Densities and Dew Points of Vapor Mixtures of Methane + Propane and Methane + Propane + Hexane Using a Dual-Sinker Densimeter

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A commercial density/sorption system has been converted to a dual-sinker densimeter and used to make density measurements for some light hydrocarbon mixtures in the compressed gas region and near dew-point conditions. Argon was used as a reference fluid for calibration of the measurement system. Experimental uncertainties in density for methane were estimated as $\pm(0.029\% + 0.013 \text{ kg m}^{-3})$, including claimed uncertainties in the argon reference data. Measured methane densities at temperatures of (273 to 313) K and pressures to 12 MPa agreed within combined uncertainties with a methane equation of state in the literature (claimed uncertainty of 0.03%). Densities are reported along isotherms in this same range for selected methane + propane and methane + propane + hexane mixtures with cricondentherms below 293 K. Estimated experimental uncertainties for these mixtures are slightly larger than those for pure methane, because of uncertainties in compositions. Additional isochoric experiments were performed on some of these mixtures to investigate the mass adsorbed on each sinker as dew-point conditions are approached. Significant adsorption occurred up to 2 K above the dew point for the binary mixtures and 5 K for the ternary mixtures. Adsorption progressively increased as the dew-point temperature was approached, resulting in changes in gas-phase composition and density. These experiments allowed dew-point conditions and densities to be estimated.

Introduction

Densities of hydrocarbon mixtures are important in the production, transport, and processing of natural gas and gas condensate fluids. Methods of experimental measurement of fluid densities have improved greatly in recent years. New techniques, based on Archimedes' principle applied to sinkers of known mass and volume, have been used to measure densities of pure fluids and selected mixtures with claimed uncertainties approaching 0.01%. Dual-sinker techniques have been developed which have the advantage of minimizing errors due to adsorption for pure gases near dew-point conditions. Wagner and co-workers have developed both single-sinker and dual-sinker density measurement techniques, using magnetic suspension mechanisms to isolate the balance from the measurement cell, and they have published pure-fluid studies in which the methods are described.[1−4]

The results of these accurate density determinations have been used to improve equations of state for both pure fluids and natural gas mixtures. For mixtures, such measurements are still quite restricted (data sources and compilations can be found in refs 5−8), and there is need for extending such measurements over wider ranges of composition and components.

The objective of the current experimental project is to extend accurate gas-phase mixture density measurements beyond typical natural gas compositions and to study

adsorption effects near the phase boundary at high pressures. In this first phase, some selected mixtures containing methane, propane, and hexane with cricondentherms below 20 °C are studied, both along isotherms away from the dew-point curve and along isochores that intersect this phase boundary.

Experimental System

The centerpiece of the density measurement equipment is a magnetic suspension microbalance system that is used for direct mass determinations of Archimedes sinkers. The instrument employed in the current study is a three-position sorption/density apparatus manufactured by Rubotherm (Bochum, Germany), modified to allow operation as a dual-sinker device. The balance can be read to 10 μg, with reproducibility and long-term stability about 20 μg. The operable temperature range is 190 K to 520 K, with pressures to 30 MPa.

The three-position mode illustrated in Figure 1 is used for dual-sinker density measurements. In the zero point (or tare) position, both sinkers are decoupled from the suspension mechanism and rest on their deposit screws. In measuring position 1, the lower (hollow) sinker is lifted. In measuring position 2, both the lower sinker and the upper (solid) sinker are lifted.

The two sinkers, the sinker-coupling rod, the deposit screw for the bottom sinker, and a measuring load cage spacer (part of the coupling housing suspension system, not shown in Figure 1) are all new elements that have been designed to convert the sorption/density apparatus into a dual-sinker density system. Both sinkers are constructed

