25 K.

The vibrating tube densimeter is an Anton Paar 512P DMA, specified by the manufacturers as capable of operating at temperatures up to  $150^\circ\text{C}$  and pressures to 70 MPa. Oscillations are excited and measured by a unit (AP DMA 48) external to the air bath cabinet. The resonant period, typically between 3900  $\mu\text{s}$  and 4100  $\mu\text{s}$ , is measured with an uncertainty of 0.001  $\mu\text{s}$ , according to the manufacturer.

The microwave resonator is the brass reentrant cavity, previously used in the variable volume system described by May et al. (2001), modified for use in the presence of mercury vapor. Previously, an indium O-ring had been used as both a high-pressure seal and to provide electrical contact between the top and bottom sections of the resonator. Goodwin et al. (1996) used a gold O-ring in a similar resonator. Due to the presence of mercury vapor, neither of these metals are suitable for use as pressure seals over an extended period of time. The indium O-ring was replaced by a viton O-ring, which allows the resonator to contain fluids at pressures to 15 MPa and temperatures to  $80^\circ\text{C}$  indefinitely. Despite the use of an insulator as the primary pressure seal, there is sufficient electrical contact (via the bolts) between the two halves of the reentrant cavity to allow microwave resonance. A vacuum resonance exists at about 644 MHz with a bandwidth of approximately 3 MHz. The resonant

frequency is measured and tracked, with an uncertainty of 0.01 MHz, using the same Pound frequency discriminator circuit described by May et al. (2001).

Several other changes have been made to the reentrant resonator. All elements that relied on the use of solder were modified. An SMA glass-to-metal feedthrough threads into the cavity lid, compressing a second viton O-ring to provide a seal. The magnetic loop probe is spot welded to the feedthrough. In additions to these modifications, great care was taken to minimise exposure of the resonator to liquid mercury. The free mercury surface in the PVT cell, controlled by pump 1, was never raised to a level less than 1 cm below valves V1 and V2.

The entire volume of the circulation loop external to the PVT cell bounded by V1, V2, V3 and V4 is approximately  $41.1 \text{ cm}^3$ , about half of which is the internal volume of the reentrant resonator. At the conditions of the measurements reported here, the sample volume within the PVT cell was of the order of  $1400 \text{ cm}^3$ . The circulation pump was used to circulate the vapor phase through the external loop containing the densimeter and resonator, ensuring that the vapor in the circulation loop is equilibrated with vapor in the PVT cell. The mixing system in the PVT cell ensures equilibrium between the liquid and gas phases.

#### 4. Experimental procedure

It is not possible to fill the external loop with the condensate using the circulation pump. For a condensate measurement, pumps 1 and 2 move the sample in the PVT cell at constant volume until the condensate level is several centimetres above valves V1 and V2. These two valves are open following completion of the vapor measurements. The free mercury surface in the bottom of the PVT cell is then isolated from pump 1 by closing V7. The lines and a  $75 \text{ cm}^3$  sample cylinder between V8 and V4 are evacuated. Valve V5 is then closed and V8 is opened and mercury is admitted and pressurised to the seat of V5 using pump 1.

Valve V4 is then opened expanding the sample slightly. The pressure in the mercury below V5 is then reduced to slightly below that of the sample before V5 is opened ensuring mercury is not forced into the

sample loop. Valve V1 is closed and pumps 1 and 2 are then slaved together. Pump 2 is advanced and pump 1 is reversed drawing approximately 50 cm<sup>3</sup> of condensate into the sample cylinder. Then valve V2 is closed and V1 is opened. Pump 1 is advanced and pump 2 is reversed until the condensate phase enters and fills the resonator and then the densimeter. The system is allowed to equilibrate for an hour before measurements of the condensate's dielectric constant and density are made.

The procedure outlined above is then reversed in order to return the condensate phase back into the PVT cell. The mercury surface driven by pump 1 is returned to, but never allowed past the seat level of V5. Valve V8 is then closed and V7 opened, so that pump 1 again controls the mercury surface in the lower half of the PVT cell. The PVT cell then translates the sample down at constant volume until the liquid vapor interface is in the sapphire viewing region. The vapor circulation pump is then employed to flush out residual condensate in the external loop. At the completion of a condensate measurement, only a very small volume of condensate in the line from V5 to just above V4 is not returned to the PVT cell.

