High-Pressure Phase Diagrams of Methane + Squalane and Methane + Hexatriacontane Mixtures

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Equilibrium data on the methane + hexatriacontane mixture at (373, 398, 423, and 453) K and on the methane + squalane (2,6,10,15,19,23-hexamethyltetracosane) mixture at (323, 370, 420) K are reported. The apparatus and the near-infrared absorption method have been previously described.

Introduction

Thermodynamic properties of crude oils and natural gases are important for optimizing operating conditions. To minimize the experimental work, thermodynamic models are used to calculate the thermodynamic behavior of fluids. Different types of thermodynamic models can be used, i.e., classical equations of state, group contribution methods, and molecular simulation. Owing to the fact that these models are not perfect for complex mixtures, use is made of interaction parameters to correctly represent the behavior of fluids. For classical equations of state, the fitted parameter is a binary interaction parameter. For group contribution methods, it is necessary to calculate specific parameters for each group in the molecule. For molecular simulation, specific potential must be estimated. In all these cases experimental data on binary mixtures are needed to tune specific parameters. These parameters will be used for modeling complex fluids.

An experimental infrared absorption method has been developed and previously described (Marteau et al., 1996) to determine phase diagrams of binary mixtures at high pressure and high temperature without sampling. Several mixtures have already been investigated: methane + benzene and methane + hexane (Marteau et al., 1997) and methane + α-methylnaphthalene (Marteau et al., 1996). In this paper, we present experimental data on methane + hexatriacontane (n-$C_{36}H_{74}$) and methane + squalane (2,6,10,15,19,23-hexamethyltetracosane) mixtures at (373, 398, 423 and 453) K and (323, 370, and 420) K.

Accuracy

The infrared absorption method gives direct access to the concentrations of each component of the mixture. Mole fractions and molar volumes are deduced from these experimental data. The spectroscopic precision can be evaluated from the reproducibility of absorption spectra, typically of the order of 1% for a grating spectrometer. Accuracy can also be deduced from results obtained for pure components according to the cross-validation method, i.e., analysis of a sample taken out of the calibration set. Concentrations of these samples have always been recovered with an uncertainty less than 1%. Our results have also been compared to those obtained using the synthetic
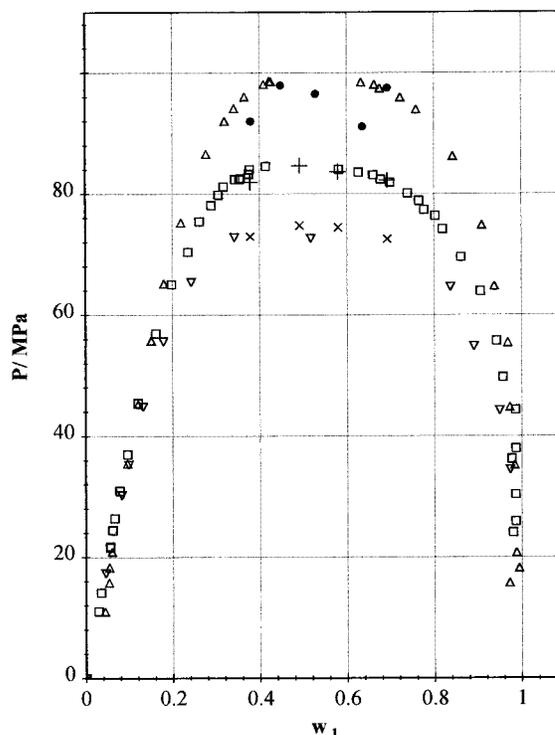

Figure 1. Phase diagram of squalane + methane at three temperatures: this work (△ 323 K, □ 370 K, ▽ 420 K); Paas et al. (● 323 K, + 373 K, × 423 K).

method. Concerning the mole fraction of methane, discrepancies no more than a few tenths of a percent were observed. Finally, the pressure measurements (pressure gauge Dynisco) with an accuracy of 0.4 MPa seem to be the most important source of uncertainty.

