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Experimental Data on Binary and Ternary Mixtures of Perfluoromethylcyclohexane with Methane and *n*-Decane at 373.15 K

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The phase and volumetric measurements of perfluoromethylcyclohexane + methane and perfluoromethylcyclohexane + *n*-decane and their ternary mixtures at 373.15 K and over a wide range of concentration are presented. The ternary mixtures are used to carry out a constant composition expansion test at 373.15 K. Measurements are made on the liquid bubble point and retrograde dew point pressures and on the single-phase density of the binary mixtures. A high-pressure high-temperature oscillating tube densitometer is used to measure the density.

Introduction

Perfluorocarbons (PFCs) have been widely used as tracers in industry to obtain important information for design and operation of many processes. The successful application of PFC compounds as tracers is due to chemical inertness, high thermal stability, and high detectability by gas chromatography using an electron capture detector (ECD). Cyclic PFCs have been used in air quality investigation to trace the air flow in environmental studies.[1] In the oil industry, tracers are employed to acquire valuable information to aid in the design of enhanced hydrocarbon recovery plans. Tracer application can provide reservoir management with the pattern and rate of movement of injected fluids in the reservoir, barriers to flow, heterogeneities in the reservoir, and sweep efficiency of the treatment.

Application of non-radioactive tracers, particularly PFCs in tracing injection gases in reservoirs, has been increasing in the oil industry since 1990. The PFC tracers have been applied in several fields in the North Sea. Two PFC tracers, including perfluoromethylcyclohexane (PMCH), were used to improve the evaluation of a water-alternating-gas (WAG) pilot in the Gullfaks field, where the results of the tracer study were used to interpret the WAG pilot mechanism and communication in the area.[2] A multiple tracer injection scheme was employed in two off-shore fields, Gullfaks and Sleipner, in the North Sea. The results from tracer injection were used to clarify fluid communication routes in the pilot area. It also proved some communication between layers and faults blocks, which had been previously neglected.[3]

Experimental data on phase and volumetric behavior of PFCs and hydrocarbons are scarce in the literature. Genco et al.[4,5] studied a series of binary systems composed of the isomers of hexane with PMCH to determine the effect of molecular structure on the phase diagrams of such mixtures. Bernardo-Gil and Soares[6] measured the mutual solubility of PMCH with some liquid hydrocarbons over a range of temperature. Bernardo-Gil et al.[7] reported vapor−liquid equilibrium data on PMCH + 1-hexene and PMCH + *n*-hexane binary mixture at 328.15 K.

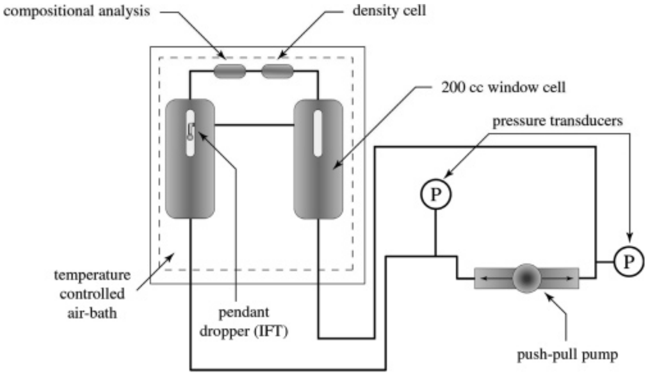

Figure 1. Schematic representation of the vapor−liquid equilibrium (VLE) experimental facility.

In this paper, experimental data on binary and ternary mixtures of PMCH, methane, and *n*-decane at 373.15 K and over a range of concentrations are presented. The measured data on the binary mixtures consist of the liquid bubble point pressures, retrograde dew point pressures, and the single-phase density. The phase and volumetric behavior of the ternary mixtures are studied through carrying out constant composition expansion tests at 373.15 K.

Experimental Section

Materials. In this study perfluoromethylcyclohexane (Apollo Scientific, 95 % by mass, impurities: other perfluorocarbons), methane (Air Products, 99.995 %, by volume), and *n*-decane (Aldrich, 99+ % by mass) were used as supplied.