## 5. Pure fluid calibration

Both the reentrant resonator and vibrating tube densimeter need to be calibrated with pure fluids prior to mixture measurements. The resonator was calibrated with helium (99.9% minimum purity) and subsequently tested with welding grade argon (99.995% minimum purity). The densimeter was calibrated with both argon and nitrogen (99.9% minimum purity) at about (12.4 MPa, 308 K) and (12.4 MPa, 318 K). The calibration measurements were conducted prior to the opening of V1 and V2 and any exposure of the external loop to mercury vapor. The effect of the calibration gas impurities is negligible compared to the other uncertainties in the measurement system.

Room temperature resonant frequencies were measured with helium at pressures to 9 MPa. The vacuum resonant frequency,  $f_0$ , of the reentrant resonator can be modelled by (Goodwin et al., 1996; Anderson et al., 2000; May et al., 2002)

$$f_0 = f_{00}(1 - \alpha t + \beta P) \quad (1)$$

where  $f_{00}$  corresponds to the vacuum value of the resonant frequency at a reference temperature (318.2 K),  $\alpha$  is the coefficient of thermal expansion of the resonator material,  $\beta$  is related to the elastic properties of the resonator,  $P$  is the absolute pressure and  $t$  is  $T/K - 318.2$ . The value for  $\alpha$  was measured previously (May et al., 2001) and found to be in excellent agreement with literature values of brass' thermal expansion coefficient. Modifications to the resonator meant that the value of  $\beta$  had to be re-measured. The method is described by May et al. (2001). The room temperature helium measurements on the modified resonator give  $\beta = (1.09 \pm 0.01) \times 10^{-4} \text{ MPa}^{-1}$ . The value of  $f_{00} = 644.31 \pm 0.02 \text{ MHz}$  was determined by direct measurement of the vacuum frequency at the reference temperature.

Dielectric constants,  $\epsilon$ , of a given fluid are obtained by measuring the cavity resonance frequency,  $f$ , when filled with the fluid in question. In the simplest model,  $\epsilon$  is related to  $f$  and  $f_0$  by

$$\epsilon = \left(\frac{f_0}{f}\right)^2 = \left(\frac{f_{00}(1 - \alpha t + \beta P)}{f}\right)^2. \quad (2)$$

The accuracy of this expression was tested with measurements on argon. Eq. (2) is used rather than the more complex forms presented by Hamelin et al. (1998) for several reasons. Firstly, our Pound tracking system does not provide a measure of the resonance's bandwidth necessary for penetration depth corrections. Furthermore, the relatively poor thermal control, pressure uncertainty and temperature uncertainty limit the expected accuracy of such a measurement. Reference values of the dielectric constant,  $\epsilon$ , were calculated from

$$P_t = \frac{1}{\rho} \left( \frac{\epsilon - 1}{\epsilon + 2} \right) = A_\epsilon + B_\epsilon \rho + C_\epsilon \rho^2 \quad (3)$$

where  $P_t$  is the molar polarizability,  $\rho$  the molar density and  $A_\epsilon$ ,  $B_\epsilon$  and  $C_\epsilon$  are the dielectric virial coefficients. Argon densities were estimated from the equation of state of Tegeler et al. (1999) and the dielectric virial coefficients of argon were taken from the 50 °C measurements of Moldover and Buckley (2001). The small temperature dependencies of the dielectric virial coefficients were

neglected. Table 1 lists the literature and measured values of the dielectric constant of argon at the measured pressure and temperature. The rms fractional deviation of the measured dielectric constants from the literature estimates is 0.09%.