Methane purity was 99.9%, and commercial compounds were used as provided by Aldrich without further purification, namely squalane (99%) and hexatriacontane (98%).

Results

Squalane + Methane Mixture. The liquid−gas equilibria of squalane + methane have been studied at (323, 370 and 420) K. Numerical values are reported in Table

Table 1. Vapor−Liquid Equilibrium Data for Squalane + Methane at (323, 370, and 420) K

P/MPa	gas phase		liquid phase	
	C_1/mol·L^{-1}	C_2/mol·L^{-1}	C_1/mol·L^{-1}	C_2/mol·L^{-1}
		$T = 323$ K		
11.1			1.843	2.201
15.8	0.007	6.747	1.794	2.644
18.3	0.002	7.494	1.759	2.632
20.8	0.004	8.597	1.742	2.928
35.4	0.008	12.711	1.591	4.424
45.0	0.016	14.504	1.504	5.427
55.6	0.020	16.049	1.401	6.550
65.0	0.043	17.015	1.311	7.602
75.0	0.067	17.632	1.198	8.875
86.4	0.128	18.016	1.045	10.582
92.0			0.945	11.722
94.0	0.217	18.009	0.895	12.248
96.0	0.258	17.768	0.839	12.761
97.4	0.313	17.229		
98.1	0.332	17.258	0.747	13.674
98.5	0.369	16.796	0.709	13.840
98.5			0.714	13.768
		$T = 370$ K		
11.0			1.786	1.406
14.2			1.742	1.635
21.7			1.646	2.580
21.7			1.647	2.571
24.3	0.006	7.526	1.630	2.805
26.1	0.004	7.850	1.603	2.994
30.6	0.005	8.906	1.560	3.485
36.6	0.009	10.315	1.491	4.168
38.0	0.005	10.672		
44.9	0.006	11.671	1.406	5.065
49.7	0.022	12.728		
56.4	0.031	13.518	1.274	6.465
64.5	0.057	14.361	1.168	7.598
70.0	0.091	14.831	1.065	8.637
74.8	0.126	15.038	0.993	9.293
76.4	0.143	15.347		
77.8	0.164	15.051	0.927	9.918
79.4	0.177	15.169	0.886	10.267
80.6	0.203	15.178	0.856	10.512
82.2	0.245	14.986	0.777	11.244
82.4	0.268	14.854	0.794	10.985
82.6			0.771	11.308
83.2	0.288	14.776	0.729	11.565
83.8	0.328	14.512	0.728	11.663
84.3	0.387	14.158	0.654	12.201
		$T = 420$ K		
17.4			1.528	1.911
17.4			1.524	1.849
30.2			1.479	3.502
34.9	0.009	8.612	1.417	4.086
44.6	0.021	10.378	1.302	5.208
55.2	0.055	11.753	1.146	6.564
65.0	0.091	12.294	0.969	8.211
72.7	0.412	11.658	0.738	10.101

Figure 2. Concentration of squalane as a function of pressure in the gas and liquid phases of squalane + methane (△ 323 K, □ 370 K, ▽ 420 K).

Figure 3. Concentration of methane as a function of pressure in the gas and liquid phases of squalane + methane (△ 323 K, □ 370 K, ▽ 420 K).

1. For each pressure the concentrations of squalane and methane in both the liquid phase and the gas phase are given. In Figure 1 pressure has been plotted versus methane mass fraction for both the liquid phase and the gas phase. Mass fractions rather than mole fractions have been used because, owing to the high molecular weight of squalane, the dew curves collapse very close to 1 in the mole fraction representation. In Figure 1 our results can be compared to those previously obtained (Paas et al.,1979) in the critical region for temperatures very close to the present ones. Good agreement is observed, except for 423 K where their results seem to be less accurate. Figures 2 and 3 show the concentrations of squalane and methane as a function of pressure in the two phases.