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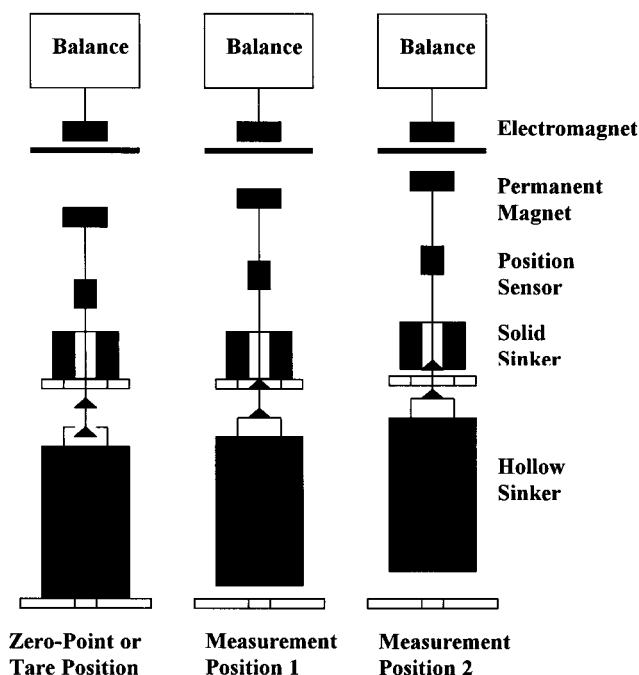† Current address: Department of Physics, University of Western Australia, Nedlands, Western Australia 6907.

Figure 1. Three-position operation for the magnetic suspension balance system.

from titanium (CP Grade 2, 99.5% minimum purity). Both have similar surface finishes, which are machined smooth but not highly polished. One is a hollow cylinder, constructed by welding flat end plates to a cylindrical section, about 1.98 cm o.d., 4.00 cm height, with a wall thickness of 0.17 cm. On the basis of construction specifications, the estimated volume, mass, and surface area of the hollow sinker are 12.3 cm³, 20.4 g, and 32.1 cm², giving an effective density of 1.66 g cm⁻³. This sinker has a titanium connector welded to its top surface, which allows it to be lifted by a cone on the bottom of the sinker-coupling rod. An adjustable deposit screw is placed in the bottom of the cell to allow the hollow sinker to be disengaged from the sinker-coupling rod when the system is operated in the zero point position.

The solid sinker (4.51 g cm⁻³ approximate density) is a short cylinder, 1.85 cm o.d., 1.94 cm height, with a 0.50 cm diameter hole along its axis. It has a number of 1.0 mm diameter holes drilled part way through to provide the required additional surface area. On the basis of construction specifications, its estimated volume, mass, and surface area are 4.5 cm³, 20.3 g, and 32.1 cm². It is lifted by a second cone, located some distance above the lower cone on the sinker-coupling rod. This solid sinker replaces the titanium sinker of similar shape that was provided with the simultaneous sorption/density apparatus, with both its deposit screw and lift mechanism remaining unchanged.

For each fixed fluid state, the balance is calibrated using its internal standard masses and then (m_0, m_1, and m_2) are determined multiple times, allowing accurate apparent mass determinations for each sinker. The apparent mass of the hollow sinker is calculated from the zero point and measuring position 1 readings of the balance as follows:

$$m_{HS}^{app} = (m_1 - m_0)\left(1 - \frac{\rho_{air}/(kg\ m^{-3})}{8000}\right) \quad (1)$$

An equation identical to eq 1, with ($m_2 - m_1$) replacing ($m_1 - m_0$), gives the apparent mass of the solid sinker. The last factor on the right hand side is needed to correct for

buoyancy effects on the balance internal calibration masses (density 8000 kg m⁻³). Air temperature, barometric pressure, and relative humidity are measured to evaluate ρ_{air} using the ideal gas law. As an alternative, this buoyancy correction factor can be evaluated by measuring the change in balance reading when two external masses (one titanium and the other tantalum) having identical volumes are interchanged on the balance.

The density of a fluid is given in terms of true mass (m^{true}), adsorbed mass (m^{ad}), apparent mass (m^{app}), and volume (V) of either sinker.

$$\rho = \frac{m^{true} + m^{ad} - m^{app}}{V} \quad (2)$$

Using the dual-sinker approach, and assuming any adsorption occurs in the same amount on both sinkers, density is related to differences in mass and volume between the two sinkers.

$$\rho = \frac{\Delta m^{true} - \Delta m^{app}}{\Delta V} \quad (3)$$

The sinker volumes are written in terms of volumes at zero pressure and standard temperature ($t_0 = 0$ °C).

$$V = V_0°(1 + \alpha t)(1 - \beta P)$$

$$\Delta V = \Delta V_0°(1 + \alpha t)(1 - \beta P) \quad (4)$$

In these equations, the four parameters (m^{true}, $V_0°$, α, and β) are different for each individual sinker and for the difference form used in the dual-sinker measurements. These parameters are determined by calibration, using argon as the reference fluid, at conditions where adsorption can be neglected. Reference densities are taken from the equation of state of Tegeler et al.,[9] which has a claimed uncertainty of 0.02%. This equation of state agrees with the data of Klimeck et al.[4] within 0.01%. To first order, this calibration eliminates such effects as nonlinearities in the balance and the magnetic coupling. For example, these and other sources of systematic error may cause the small values of α determined by calibration to differ somewhat from the coefficients of thermal expansion listed in standard references for pure titanium.