The precision to which the dielectric constants of hydrocarbon fluids can be measured using the reentrant resonator technique is generally limited by the uncertainty in the value of the parameter  $f_{00}$ . We have observed in other reentrant resonators that this parameter can be changed by up to a few tens of kilohertz by mechanisms such as mechanical shock or back streaming from vacuum pumps. Because of the sensitivity of  $\varepsilon$  on the parameter  $f_{00}$  in Eq. (2), the vacuum frequency at the reference temperature was re-measured at the conclusion of the condensate measurements and found to have decreased to 642.70 MHz. The reason for the fractional shift of approximately  $-3 \times 10^{-3}$  became apparent when the resonator was disassembled. The colour of the internal brass surfaces had changed to a pasty white. We hypothesise that the presence of small amounts of mercury vapor in the brass cavity resulted in the build up of an amalgam similar to that observed by Fleming et al. (1972), increasing the reentrant resonator's principal capacitance and thus decreasing the resonant frequency. Furthermore, the presence of a small amount of mercury vapor would shift the measured dielectric constant of the hydrocarbon fluid. For the hydrocarbon mixture dielectric constant measurements, we estimate that these two effects result in an uncertainty of  $5 \times 10^{-3}$ . While this is a relatively large uncertainty compared to other dielectric constant measurements in fluids (Hamelin et al., 1998; Moldover and Buckley, 2001), it is still more than adequate for the purposes of these measurements.

Laznickova and Huemer (1998) present a detailed analysis and calibration procedure for gas density measurements in vibrating tube densimeters. However,

Table 1  
Measured and literature (Tegeler et al., 1999; Moldover and Buckley, 2001) dielectric constants of argon

$P$ (MPa)	$T$ (K)	$\varepsilon$ lit.	$\varepsilon$ meas.
5.04	318.3	1.0243	1.0242
9.07	318.3	1.0445	1.0443
12.36	318.3	1.0612	1.0609
12.53	307.9	1.0649	1.0640

Table 2

Densimeter parameters determined from calibration with argon and nitrogen

$P$ (MPa)	$T$ (K)	$A$	$B$
12.43	307.9	$6.243 \times 10^{-4}$	$9.565 \times 10^{-3}$
12.43	318.3	$6.178 \times 10^{-4}$	$9.490 \times 10^{-3}$

due to the short time frame and relaxed precision required operationally in the field, we followed the simple calibration procedure suggested by the manufacturer. The mass density,  $\rho_m$ , of the fluid contained in the vibrating tube can be calculated from the resonant period,  $\tau$ , of the oscillations through the equation

$$\rho_m = A\tau^2 - B. \quad (4)$$

Parameter  $A$  of Eq. (4) depends on the effective spring constant and inner volume of the vibrating tube, while parameter  $B$  depends on the inner volume and mass of the empty tube (Laznickova and Huemer, 1998). Both parameters are pressure and temperature dependent. The simplest calibration scheme for vibrating tubes involves measuring the resonant period at the required pressure and temperature with at least two fluids of known density. This was done with argon and nitrogen at the pressures and temperatures listed in Table 2 using the equations of state of Tegeler et al. (1999) and Span et al. (2000).

At the conclusion of the experiment, the vacuum resonant period of the densimeter was re-measured. Its value had not changed within the limits imposed by the experimental uncertainty in the measured temperature and pressure. The control and resolution of the system's temperature and pressure dominate the uncertainty in the density measurements. The total uncertainty in the mixture density measurements reported here, including the small differences between the mixture and calibration fluid conditions, is estimated to be 2%.

## 6. Composition measurements

Both cylinders containing the separator's vapor phase were sampled for gas chromatography (GC) analyses. The samples were found to be identical to within the uncertainty of the GC. The resolution of the



GC technique used is 0.01% by mole. Alkanes to C<sub>9</sub> were detected in the vapor samples. No water was detected in this or any other subsequent measurements. Nitrogen and carbon dioxide were detected at  $2.69 \pm 0.09\%$  and  $1.89 \pm 0.07\%$ . The methane fraction was  $83.5 \pm 0.3\%$ .