Apparatus. A vapor−liquid equilibrium (VLE) facility was used to make the measurements. Figure 1 gives the general layout of the main components of the VLE experimental facility. The rig consists of two inter-connected PVT windowed cells of approximately 200 cm^3 volume. The pressure medium is mercury, and it is generated by two electrically driven single-piston pumps, each has a volume of 250 cm^3. The equilibrium pressure is measured using two Quartzdyne pressure transducers that can measure pressure to within 6 Pa with a maximum full-scale error

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Table 1. Molar Composition and Saturation Pressure (p_{sat}) of PMCH + Methane Mixture at 373.15 ± 0.1 K

PMCH	methane	p_{sat}	
%	%	MPa	type[a]
79.90 ± 0.06	20.10 ± 0.06	4.90 ± 0.06	p_b
49.99 ± 0.07	50.01 ± 0.16	12.76 ± 0.03	p_b
30.00 ± 0.06	70.00 ± 0.25	16.56 ± 0.02	p_b
25.00 ± 0.06	75.00 ± 0.28	16.73 ± 0.02	p_b
20.01 ± 0.05	79.99 ± 0.30	16.69 ± 0.02	p_d
15.00 ± 0.04	85.00 ± 0.33	16.15 ± 0.03	p_d
10.08 ± 0.03	89.92 ± 0.36	13.86 ± 0.03	p_d

[a] p_b = bubble point pressure, p_d = Retrograde dew point pressure.

of 0.006 %. The transducers are self-adjusting for the atmospheric temperature and pressure, and they are calibrated against fully traceable standards (NAMAS standards). The pumps are fitted with two Mitutoyo linear scales that allow volume to be displayed on a Mitutoyo digital readout to a resolution of 0.01 cm^3. The upper pressure limitation is approximately 38 MPa, which is governed by the operational limit of valves and piping work for composition and density measurements (online density/compositional sampling).

Between the two PVT cells is located an Anton Paar 512 density cell, which allows for the direct measurement of vapor and liquid density at test conditions. The upper pressure limit of this unit is 40 MPa, and the temperature operating range is from 253.15 K to 423.15 K.

The VLE experimental facility is equipped with a direct sampling system, located between the two PVT cells, allowing online phase composition measurements.[8] The general layout, valve configurations and pressure, and temperature limitations of this unit can be found elsewhere.[9]

The majority of these components are held inside a temperature-controlled air bath, the temperature of which can be maintained to ± 0.1 K. The four electrical heaters within the air bath are controlled by an Eurotherm 2404 precision controller.

Light is provided within the VLE facility by an electronic fiber optic light source. The principal advantage of this system being that the light provided is from a "cold source" so any possibility of the light source acting as a source of heat is eliminated, which allows for much greater temperature stability within the oven.

Visual information from the cells is obtained by the use of a color video camera, which is mounted on a moveable platform on the front of the VLE facility. This allows the camera to be moved up and down so that volumetric measurements and visual observations of the study fluid can be obtained from within the cells. The image is displayed on a high-resolution monitor and can be recorded onto videotape using a video recorder.