If measurements are made under conditions where adsorption on the sinkers is significant, then different densities are calculated for the solid sinker and the hollow sinker (based on eq 2, neglecting the adsorption term). Assuming the adsorbed amount is the same on both sinkers, the mass adsorbed on either of the sinkers can be estimated from any of the following relations, where ρ is the dual-sinker density:

$$m^{ad} = \frac{(\rho_{HS} - \rho_{SS})}{\left(\frac{1}{V_{SS}} - \frac{1}{V_{HS}}\right)} = V_{HS}(\rho - \rho_{HS}) = V_{SS}(\rho - \rho_{SS}) \quad (5)$$

Pressures are measured with an oscillating quartz gauge, calibrated against an oil-operated piston gauge, and are believed to have an uncertainty of ±(0.015% + 0.001 MPa). The temperature of the density measurement cell is controlled by circulation of a constant temperature fluid through jackets surrounding the cell and coupling housing. These jackets are insulated from the surroundings. Temperatures are measured with a calibrated platinum resistance thermometer and have an estimated uncertainty of ±0.02 K.

Table 1. Argon Calibration Results for Sinker Parameters

	single sinker			dual sinker	
parameter	hollow sinker parameter	solid sinker parameter	parameter	from calibration	from single-sinker parameters
$\alpha/°C^{-1}$	1.504×10^{-5}	1.707×10^{-5}	$\alpha/°C^{-1}$	1.392×10^{-5}	1.388×10^{-5}
β/MPa^{-1}	0.910×10^{-5}	0	β/MPa^{-1}	1.450×10^{-5}	1.432×10^{-5}
m^{true}/g	20.98629	20.45639	$\Delta m^{true}/g$	0.52988	0.52990
$V_0°/cm^3$	12.4376	4.5361	$\Delta V_0°/cm^3$	7.9015	7.9015
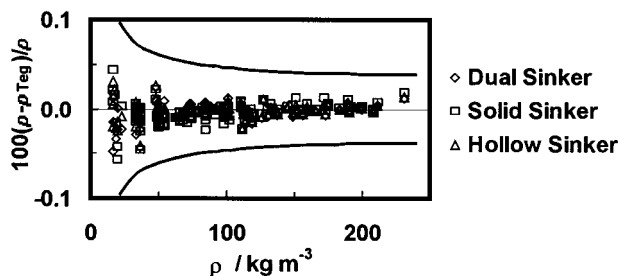
Figure 2. Percent differences between regressed experimental argon densities (ρ) and reference values from the equation of state of Tegeler et al.[9] (ρ_{Teg}): $-$, estimated uncertainties in the current measurements.

Figure 3. Percent differences between experimental methane densities (ρ) and values from the equation of state of Setzmann and Wagner[11] (ρ_{Set}): $-$, estimated uncertainties in the current measurements.

Gas mixtures are prepared directly by mass in high-pressure 500 cm^3 sample cylinders, using a 2 kg capacity balance with an uncertainty of $\pm$2 mg. Mixing is accomplished by shaking, a metal ball having been placed inside each cylinder. Mixture mole fractions have an estimated uncertainty of $\pm$0.0001.

Calibration Results

Experiments were performed on research grade argon with a stated minimum purity of 99.9995 mol %. Impurities have been estimated to have a negligible effect on reported densities. Altogether, 98 data points were measured on five evenly spaced isotherms between 273 K and 313 K, with pressures to 12 MPa.