In order to determine the composition of the separator's liquid phase, the condensate sample was flashed to laboratory conditions. The sample cylinder was connected to a four liter gasmeter (ROP Training Center, 1987) and condensate volume trap. The gasmeter allows automatic measurement of gas volumes at constant pressure. Sample was bled through the cylinder's valve until 10.0 cm<sup>3</sup> of liquid had formed at atmospheric conditions in the condensate volume trap. The corresponding 1328.2 cm<sup>3</sup> of evolved gas at atmospheric pressure and temperature was contained and measured by the gasmeter; changes in pressure inside the gasmeter are automatically compensated by the movement of a piston. The evolved gas was displaced with the piston into an evacuated cylinder and its composition was measured with a gas chromatograph. Alkanes to C<sub>9</sub> were again

detected, nitrogen and carbon dioxide were measured at  $2.08 \pm 0.08\%$  and  $1.96 \pm 0.06\%$  and the methane fraction was measured to be  $48.8 \pm 0.3\%$ . International Standard ISO 6976 was used with the measured composition, pressure and temperature to determine that the compressibility of the evolved gas was 0.9902. Thus, the equivalent volume of an ideal gas at standard temperature and pressure is 1236.1 cm<sup>3</sup>. The volume of evolved gas corresponds to 0.0552 mol.

The 10.0 cm<sup>3</sup> of liquid was directly weighed and found to have a mass of 7.366 g. Two analyses of the evolved liquid sample were conducted: both used the same GC column, but one employed a mass spectrometer and the other used a flame ionisation detector. The former detector allowed the identification of over 128 species while the latter provided a more accurate measurement of the composition. Alkanes to C<sub>22</sub> were detected, the methane fraction was  $0.26 \pm 0.01\%$  and the composition distribution peaked at C<sub>8</sub> ( $24.02 \pm 0.01\%$ ). The molecular mass of the evolved liquid was approximately 103.98, and thus the 10.0 cm<sup>3</sup> of evolved liquid contained 0.0708 mol.

Table 3

Measured bulk composition of recombined reservoir fluid and predicted EOS phase compositions at pressures and temperatures in Table 4

Component	Measured bulk composition (mol%)	EOS phase composition predictions (mol%)			
		Vapor 1	Vapor 2	Condensate 1	Condensate 2
CH <sub>4</sub>	74.4 ± 0.3	83.09	83.72	42.00	40.05
C <sub>2</sub> H <sub>6</sub>	6.18 ± 0.19	5.97	5.86	7.31	6.96
C <sub>3</sub> H <sub>8</sub>	3.58 ± 0.11	2.87	2.73	6.56	6.35
i-C <sub>4</sub>	0.97 ± 0.03	0.64	0.60	2.26	2.24
n-C <sub>4</sub>	1.60 ± 0.04	0.97	0.88	4.08	4.07
neo-C <sub>5</sub>	0.03 ± 0.01	Not simulated (lumped with n-C <sub>5</sub> )			
i-C <sub>5</sub>	0.82 ± 0.01	0.39	0.34	2.49	2.54
n-C <sub>5</sub>	0.84 ± 0.01	0.37	0.32	2.74	2.81
C <sub>6</sub>	1.30 ± 0.01	0.37	0.31	4.73	4.98
C <sub>7</sub>	1.67 ± 0.01	0.30	0.25	6.62	7.10
C <sub>8</sub>	2.07 ± 0.01	0.23	0.18	8.59	9.35
C <sub>9</sub>	0.93 ± 0.01	0.06	0.05	3.97	4.35
C <sub>10</sub>	0.65 ± 0.01	0.03	0.02	2.80	3.09
C <sub>11</sub>	0.30 ± 0.01	0.01	0.01	1.30	1.44
C <sub>12</sub>	0.20 ± 0.01	0.00	0.00	0.89	0.99
C <sub>13</sub>	0.12 ± 0.01	0.00	0.00	0.52	0.58
C <sub>14</sub>	0.10 ± 0.01	0.00	0.00	0.43	0.47
C <sub>15</sub>	0.06 ± 0.01	0.00	0.00	0.28	0.31
C <sub>16</sub>	0.01 ± 0.01	0.00	0.00	0.05	0.06
C <sub>17+</sub>	0.01 ± 0.01	0.00	0.00	0.07	0.07
N <sub>2</sub>	2.44 ± 0.09	2.87	2.92	0.76	0.73
CO <sub>2</sub>	1.74 ± 0.07	1.81	1.80	1.55	1.46