Results

Perfluoromethylcyclohexane* + *Methane. In the first series of measurements, the saturation pressure of perfluoromethylcyclohexane (PMCH) + methane (C_1) binary mixtures was measured at 373.15 K. The mixture was prepared by loading the VLE facility with a known volume of PMCH. After stabilization at 373.15 K, the density of PMCH was measured at 34.47 MPa to be 1770 (± 0.5) kg/m^3. Known volumes of methane (at 373.15 K and 34.47 MPa) were then added to the system in several stages to generate PMCH + C_1 binary mixtures with various concentrations of constituents. At each stage after methane addition, the mixture was pressurized to single-phase, and it was thoroughly mixed. Then the saturation pressure of the mixture was measured visually at each stage. Table 1 presents the measured saturation pressure of the mixtures along with their molar composition. The measured saturation pressure data are also plotted against concentration of methane in the mixture in Figure 2. The binary mixtures containing (70 to 80) mol % methane exhibited a near critical behavior at the test conditions, with major phase changes by lowering the pressure below the saturation value. Therefore, the accuracy of the measured saturation pressure of these mixtures was within the accuracy of the pressure measurement. The mixture containing 75.00 mol % methane exhibited liquidlike behavior with the bubble point measured at 16.73 MPa, whereas the mixture containing 79.99 mol % methane exhibited gaseous behavior with a retrograde dew point pressure measured at 16.69 MPa (Table 1 and Figure 2). This suggests the critical composition of PMCH + methane binary mixture at 373.15 K should be between the above-mentioned concentrations of methane with the critical pressure around 16.71 MPa.

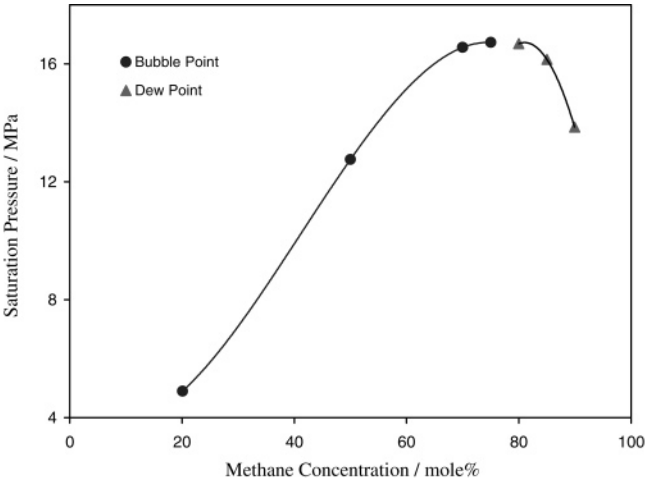

Figure 2. Measured saturation pressure of PMCH + methane mixtures at 373.15 ± 0.1 K.

Table 2. Molar Composition, Single-Phase Density, and Bubble Point Pressure (p_b) of PMCH + *n*-Decane Mixture at 373.15 ± 0.1 K

PMCH	*n*-decane	density[a]	p_b
%	%	kg/m^3	MPa ± 0.005
80.01 ± 0.04	19.99 ± 0.02		0.300
43.72 ± 0.03	56.28 ± 0.05	1115 ± 0.5	0.287
19.99 ± 0.01	80.01 ± 0.07		0.258

[a] At 34.47 MPa.

Table 3. Constant Composition Expansion Test of PMCH + *n*-Decane (56.28 mol %) Mixture at 373.15 ± 0.1 K

p/MPa ± 0.02	total vol[a] ± 0.1 %	liquid fraction (V_{liquid}/V_{total}) % ± 0.05
0.58	0.998	
0.46	0.998	
0.37	0.998	
0.32	0.999	
0.29	1.000	100.00
0.28	1.017	
0.27	1.108	88.66
0.26	1.226	80.20
0.24	1.418	69.39
0.23	1.573	62.67
0.23	1.670	59.05

[a] Relative to the volume at the bubble point.

Table 4. Molar Composition, Single-Phase Density, and Saturation Pressure (p_{sat}) of PMCH + Methane + *n*-Decane Mixture at 373.15 ± 0.1 K

PMCH	*n*-decane	methane	density[a]	p_{sat}	
%	%	%	kg/m^3	MPa	type
34.86 ± 0.03	44.87 ± 0.04	20.27 ± 0.05	1058 ± 0.5	4.52 ± 0.02	p_b
19.58 ± 0.03	25.20 ± 0.05	55.22 ± 0.19	883 ± 0.5	15.17 ± 0.02	p_b
1.38 ± 0.01	1.78 ± 0.01	96.84 ± 0.41	234 ± 0.5	20.96 ± 0.1	p_d
11.21 ± 0.07	1.60 ± 0.01	87.19 ± 0.35	549 ± 0.5	23.01 ± 0.05	p_d

[a] At 34.47 MPa.