Hexatriacontane + Methane Mixture. This binary system has been studied at four temperatures: (373, 398,
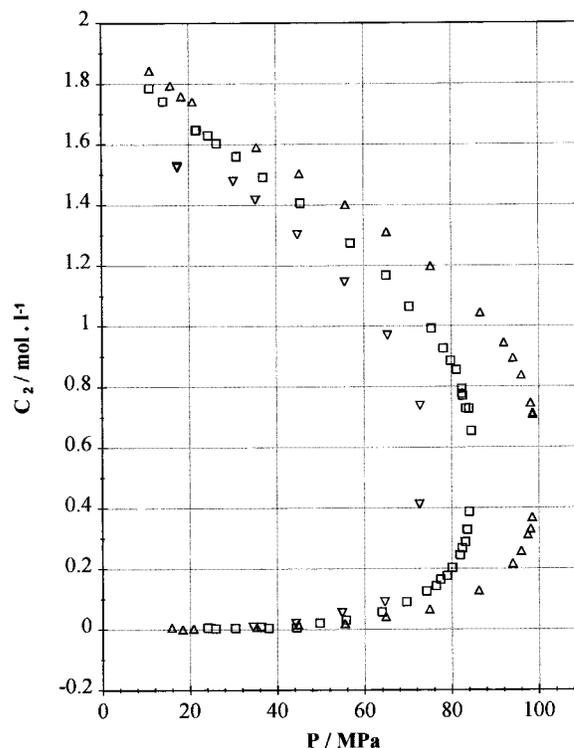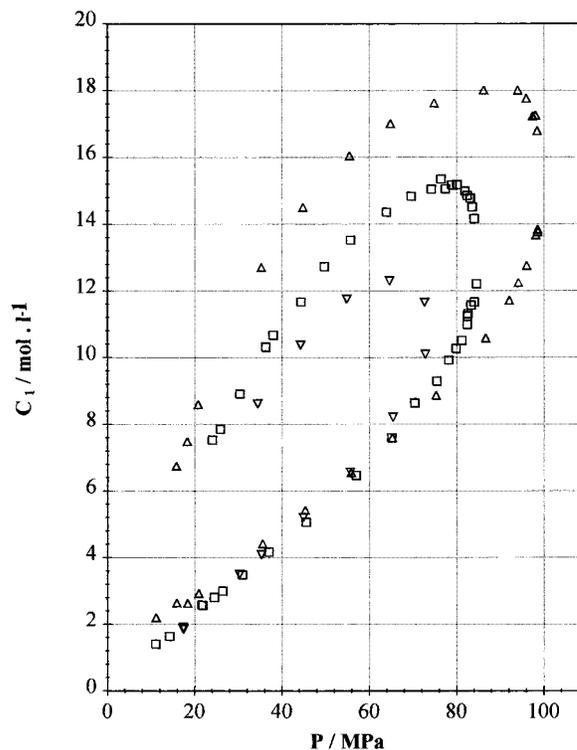
423, and 453) K. Numerical results are reported in Table 2. Figure 4 shows the phase diagrams at the four temperatures. Bubble-point measurements at medium pressure (up to 45 MPa) have also been performed using a more conventional technique in the French Institut of Petroleum. The break in a pressure−volume curve has been recorded
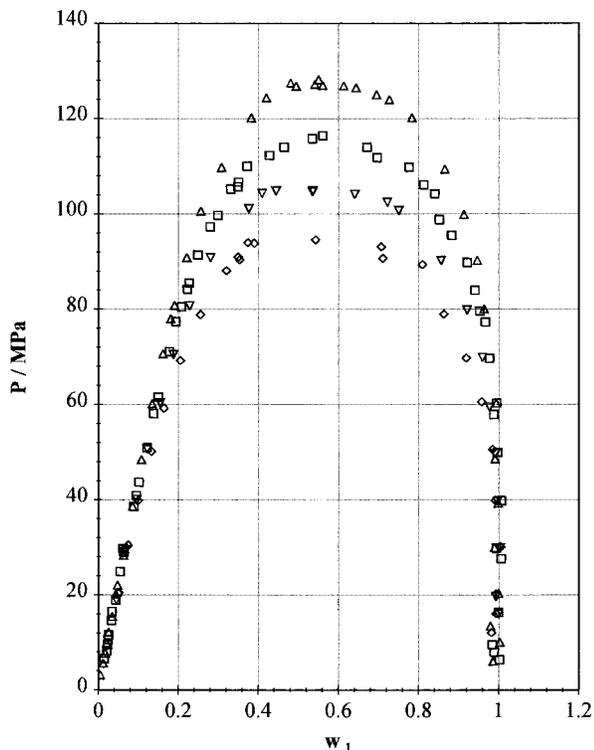
Figure 4. Phase diagram of hexatriacontane + methane at four temperatures ($\triangle$ 373 K, $\square$ 398 K, $\triangledown$ 423 K, $\diamond$ 453 K).