The measured compositions of the evolved gas and liquid were combined according to the ratio of the number of moles evolved in each phase to give the composition of the separator liquid sample. The methane fraction in the separator liquid was  $21.5 \pm 0.3\%$ . The condensate-to-gas ratio (CGR) of the test separator was quoted by the production company as 168.840 sepbbl/mmscf. This CGR was used to combine the compositions measured from the separator vapor and liquid samples to produce a well head composition. Table 3 contains the composition for the recombined reservoir fluid. The composition reported here is based on an end-point cut, where the end-point is determined by the elution of the alkane for that cut. Due to the uncertainty of the composition measurements, only alkanes to  $C_{17}$  are presented in Table 3; however, traces of alkanes to  $C_{22}$  were detected during the composition measurements.

## 7. Sample quality and dew point measurements

The reported temperature and pressure of the separator from which the samples were taken was (7.21 MPa, 313.8 K). The uncertainty of these values is unknown. In the laboratory, the sample cylinders were placed in an oven (separate and distinct from the PVT cell) and the bottle-opening pressures of each

cylinder were measured at the reported separator temperature. The two gas cylinders returned a pressure of 7.24 MPa, while the condensate sample cylinder pressure was 6.76 MPa.

The bubble point pressure of the condensate sample at 313.8 K ( $T_{\text{separator}}$ ) was measured by connecting one of the PVT cell's mercury pumps to the sample cylinder. By operating the mercury pump in constant pressure servo mode and recording the volume of mercury displaced to achieve the pressure set point, the compressibility of the condensate sample could be measured. Fig. 2 shows a plot of set point pressure as a function of the volume of mercury displaced. The obvious slope discontinuity indicates that the condensate sample's bubble point was  $6.76 \pm 0.02$  MPa.

It is not generally recognised that accurate measurement of the bubble point requires long equilibration time in the two-phase region. The two points Y and Z in Fig. 2 required more than 24 h to reach equilibrium. In the single-phase region, it is merely the compressibility that is being measured and the experimental points there required only a few minutes for the pressure to stabilise after a 0.1 MPa decrement.

Prior to transfer into the PVT cell, all sample cylinders were heated in the separate oven to a temperature that ensured they were in the single phase. The sample cylinder contents were then convectively mixed for at least 48 h using heating tape

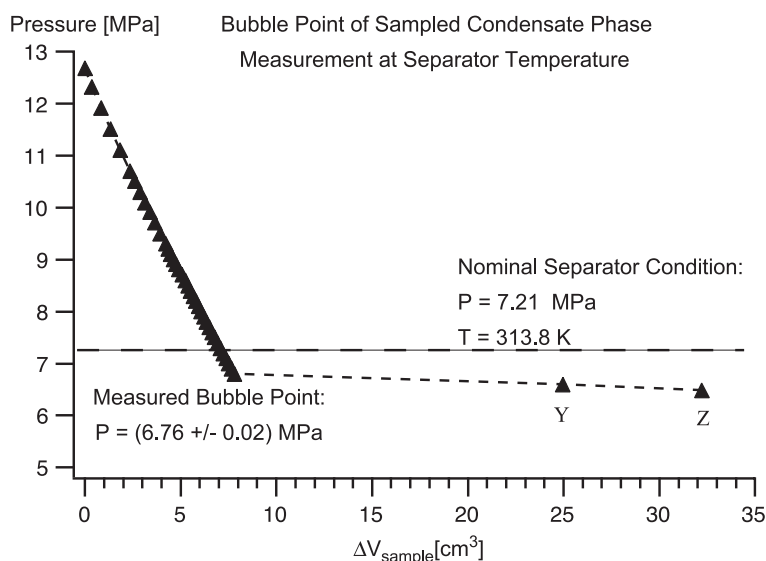


Fig. 2. Bubble point measurement of the condensate sample.



wound around the bottom of the cylinder to establish an 11 K difference along the cylinder's height. All transfer lines connecting the cylinder to the PVT cell were heated to ensure single-phase conditions during transfer.