Measured argon densities were forced to agree with the reference equation of state[9] by using the method of least squares to determine the best values of the sinker parameters. Three separate fits were made, one for each individual sinker and one for the dual-sinker system. The parameters determined are listed in Table 1 (columns two, three, and five). Also listed are dual-sinker parameters calculated from the single-sinker parameters (column six). As can be seen, there is internal consistency between the three sets of parameters. The standard deviation for the dual-sinker fit was 0.01%, and the standard uncertainties in the primary coefficients were $\pm$0.000 03 g for Δm^{true} and $\pm$0.0008 cm^3 for $\Delta V_0°$.

In addition, the true masses of the individual sinkers were directly measured under vacuum conditions in nine separate experiments, over a range of temperatures, with the mean values obtained within (20 to 30) μg of the calibration results shown above. The mean of the differences in mass between the two sinkers was found to be 0.529 90 g (with a standard deviation of 20 μg), which agrees with the dual-sinker calibration Δm^{true} within $\pm$20 μg.

A residual plot for all the argon data is shown in Figure 2. There are points for each individual sinker and for the dual-sinker approach. The three regressions bring the residuals for all data points well within the estimated experimental uncertainties for argon densities of $\pm$(0.028% + 0.018 kg m^{-3}). Slightly greater scatter occurs for the solid sinker.

Improved accuracies are possible, using sinkers of greater volume difference. This could be accommodated by using
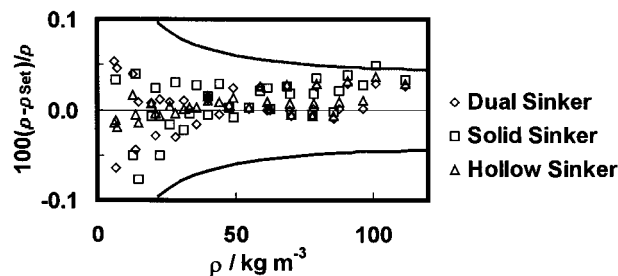
different density materials for construction of the sinkers, combined with identical plating of both, as suggested by McLinden and Frederick.[10]

At one point during the subsequent mixture measurements, it became apparent that the mass of the solid sinker had suddenly decreased by about 200 μg, probably by having lost a very small filing from one of the holes. Additional pure fluid and vacuum density data were taken to provide modified sinker true masses, with little change in estimated accuracy for the density measurements reported.

Methane Measurements

To evaluate the measurement system, densities were determined for research grade methane (99.99% minimum purity). Using the maximum possible concentrations for the impurities ethane, propane, carbon dioxide, and nitrogen (as stated by the gas supplier), the maximum effect of impurities on densities in the range of the current measurements was estimated to be 0.004%. The estimated uncertainties for measured densities of methane are $\pm$(0.029% + 0.013 kg m^{-3}). This includes estimates of uncertainties in sinker parameters, temperature, pressure, composition, reference densities, and fit to the reference densities. Densities were measured at a total of 45 different conditions, over the same temperature and pressure ranges as used in the argon calibration.

The methane data have been compared with the equation of state of Setzmann and Wagner,[11] which has a claimed uncertainty of $\pm$0.03%. By using the dual sinker, the hollow sinker, and the solid sinker methods, the average absolute deviations between the current results and the literature equation of state are 0.02%, 0.01%, and 0.03%, respectively. In Figure 3, the deviations are plotted against density for all temperatures and pressures. All except one solid sinker point lie within the estimated experimental uncertainty curves. All points lie within the combined uncertainties of the experiments and the equation of state. There does appear to be a small systematic trend in the deviations with increasing density.

Mixture Densities on Isotherms

All mixtures were prepared using the same research grade methane used for the pure methane studies. Re-

Table 2. Mixture Mole Fraction Compositions and Average Molecular Weights

	mixture 1	mixture 2	mixture 3	mixture 4	mixture 5
methane	0.9330	0.8419	0.7931	0.9150	0.9397
propane	0.0670	0.1581	0.2069	0.0790	0.0525
hexane				0.0060	0.0078
avg MW	17.923	20.478	21.847	18.680	18.063

