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Bubble Point Pressures of Some Petroleum Fractions in the Presence of Methane or Carbon Dioxide

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In this work, the bubble point pressures of a number of petroleum fractions were measured in the presence of carbon dioxide or methane. These petroleum fractions had a maximum boiling range of 40 K. The most volatile fraction has a boiling range of 353.15 K to 373.15 K, while the least volatile boils within the temperature range of 453.15 K to 493.15 K. The densities of these petroleum fractions varied from 690 kg/m^3 to 790 kg/m^3. Measurements were carried out in the Cailletet apparatus within a temperature range of 312 K to 470 K.

Introduction

For the developing of predictive methods of phase behavior of gas condensates and petroleum fractions, experimental data are needed. This type of experimentation is time-consuming and laborious; consequently, experimental data are not abundantly reported in the literature (Wang et al., 1991). Among the available data, those of White and Brown (1942) belong to the best and most complete. They carried out equilibrium vaporization measurements on mixtures of light naphtha and furnace oil.

The experimental work reported in this contribution was carried out in order to have some additional reliable experimental data on petroleum fractions in order to characterize C_6^+ fractions. For this purpose, four petroleum fractions with different boiling ranges were selected and mixed with carbon dioxide or methane. The bubble point pressures of the six resulting systems were measured at temperatures between 312 K and 470 K.

Experimental Section

(a) Apparatus and Procedure. The experiments were performed using a so-called Cailletet apparatus. A mixture of known composition was contained in a glass measuring cell. At a fixed temperature the pressure at which the first bubble appears, or the last bubble disappears, could be determined visually.

The pressure was measured using a dead-weight pressure gauge with an accuracy within ±0.003 MPa. A platinum resistance thermometer with an accuracy of ±0.01 K was used to measure the temperature. During the experiments the temperature in the silicon oil thermostat was maintained constant within ±0.03 K. A more detailed description of the apparatus and the experimental procedure can be found in the literature (de Loos et al., 1986; Peters et al., 1987a,b, 1993; Coorens et al., 1988.

(b) Materials. All the petroleum fractions used in this work were from MERCK. The specifications of these fractions are given in Table 1. The normal boiling ranges and densities (at 293.1 K) of these fractions were reported by MERCK, while the molecular weights of these fractions were estimated using the Kesler and Lee (1976) or Riazi and Daubert (1986) correlations.

Table 1. Petroleum Fractions Specifications

fraction no.	boiling range,[a] K	density,[a] kg/m^3	M_W
1	353.15−373.15	690	101.65[b]
2	373.15−413.15	740	115.66[b]
3	419.15−443.15	790	135.17[b]
4	453.15−493.15	760	159.16[c]

[a] Has been reported by MERCK. [b] Using the Kesler and Lee correlation (Kesler and Lee, 1976). [c] Using the Riazi and Daubert correlation (Riazi and Daubert, 1986).

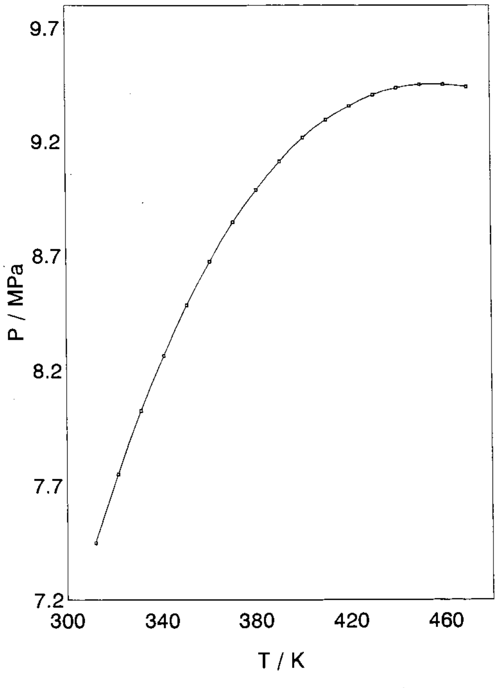

Figure 1. Experimental bubble point curve of system 5 (25.43 mol % methane + 74.57 mol % petroleum fraction 3).

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Table 2. Experimental Bubble Point Pressures of the Mixtures 1 to 6