Approximately 500 cm<sup>3</sup> of the separator's vapor sample was transferred to the PVT cell from one of the cylinders at (7.00 MPa, 333.0 K). A constant composition expansion at 313.8 K ( $T_{\text{separator}}$ ) was performed from 10 to 5 MPa as a comparative check between the sample's dew point and the separator conditions. Unexpectedly, no liquid phase was observed to condense at any point. A similar scan at 303.2 K also produced no liquid phase. The two-phase condition was finally observed during a scan at 293.2 K; a liquid volume of 0.30 cm<sup>3</sup> was observed at (6.66 MPa, 293.2 K).

In order to obtain reliable phase behaviour information about a reservoir fluid, accurate sampling is essential. It is also one of the most problematic and difficult elements of the measurement process. The above measurements were made to determine the quality and mutual consistency of the vapor and condensate samples. The 6% discrepancy between the bottle opening pressure of the condensate sample and the vapor samples, and the fact that the vapor sample was not at its dew point highlight the sampling problem. The failure of the sample dew point to coincide with the separator conditions could have resulted from temperature differences between

the separator and the flow lines leading to the sample cylinder, which would lead to drop out of heavy end components. As is well known the location of the phase envelope, and especially the cricondentherm, is sensitively dependent on trace amounts of heavy hydrocarbons. On the positive side, both vapor samples had identical compositions and the bubble point of the condensate sample was near separator conditions.

In order to produce a sufficient quantity of recombined fluid representative of the reservoir, an additional volume of the vapor sample was transferred to the PVT cell, resulting in a final vapor volume of 1747.66 cm<sup>3</sup> at 7.96 MPa, 323.2 K. The difference in pressure and temperature between this and the separator condition required an adjustment to the CGR, which was recalculated to be 168.236 sepbbl/mm scf. One of the mercury pumps was connected to the base of the condensate sample cylinder allowing the sample to be pressurised as necessary. Heated lines connecting the condensate sample bottle to the PVT cell were then opened and a volume of 134.51 cm<sup>3</sup> of condensate was transferred at pressure to the PVT cell. This volume was measured by injecting an equal volume of mercury into the sample cylinder, using the precise volumetric pump.

The recombined sample was then mixed for 10 h in the PVT cell at 10.27 MPa, 384.2 K, the temperature corresponding to that of the reservoir. Once the recombined sample had been thoroughly mixed the

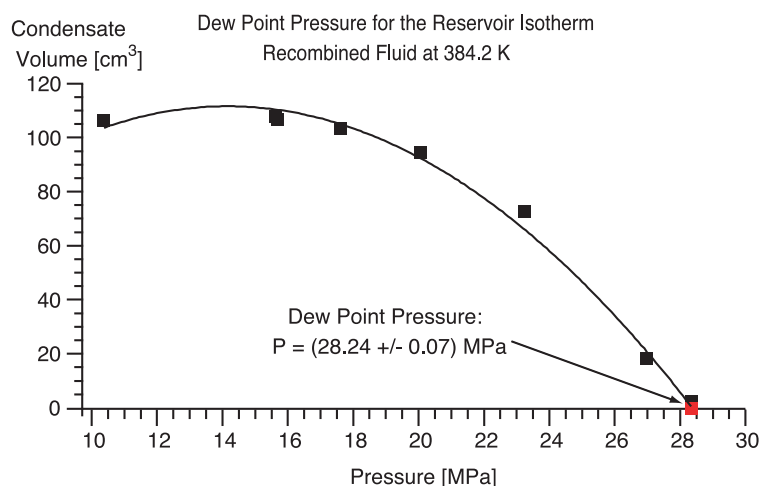


Fig. 3. Dew point determination for the recombined fluid along the reservoir isotherm.

condensate volume was measured to be  $106.37 \text{ cm}^3$  in a total sample volume of  $1765.71 \text{ cm}^3$ . The pressure was then increased toward the upper dew point and the liquid volume at each pressure was recorded. A plot of these measurements is shown in Fig. 3. The sample was mixed for 24 h after each pressure change and prior to the measurement of liquid volume. The minimum liquid volume observed was  $0.03 \text{ cm}^3$  in a total sample volume of  $755.09 \text{ cm}^3$  at 28.24 MPa. A quadratic was regressed to the data and the dew point pressure for the reservoir isotherm was estimated to be  $28.24 \pm 0.07 \text{ MPa}$ .