Table 3. Mixture Densities on Isotherms

	T/K	P/MPa	ρ/kg m^{-3}	T/K	P/MPa	ρ/kg m^{-3}
mixture 1	289.98	2.346	18.50	313.02	0.936	6.57
	289.99	3.013	24.18	313.02	2.020	14.45
	290.00	4.193	34.72	313.03	3.019	22.01
	289.99	5.105	43.31	313.02	4.022	29.88
	289.98	6.123	53.39	313.02	5.025	38.03
	289.99	7.056	63.05	313.02	6.021	46.41
	289.98	7.123	63.76	313.02	7.031	55.16
				313.03	7.903	62.90
mixture 2	278.30	2.841	28.30	297.08	6.994	73.86
	278.30	4.248	45.31	297.08	7.982	87.31
	278.30	5.111	57.04	297.08	8.741	98.09
	278.31	5.990	70.15	313.13	2.128	17.67
	278.31	6.989	86.54	313.13	3.029	25.76
	278.31	7.834	101.57	313.13	4.073	35.67
	297.08	2.993	27.31	313.13	5.048	45.43
	297.06	3.993	37.76	313.13	6.082	56.35
	297.08	4.994	48.98	313.13	7.370	70.72
	297.10	6.017	61.26	313.12	8.093	79.13
	297.09	6.993	73.85	313.12	9.491	95.97
mixture 3	284.58	2.972	31.40	288.20	9.633	142.06
	284.60	4.004	44.71	293.36	1.917	18.44
	284.62	5.011	59.35	293.36	3.005	30.30
	288.17	3.019	31.37	293.36	4.032	42.60
	288.17	4.004	43.72	293.35	5.026	55.78
	288.19	5.008	57.71	293.34	6.023	70.34
	288.20	6.020	73.55	293.35	7.019	86.27
	288.20	7.027	91.02	293.35	8.184	106.64
	288.21	8.028	110.01	293.35	8.971	121.12
	288.20	9.033	130.00	293.35	10.049	141.33
mixture 4	293.93	2.915	23.98	303.11	9.007	82.40
	293.93	4.317	36.95	303.10	9.720	90.18
	293.93	5.150	45.11	313.16	2.080	15.59
	293.93	6.344	57.47	313.15	4.028	31.27
	293.93	8.086	76.94	313.15	5.073	40.21
	303.11	3.007	23.84	313.15	6.195	50.23
	303.11	4.011	32.59	313.15	7.173	59.32
	303.12	5.009	41.73	313.15	8.266	69.86
	303.11	6.009	51.31	313.15	9.439	81.61
	303.11	7.010	61.33	313.15	10.179	89.13
	303.11	8.020	71.83			
mixture 5	297.56	1.944	14.65	297.57	7.259	62.68
	297.65	3.011	23.48	297.58	8.128	71.58
	297.58	4.047	32.37	297.58	9.138	82.28
	297.57	5.030	41.18	297.58	10.082	92.57
	297.58	6.660	56.71			

search grade propane was used with a minimum stated purity of 99.991 mol %. The hexane was actually a mixture of C_6 hydrocarbons, containing 86.1% hexane, 9.7% methylcyclopentane, and 4.2% 3-methylpentane. Other compounds totaled less than 0.1 mol %, and the water content was less than 0.002%. This hexane sample was obtained from the supplier in a sealed container under nitrogen gas, and it was degassed by freezing and evacuation before use. The difference between pure hexane and the C_6-blend used is estimated to affect the reported densities by less than ±0.02% and dew points by less than ±0.05 K.

Five mixtures were studied, three methane + propane mixtures and two methane + propane + hexane mixtures. The mole fraction compositions and average molecular weights are given in Table 2. Estimated experimental uncertainties in measured densities are ±(0.036% + 0.013 kg m^{-3}) for the methane + propane mixtures and ±(0.058% + 0.013 kg m^{-3}) for methane + propane + hexane mixtures. These mixture uncertainties are larger than those for pure methane due to larger effects of uncertainties in mixture compositions.

All mixtures were studied along isotherms at conditions far enough from the dew point curve so that adsorption effects were negligible. The isothermal dual-sinker density data under such conditions are presented in Table 3.

Mixture 1 was studied to compare results from the current experimental system with previous accurate mixture measurements using a dual-sinker densimeter (see Ruhrgas data in ref 5). Densities were measured along two isotherms (near 290 K and 313 K), at pressures to 8 MPa. The cricondentherm for this mixture is near 240 K; thus, these studies were at conditions well away from the two-phase region. Since the composition of mixture 1 is not exactly the same as that studied previously, intercomparisons were done by comparing deviations from the model of Lemmon and Jacobsen.[6,7] In Figure 4, best estimates of percent deviations of the mixture 1 data from the Ruhrgas data are plotted versus density for the two isotherms studied in the current work. All deviations are within the estimated uncertainties for the current work (shown as solid curves in Figure 4), with average absolute deviations of 0.03% at 290 K and 0.05% at 313 K. The larger value at 313 K is heavily influenced by the current measurement at 6.6 kg m^{-3}, which has an estimated experimental uncertainty of ±0.24%.