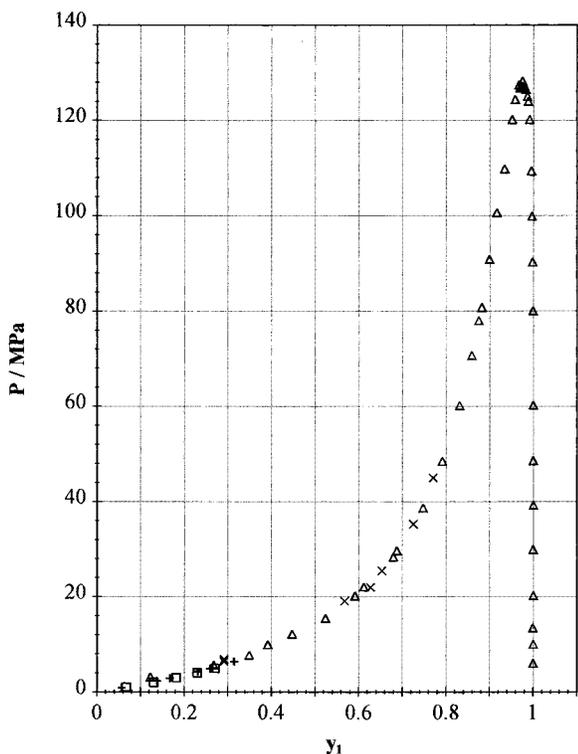**Figure 5.** Pressure as a function of the methane mole fraction in the two phases of the hexatriacontane + methane system at 373 K ($\triangle$ present work; $\square$ Tsaï et al., 1987; + Darwish et al., 1993; $\times$ present work by synthetic method).

Figure 6. Concentration of hexatriacontane as a function of pressure in the gas and liquid phases of the hexatriacontane + methane ($\triangle$ 373 K, $\square$ 398 K, $\triangledown$ 423 K, $\diamond$ 453 K).
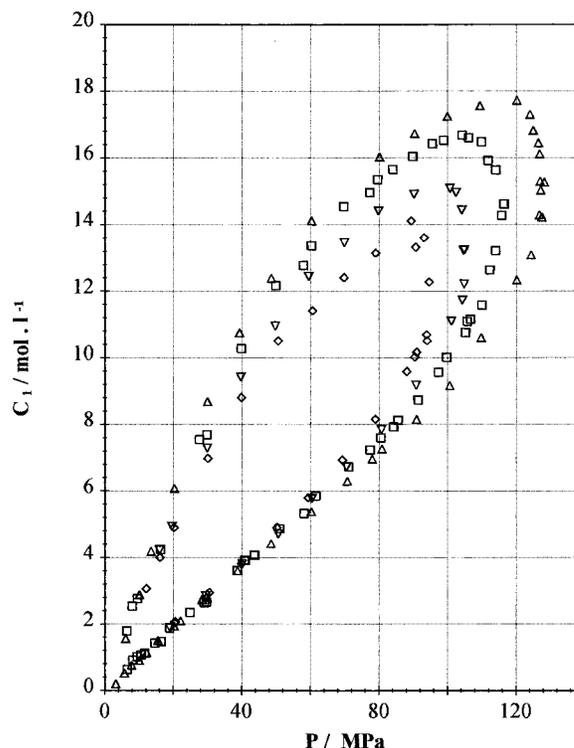
Figure 7. Concentration of methane as a function of pressure in the gas and liquid phases of the hexatriacontane + methane ($\triangle$ 373 K, $\square$ 398 K, $\triangledown$ 423 K, $\diamond$ 453 K).