## 8. Density, dielectric constant and PVT measurements

At the completion of the dew point measurements, the system was taken to well head conditions (12.46 MPa, 318.9 K) and mixed for 24 h. The condensate volume and total sample volume were measured and then valve V1 was opened allowing the fluid to expand into the evacuated external loop containing the densimeter and resonator. The volumetric pumps were then operated in servo mode until the pressure returned to 12.46 MPa. The circulation pump was then activated for 2 h before being switched off. The frequency of the resonator and vibration period of the densimeter were recorded after a further 0.5 h. The remaining measurements of dielectric constant and density were then conducted as described in Section 4. Table 4 lists the measured temperatures, pressures, liquid and sample volumes, resonant frequencies and vibration periods recorded.

The Pound frequency discriminator circuit utilised in tracking the frequency of the resonator can maintain a lock if the frequency does not shift by more than a few hundred kilohertz in less than a few seconds. If frequency track is lost, the resonant frequency must be

re-found manually; this occurred when the evacuated resonator was filled with the vapor phase. The tracking of the frequency was maintained however when the resonator was filled with the condensate phase by varying the filling rate determined by volumetric pump 1. This pump can displace mercury at a rate as low as  $0.01 \text{ cm}^3 \text{ min}^{-1}$ , and this minimum rate was required when the condensate phase started to fill the resonator's high capacitance region—the vertical 1 mm annular gap. Fig. 4 shows the measured frequency of the cavity as it changed from containing only the vapor phase to being completely full of condensate.

The distribution of electric field intensities within a reentrant resonator can be used to infer the location of the liquid–vapor interface (May et al., 2001). This in turn allows the volume of liquid in the cavity to be estimated. A somewhat different illustration of this effect occurred when the rate at which the condensate phase could be displaced had to be varied in order to maintain frequency track. The rate of volumetric displacement corresponded to a rate of change in the effective dielectric constant within the cavity. The rate of change of the effective dielectric constant is determined by the electric field intensity at the liquid–vapor interface. Thus, the location of the interface could be qualitatively inferred from the rate at which condensate could be displaced while still maintaining frequency track.

Eqs. (2) and (4) were used to convert the measured vibration periods and frequencies to the densities and dielectric constants of the vapor and condensate phases. Table 5 shows these calculated values at the corresponding pressures and temperatures, together with their estimated uncertainties resulting from the deviation between the measurement and calibration conditions and from the temperature and pressure uncertainties.

The commercial thermodynamic modelling package, HYSYS, was used to estimate the density, composition and dielectric constant of each phase at the measurement conditions. The modelling package used the Peng–Robinson equation of state (EOS) together with the experimentally determined reservoir fluid compositions. A modified version of Eq. (3) was used to predict the dielectric constant based on the EOS phase densities and compositions together with component molar polarizabilities. For the purposes of this simulation, component polarizabilities,  $P_{ii}$ , were

Table 4

Measured PVT, densimeter and resonator parameters for vapor and condensate phases

Phase	$P$ (MPa)	$T$ (K)	$V$ ( $\text{cm}^3$ )	$\tau$ ( $\mu\text{s}$ )	$f$ (MHz)
Vapor 1	12.46	318.9	1320.53	3944.80	601.54
Vapor 2	12.43	308.2	1199.43	3940.40	597.66
Condensate 1	12.41	307.3	163.83	4038.77	475.48
Condensate 2	12.41	319.1	155.40	4044.59	476.18

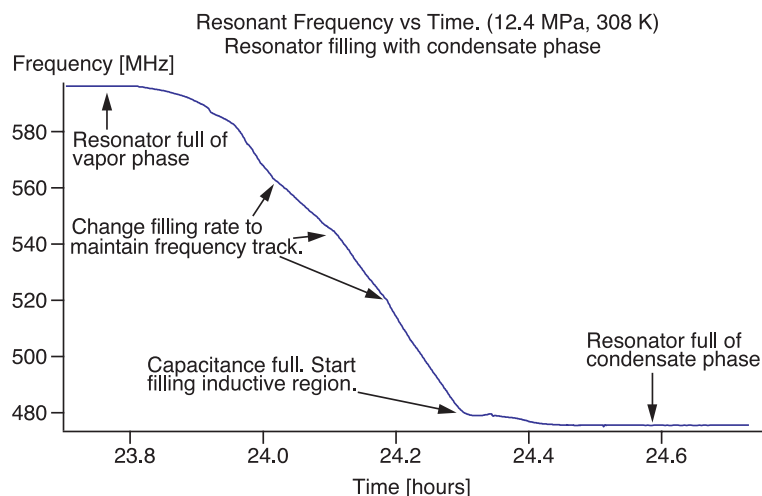


Fig. 4. Resonant frequency as condensate fills the resonator.