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
Mixture 1: CO_2 (1) + Fraction 1 (2), $Z_1 = 0.2653$					
314.55	2.6468	371.30	4.3141	430.65	5.7946
321.86	2.8669	381.19	4.5840	440.52	5.9999
331.71	3.1669	391.06	4.8492	450.47	6.1951
341.53	3.4534	400.96	5.0993	460.41	6.3743
351.39	3.7487	410.85	5.3443	470.37	6.5250
361.34	4.0340	420.78	5.5744		
Mixture 2: CO_2 (1) + Fraction 2 (2), $Z_1 = 0.2440$					
312.01	2.3646	371.23	3.9039	430.62	5.2050
321.79	2.6247	381.14	4.1441	440.53	5.3952
331.65	2.8897	391.03	4.3741	450.48	5.5702
341.47	3.1486	400.93	4.5893	460.38	5.7356
351.32	3.4037	410.83	4.8045	470.33	5.8910
361.23	3.6537	420.76	5.0098		
Mixture 3: CO_2 (1) + Fraction 3 (2), $Z_1 = 0.2519$					
313.05	2.7284	371.19	4.4598	430.67	5.8866
321.89	2.9936	381.09	4.7256	440.58	6.0767
331.71	3.2993	390.98	4.9807	450.52	6.2517
341.56	3.6045	400.89	5.2258	460.44	6.4168
351.37	3.8946	410.83	5.4560	470.43	6.5669
361.27	4.1798	420.70	5.6814		
Mixture 4: CO_2 (1) + Fraction 4 (2), $Z_1 = 0.2627$					
314.56	2.5028	371.22	4.0533	430.60	5.3685
321.88	2.7078	381.13	4.3044	440.59	5.5351
331.72	2.9831	391.03	4.5446	450.54	5.6949
341.56	3.2631	400.94	4.7721	460.44	5.8399
351.42	3.5331	410.84	4.9821	470.43	5.9701
361.32	3.8032	420.79	5.1798		
Mixture 5: CH_4 (1) + Fraction 3 (2), $Z_1 = 0.2543$					
312.03	7.4496	371.23	8.8454	430.65	9.4053
321.84	7.7497	381.15	8.9856	440.56	9.4353
331.68	8.0248	391.07	9.1107	450.42	9.4504
341.52	8.2650	400.96	9.2158	460.37	9.4505
351.39	8.4851	410.93	9.2952	470.33	9.4405
361.30	8.6753	420.72	9.3551		
Mixture 6: CH_4 (1) + Fraction 4 (2), $Z_1 = 0.2267$					
312.08	5.5466	371.20	6.7215	430.71	7.2251
321.86	5.7913	381.13	6.8515	440.61	7.2602
331.70	6.0263	391.07	6.9482	450.52	7.2852
341.57	6.2263	400.98	7.0432	460.42	7.2953
351.41	6.4214	410.88	7.1186	470.38	7.2954
361.29	6.5814	420.80	7.1788		

Carbon dioxide and methane were obtained from Air Products with a minimum purity of 99.95 and 99.995 mol %, respectively. Both gases were used without any further purifications.

In this work, six mixtures were prepared. For each mixture, carbon dioxide or methane was injected into the liquid petroleum fraction. The amount of liquid petroleum fraction was measured as mass whereas the amount of gaseous substance was obtained by measuring the pressure, the temperature, and the volume of the gas filled into the Cailletet tube. Owing to technical problems, only the two heaviest fractions were mixed with methane. For each mixture, the composition of the injected gas in the mixture is given in Table 2. The accuracies of the compositions depend on the accuracies of the correlations that were selected for determining the molecular weights of the petroleum fractions.

Results and Discussions

The experimental bubble point pressures for the systems 1 to 6 are given in Table 2. The bubble point curves of systems with carbon dioxide have less curvature than those of systems with methane. This behavior may follow from the fact that at the experimental conditions, the critical temperature of methane is much farther removed from the temperature region of interest in this study than the critical temperature of carbon dioxide. As a consequence, the mixtures with methane show already a cricondenbar (see Figures 1 and 2), which is not the case with the mixtures with carbon dioxide. Owing to the temperature limitations of the particular apparatus used in this work, it was not possible to measure the phase envelope up to higher temperatures.

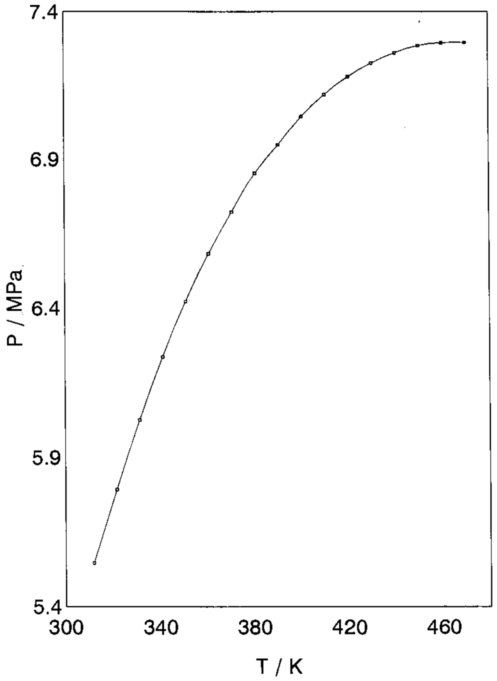

Figure 2. Experimental bubble point curve of system 6 (22.67 mol % methane + 77.33 mol % petroleum fraction 4).

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