with various amounts of methane. The resulting measurements at (273, 398, and 423) K are presented in Table 3. Some of the data shown have been measured with a DMA densimeter, which allowed us to record simultaneously the saturated liquid density. The methane mole fraction versus pressure at 373 K is shown in Figure 5 in order to
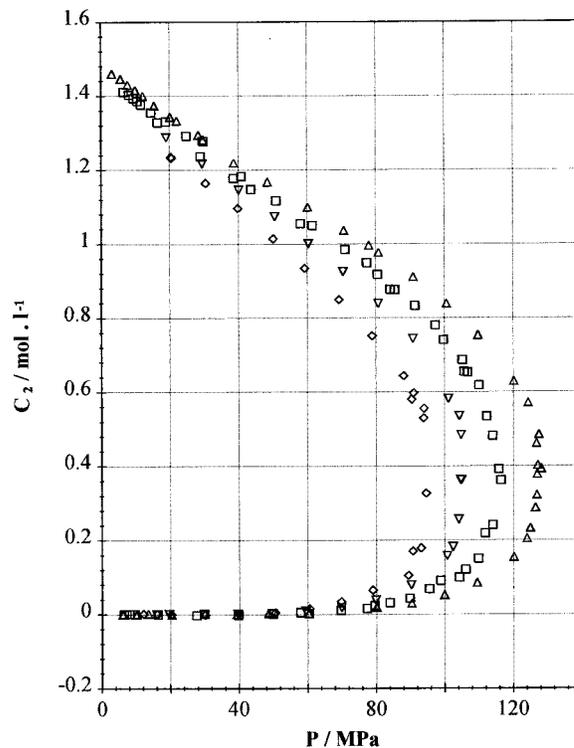
illustrate the good agreement between our spectroscopic results and those obtained at low pressures (Tsaï et al., 1987; Darwish et al., 1993) and at pressures up to 45 MPa in French Institut of Petroleum. The concentrations versus pressure of hexatriacontane and methane are shown in Figures 6 and 7, respectively.

Table 2. Vapor−Liquid Equilibrium Data for Hexatriacontane + Methane at (373, 398, 423 and 453) K