taken to be constant with pressure and temperature. For methane, nitrogen and carbon dioxide, the polarizability was taken to be the zero density limit,  $A_e$ , determined by Moldover and Buckley (2001). For the remaining alkanes, the polarizabilities were estimated from refractive index data for liquid alkanes (American Petroleum Institute, 1976). The dielectric constant of the vapor phase,  $\epsilon_v$ , was then calculated at each condition according to

$$\frac{1}{\rho_v} \left( \frac{\epsilon_v - 1}{\epsilon_v + 2} \right) = \sum_i y_i P_{ti} \quad (5)$$

where  $\rho_v$  is the vapor's molar density and  $y_i$  is the mole fraction of the  $i$ th component in the vapor at that pressure and temperature. This mixing rule for the polarizability has been investigated in liquid and vapor mixtures of non-polar species and found to be accurate to 0.6% or better (May et al., 2002; Pan et al., 1975; Thompson and Miller, 1980; Luo and Miller,

1981). A similar equation was used to calculate the EOS dielectric constant of the liquid phase. The EOS predictions for the densities and dielectric constants are presented in Table 5, while the predicted phase compositions are listed in Table 3.

## 9. Discussion and conclusion

The EOS used to estimate the densities and dielectric constants in Table 5 is a simple cubic form, untuned to any experimental data. Nevertheless, its prediction of the vapor phase densities agrees with the measured values within the experimental uncertainties. Its prediction of the liquid phase densities is, as may be expected, somewhat poorer; the discrepancy is approximately 10%. It is well known that the major failing of cubic equations of state is that they provide only very rough predictions of liquid density (Assael et al., 1999). The experimental determination of the liquid densities serves an additional purpose in that volume translation corrections, as per the method of Peneloux et al. (1982), can now be determined for the mixture. At least within the temperature range of the measurements, these volume translation corrections will enhance the performance of the EOS for this mixture.

Prediction of the dielectric constant is more sensitive to the prediction of the density than to the EOS composition used to estimate the polarizability. The EOS vapor dielectric constants essentially agree with

Table 5

Measured densities and dielectric constants and predicted EOS values at pressures and temperatures in Table 4

Phase	Measured values		EOS predictions	
	$\rho$ (kg m <sup>-3</sup> )	$\epsilon$	$\rho$ (kg m <sup>-3</sup> )	$\epsilon$
Vapor 1	124 ± 3	1.151 ± 0.006	125	1.148
Vapor 2	128 ± 2	1.166 ± 0.006	131	1.155
Condensate 1	619 ± 11	1.842 ± 0.009	545	1.711
Condensate 2	617 ± 15	1.836 ± 0.009	544	1.708

the measured values while the condensate dielectric constants differ by about 7%. With the application of the volume translation corrections derived from the liquid density measurement, an improvement in the prediction of condensate dielectric constants is to be expected, at conditions near or within the  $(T,P)$  range of the measurements.

Currently, an investigation between the degree of agreement between measured values and the predictions of various correlations and equations of state is being conducted. The combination of the industrial type PVT cell and densimeter with a microwave resonator represents a marriage of two significantly different technologies. The experimental system described here is a unique tool that provides the comparison basis for EOS-derived densities and dielectric constants.

Ultimately, however, the necessary accuracy and precision is determined by financial considerations. In a reservoir owned by a consortium, the distribution of costs and profits is based largely on the productivity of each well. The effect that the uncertainty of the flow measurements has upon the accuracy and equity of that distribution needs to be assessed, as this will determine the calibration accuracy requirements for multiphase flow meters.

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