Isothermal densities for all binary mixtures are compared with the Lemmon model in Figure 5. As propane content increases, the deviations between experiment and model become progressively larger, averaging about 0.3% for mixture 3. Also, there appears to be significant temperature dependence to the deviations. It should be noted that high-accuracy data were not available for propane contents larger than 10 mol % when the model was developed.

For mixture 3, three isotherms were measured. No significant adsorption (m^{ad} detection limit ≈ 100 μg) was observed for the 293.4 K isotherm. On the 288.2 K isotherm, small amounts of adsorption could be detected (m^{ad} ≈ 300 μg) at pressures near 8 MPa, with negligible
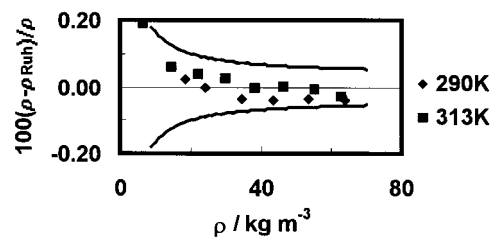

Figure 4. Estimated percent deviations of mixture 1 measured densities (ρ) from the Ruhrgas[5] measured densities (ρ_{Ruh}) at similar compositions and temperatures: −, estimated uncertainties in the current measurements.

amounts both above and below this pressure. The 284.6 K isotherm is very close to the cricondentherm temperature. The calculated adsorbed mass on each sinker was negligible at low pressures and increased at pressures above 5 MPa, to 1400 μg at 6.6 MPa, where this isotherm was terminated. Densities at pressures above 5 MPa are not reported for this isotherm because of this effect.

Isothermal densities are compared with the Lemmon model for the two ternary mixtures in Figure 6. Deviations from the model are similar for both mixtures, within about 0.1%, which is an indirect indication of internal agreement in the measured densities for these mixtures. The average absolute deviation between experiment and model is about
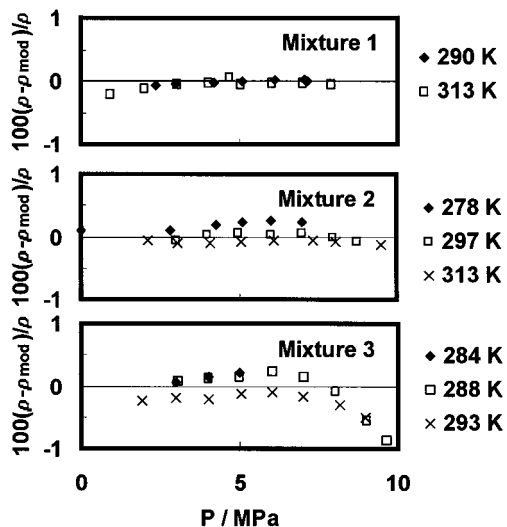
Figure 5. Percent differences between experimental densities (ρ) and Lemmon[7] model predictions (ρ_{mod}) for binary mixtures.
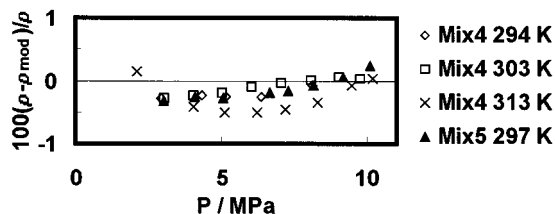

Figure 6. Percent differences between experimental densities (ρ) and Lemmon[7] model predictions (ρ_{mod}) for ternary mixtures.

0.3%, similar to that for the 20 mol % propane binary mixture.

Isochoric Densities and Dew Points

All mixtures except mixture 1 were studied along at least one "isochore", by isolating a sample in the density cell and varying the temperature from well above the dew point to well inside the two-phase region. The primary purpose of taking these data was to investigate adsorption phenomena and dew-point conditions for these mixtures at high pressures. The isochoric density data are not presented here, because the points at temperatures where negligible adsorption was present do not add significantly to the isothermal data. Densities at conditions with significant adsorption are specific to the particular experimental system used and are not reproducible in other equipment.