Table 5. Constant Composition Expansion Test of PMCH + *n*-Decane + Methane Mixture at 373.15 ± 0.1 K[a]

p/MPa ± 0.02	total vol[b] ± 0.1 %	liquid fraction (V_{liquid}/V_{total}) % ± 0.05
6.72	0.988	
5.62	0.993	
4.92	0.996	
4.69	0.998	
4.52	1.000	100.00
4.49	1.001	
4.35	1.026	
4.14	1.065	91.55
4.07	1.079	89.97
3.79	1.141	84.29
3.45	1.231	77.58
3.10	1.342	70.56

[a] PMCH: 34.86 mol %, n-C$_{10}$: 44.87 mol %. [b] Relative to the volume at the bubble point.

Table 6. Constant Composition Expansion Test of PMCH + *n*-Decane + Methane Mixture at 373.15 ± 0.1 K[a]

p/MPa ± 0.02	total vol[b] ± 0.1 %	liquid fraction (V_{liquid}/V_{total}) % ± 0.05
34.47	0.907	
19.31	0.972	
17.24	0.985	
16.55	0.990	
15.86	0.995	
15.17	1.000	100.00
14.48	1.033	90.77
13.79	1.069	85.39
13.10	1.109	80.04
12.41	1.155	75.16
11.72	1.204	70.80

[a] PMCH: 19.58 mol %, n-C10: 25.20 mol %. [b] Relative to the volume at the bubble point.

Perfluoromethylcyclohexane + n-Decane. The VLE facility was used to measure phase and volumetric behavior of perfluoromethylcyclohexane (PMCH) + *n*-decane mixture at 373.15 K. The binary mixture was prepared, where a known amount of PMCH was loaded into the cell and its density measured at 34.47 MPa and 373.15 K using our in-line high-pressure, high-temperature densitometer (1770 (± 0.5) kg/m^3). Known volumes of *n*-decane (n-C$_{10}$, at 373.15 K and 34.47 MPa) were then added to the cell in three stages, and the bubble point pressure of the resulted mixtures were visually measured. Table 2 presents the single-phase composition and the measured bubble point pressures of the studied mixtures. The measured bubble points are considerably higher than the vapor pressure of PMCH (0.202 MPa) and *n*-decane (9.56 kPa) at this temperature.[10,11]

The single-phase density of one of the mixtures (containing 43.72 mol % PMCH) was also measured at 1115 (± 0.5) kg/m^3 (at 34.47 MPa). A constant composition expansion (CCE) test was made on this mixture, which confirmed the observed saturation pressure. The measured volumetric CCE data of the mixture containing 43.72 mol % PMCH are presented in Table 3.

Perfluoromethylcyclohexane + Methane + n-Decane. The phase and volumetric behavior of four PMCH + n-C$_{10}$ + C$_1$ ternary mixtures was investigated at 373.15 K using the VLE facility. The phase and volumetric behavior of hydrocarbon binary n-C$_{10}$ + C$_1$ is reported in the lieterature.[12] A previously studied PMCH + n-C$_{10}$ mixture (containing 43.72 mol % PMCH, see previous section) was used as a base, and known volumes of methane were incrementally added (at 373.15 K and 34.47 MPa) to the system in three stages. In the fourth stage, PMCH (at 373.15 K and 34.47 MPa) was added to the mixture to generate a retrograde gas system. In each stage, the mixture was thoroughly mixed and stabilized prior to saturation pressure and single-phase density measurements. The measured data and molar composition of studied mixtures are given in Table 4.