Isochoric measurements were fully automated, with temperature programmed and measurements taken every 15 min, so that the approach to equilibrium could be observed in all cases. It was determined that 4 h was sufficient equilibration time after a small temperature change, and this was used for all measurements. At temperatures above the dew point, only minor differences were noted between data taken with increasing temperature and data taken with decreasing temperature.

To smooth the data and make determinations of dew points more accurate, small corrections (less than 0.05%) were made to the "isochoric" dual-sinker densities for variations in room temperature. A small fraction of the sample volume is outside the thermostat, resulting in changes in system pressure as room temperature changes, even at constant cell temperature. These corrections were based on isochoric measurements with pure methane in the cell, under varying room-temperature conditions, in
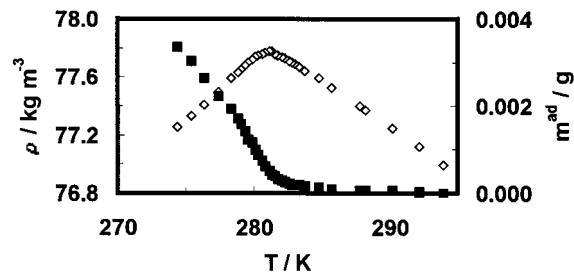

Figure 7. Density (ρ, $\diamond$) and mass adsorbed (m^{ad}, $\blacksquare$) on each sinker versus temperature for an "isochore" (ternary mixture 4).

essence allowing the volume ratio to be determined for lines external and internal to the thermostat.

A typical isochore is shown in Figure 7. Plots of dual-sinker density and mass adsorbed versus temperature are presented for ternary mixture 4. For all isochores, as the temperature decreases from the highest temperature, the single-phase density actually increases slightly, due to contractions in the density cell, combined with a shift in distribution of sample between the small room-temperature portion and the large thermostated portion of the cell. At some distance above the dew point, significant adsorption starts to appear on the sinkers, and the measured densities start to fall below a straight-line relationship with temperature.

The cause of these density deviations is adsorption on the sinkers and cell internal walls. As adsorption on these surfaces increases, the total amount of material in the gas phase decreases and, thus, the density decreases. Furthermore, this adsorption causes the composition of the remaining gas-phase sample to change. Thus, even though the dual-sinker densities measured at temperatures just above the dew point are presumably correct, they are for fluids with compositions depleted of the heavier components as compared to the original mixture. This phenomenon was described by Pieperbeck et al.[2] and represents an inherent systematic error when a finite-volume system is used to measure dew points.

Pressure versus temperature plots along the isochores of the current work are very nearly straight lines, with no appreciable change in slope at the dew point. The tendency for the pressure to drop as adsorption/condensation occurs, resulting in fewer total moles in the gas phase, is compensated by the pressure increase due to increasing gas-phase mole fraction of methane. Rowlinson and co-workers[12] have shown this straight-line behavior to be rigorous, if the isochore has a dew point at the cricondentherm temperature.

For the binary mixtures, significant adsorption was measured at temperatures less than about 2 K above the dew point, whereas, for the two ternary mixtures, this region was larger, about 5 K. That is, the addition of hexane to the sample results in a longer adsorption tail at temperatures above the dew point.

In fact, the adsorbed film thickness on the sinkers can be estimated from the measured mass adsorbed, assuming uniform coverage. Such an estimate results in a film thickness of the order 10^{-7} m (roughly 100 molecular layers), corresponding to the limit of detection of adsorption (about 100 μg). If the assumption of uniform coverage were true, there would already exist vapor–liquid equilibrium in these systems at temperatures significantly above the conventional dew points.

It is more likely that the measured adsorption occurs in areas of imperfections (roughness, scratches, and/or sharp internal angles) on the sinkers, and the phase equilibrium
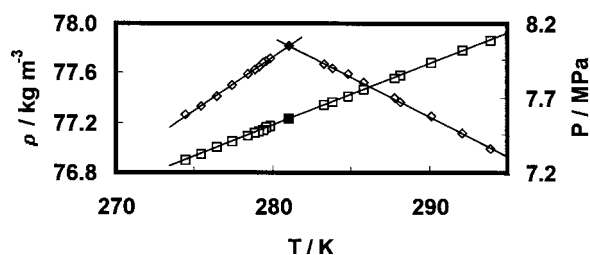
Figure 8. Density (ρ, $\diamond$) and pressure (P, $\square$) versus temperature along an "isochore": an illustration of dew point properties estimation (solid points) for ternary mixture 4.

Table 4. Estimated Dew Point Properties with Estimated Uncertainties

	T/K	P/MPa	ρ/kg m^{-3}
mixture 2	272.9 ± 0.2	7.474 ± 0.016	101.55 ± 0.12
mixture 3	284.6 ± 0.2	6.591 ± 0.007	86.25 ± 0.14
mixture 4	281.0 ± 0.2	7.557 ± 0.006	77.82 ± 0.05
mixture 5	288.6 ± 0.4	4.862 ± 0.010	41.61 ± 0.04

is modified by curved liquid surfaces. The scale of roughness (machine marks and other imperfections) on the current sinkers is likely on the order of 10^{-6} m, providing a highly uneven surface for a film with an order of magnitude smaller average thickness. When the measured adsorption becomes as large as (2 to 3) mg (Figure 7), then there are likely areas of continuous liquid film on the sinkers. A rather uniformly distributed "roughness" effect, as discussed extensively by Mehl and Moldover[13] relative to acoustic resonator experiments, could account for the fact that the measured adsorption is nearly the same on both sinkers (various forms of eq 5). If significant, scratches or sharp angles likely would lead to different adsorption behavior for the two sinkers used in the current work. These effects need to be studied using sinkers with smoother surfaces and simpler geometry.

At temperatures below the dew point, measured densities decrease with a decrease in temperature, as progressive condensation occurs in the two-phase region (again refer to Figure 7). It was possible to take the two-phase system at the lowest temperature measured, increase the temperature back to the highest temperature on the isochore, hold this temperature for 24 h, and closely reproduce the measured single-phase density at that point. This was accomplished for both mixtures 4 and 5, without any active mixing in the cell. Duplicate isochores were determined for mixture 5, with differences in results only noticeable in the two-phase region. Also, a second sample of mixture 5 was isolated in the cell at nearly the same conditions, and a third isochore was determined. When corrected for small pressure differences, the density versus temperature curve was nearly identical to the previous isochores.

Dew points can be estimated from the intersection of lines drawn through the straight-line portions of the density curves above and below the maximum density point. The method is illustrated in Figure 8 for mixture 4, where density and pressure are plotted versus temperature, and linear fits of the selected data are used to estimate dew-point conditions. The adsorption curve can be used in conjunction with the density curve to confirm estimates of dew points. Note that the dew point (Figure 8) is near a rather dramatic rise in the adsorption curve (Figure 7). This rise was even more dramatic for methane + propane mixtures, and the adsorption curves showed more irregular behavior in the two-phase region for these binary mixtures.

Dew points were estimated from the isochoric measurements for mixtures 2–5, and these data are presented in Table 4. The estimated accuracy of the reported dew-point temperatures varies from 0.2 K to 0.4 K (0.07% to 0.14%), depending on the amount and extent of data taken for each isochore. The corresponding percentage uncertainties in the reported pressures and densities are about 0.1% to 0.2%. By taking sufficient data, dew points (P, T, ρ) can be

obtained from the current experimental system with uncertainties of 0.1% or better in all three properties.

All reported dew-point temperatures are within 0.5 K of calculations based on the Peng–Robinson equation of state, except for mixture 5, where the experimental value is 2.5 K below the equation of state prediction. Due to the close proximity of this sample to its dew-point temperature when held at room temperature, it is possible that adsorption on the sample cylinder walls caused the actual mixture in the density cell to be very slightly leaner than indicated by the reported composition. Binary parameters for all Peng–Robinson calculations were taken as 0.007 48, 0.023 98, and 0.005 57 for methane + propane, methane + hexane, and propane + hexane, respectively.

Recent dew-point measurements of Blanco et al.[14] for (0.89 methane + 0.07 ethane + 0.04 butane) are 2 K to 5 K higher than Peng–Robinson calculations in the range of pressures in Table 4. These differences are 4–10 times larger than uncertainties due to composition for their mixture. Unfortunately, no total experimental uncertainties were reported.

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