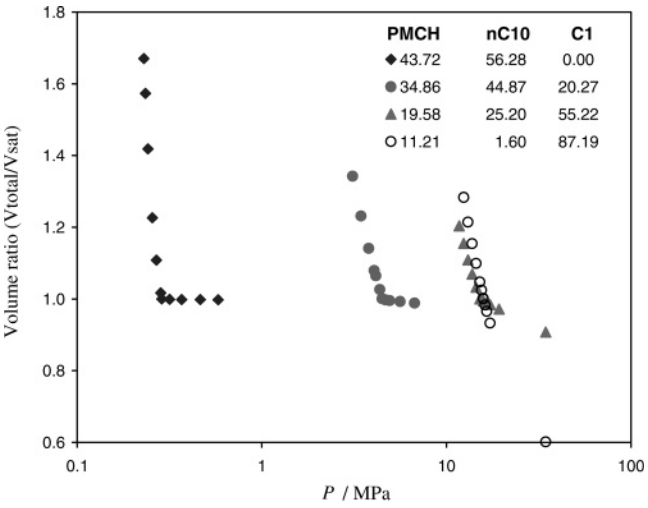

Figure 3. Measured $p-V$ data of PMCH + *n*-decane + methane mixtures at 373.15 ± 0.1 K. Molar composition of PMCH, *n*-decane, and methane in the mixtures, respectively: ◆, (43.72, 56.28, 0.00); ●, (34.86, 44.87, 20.27); ▲, (19.58, 25.20, 55.22); ○, (11.21, 1.60, 87.19)].

Mixtures exhibiting liquid behavior (containing 20.27 and 55.22 mol % methane) were used to carry out constant composition expansion (CCE) tests at 373.15 K, where the result confirmed the visually measured bubble point pressures within the given accuracy. The measured volumetric data of pertinent mixtures from the CCE test are presented in Tables 5 and 6. They are also plotted against pressure in Figure 3.

Mixture containing 96.84 mol % methane (the last stage of methane addition) behaved as a very lean gas condensate with the retrograde dew point pressure visually measured at 20.96 MPa. In the last stage, PMCH was added to the mixture (lean gas condensate) to prepare a gas condensate mixture with a PMCH concentration of 11.21 mol %. The single-phase density and the retrograde dew point pressure of the mixture were measured, where the data are also

Table 7. Constant Composition Expansion Test of PMCH + *n*-Decane + Methane Mixture at 373.15 ± 0.1 K[a]

p/MPa ± 0.02	total vol[b] ± 0.1 %	liquid fraction ($V_{\text{liquid}}/V_{\text{total}}$) % ± 0.05
34.47	0.601	
17.24	0.933	
16.55	0.966	
16.20	0.983	
15.86	1.000	0.00
15.83	1.002	0.23
15.51	1.024	2.27
15.17	1.048	3.84
14.48	1.099	5.87
13.79	1.154	6.72
13.10	1.214	6.93
12.41	1.283	6.89

[a] PMCH: 11.21 mol %, *n*-C10: 1.60 mol %. [b] Relative to the volume at the bubble point.

summarized in Table 4. The mixture was also subjected to a CCE test with the measured volumetric data are given in Table 7 and plotted in Figure 3. A maximum liquid fraction of 6.93 % was recorded at 13.10 MPa.

Figure 3 compares the measured total volume (relative to the volume at saturation pressure) of the studied mixtures against the pressure. It can be seen as the compressibility of the system increases, the departure from single-phase to two-phase becomes less obvious, and it diminishes for the gaseous mixture (mixture containing 11.21 mol % PMCH). This confirms that the pressure−volume plot can be a reliable method for measuring the bubble point pressure whereas it may not be used for dew point pressure measurements.

Conclusions

Experimental data on phase and volumetric behavior of perfluoromethylcyclohexane + methane, perfluoromethylcyclohexane + *n*-decane, and perfluoromethylcyclohexane + methane + *n*-decane at 373.15 K have been presented. Liquid bubble point pressures, retrograde dew point pressures, and single-phase density data have been generated on PMCH + C_1 and PMCH + n-C_{10} binary mixtures. Constant composition expansion tests have been made on PMCH + C_1 + n-C_{10} ternary systems with various PMCH concentrations. The results would be of value in developing phase behavior models for PFC-hydrocarbon systems.

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