	gas phase		liquid phase			gas phase		liquid phase	
P/MPa	C_1/mol·L^{-1}	C_2/mol·L	C_1/mol·L	C_2/mol·L	P/MPa	C_1/mol·L	C_2/mol·L	C_1/mol·L	C_2/mol·L
					$T = 373$ K				
3.2			1.461	0.204	78.0			0.997	6.964
5.9	0.001	1.571	1.447	0.53	80.5	0.019	16.032	0.977	7.268
7.8			1.431	0.769	90.6	0.03	16.739	0.911	8.159
10.1	0	2.885	1.416	0.912	100.3	0.052	17.251	0.839	9.17
12.2			1.401	1.135	109.6	0.086	17.566	0.754	10.608
14.5	0.003	4.192	1.374	1.511	120.2	0.155	17.723	0.63	12.335
20.3	0	6.082	1.344	1.945	124.2	0.205	17.305	0.572	13.089
22.1			1.334	2.1	125.0	0.233	16.823		
28.4			1.295	2.743	126.7	0.288	16.456	0.462	14.293
29.9	0.003	8.69	1.282	2.816	126.9	0.322	16.117		
39.0	0	10.758	1.22	3.604	127.0	0.379	15.302		
48.6	0.004	12.394	1.168	4.423	127.4	0.403	15.028	0.486	14.22
60.3	0.003	14.115	1.1	5.386	128.2	0.394	15.272		
70.7			1.037	6.296					
					$T = 398$ K				
6.5	0	1.791	1.411	0.633	61.0	0.002	13.371	1.05	5.842
8.1	0.001	2.536	1.403	0.917	70.4	0.011	14.535	0.985	6.725
9.5	0.001	2.766	1.394	1.017	77.4	0.016	14.956	0.949	7.234
10.6			1.386	1.073	80.1	0.024	15.349	0.917	7.594
11.6			1.377	1.121	84.1	0.031	15.653	0.877	7.932
14.6			1.355	1.427	85.5			0.876	8.125
16.4	0	4.241	1.329	1.471	90.6	0.043	16.039	0.833	8.725
18.9			1.331	1.877	96.4	0.069	16.424	0.78	9.569
24.9			1.292	2.348	99.3	0.091	16.526	0.741	10.011
27.6	0	7.544			104.7	0.1	16.678	0.687	10.758
29.4	0.001	7.692	1.237	2.643	105.7			0.655	11.088
29.7			1.278	2.661	106.4	0.121	16.605	0.653	11.154
38.6			1.178	3.618	109.9	0.15	16.483	0.618	11.577
39.8	0	10.285	1.183	3.923	112.1	0.219	15.913	0.534	12.633
43.7			1.148	4.077	114.0	0.241	15.631	0.482	13.213
50.5	0.001	12.164	1.117	4.87	116.1	0.362	14.615	0.392	14.268
58.0	0.005	12.772	1.055	5.325					
					$T = 423$ K				
16.0	0	4.221			80.3	0.039	14.407	0.839	7.841
19.3	0.001	4.94	1.288	1.893	90.5	0.079	14.909	0.744	9.176
29.7	0.0	7.295	1.217	2.857	100.9	0.158	15.077	0.582	11.094
39.9	0.001	9.425	1.146	3.816	102.4	0.182	14.958		
50.2	0.003	10.958	1.074	4.71	104.2	0.256	14.429	0.535	11.726
60.0	0.009	12.443	1.001	5.775	104.7	0.363	13.223	0.484	12.216
70.2	0.018	13.464	0.925	6.732	104.9	0.363	13.24		
					$T = 453$ K				
12.1	0.002	3.069			69.6	0.035	12.413	0.85	6.936
16.1	0.001	4.007			79.0	0.066	13.147	0.752	8.159
20.3	0.001	4.908	1.236	2.035	88.8	0.105	14.113	0.644	9.592
20.5			1.233	2.079	90.4			0.581	10.032
30.3	0	6.985	1.165	2.955	90.9	0.171	13.327	0.598	10.176
39.9	0.002	8.811	1.097	3.819	93.5	0.179	13.609	0.53	10.692
50.4	0.005	10.51	1.015	4.909	94.3	0.327	12.275	0.556	10.515
60.0	0.016	11.415	0.935	5.796					

Table 3. Bubble Pressure (P_b) Measurements with the Conventional $P-V$ Technique for Methane + Hexatriacontane

	P_b/MPa		
x_2	$T = 273$ K	$T = 398$ K	$T = 423$ K
0.2915[a]	6.4	6.8	6.9
	752.2 kg·m^{-3}	737.2 kg·m^{-3}	723.2 kg·m^{-3}
0.568	18.1		
0.627	2.2		
0.653	2.55		
0.725	3.53		
0.77	4.50		

[a] Measurements at the mole fraction of 0.2915 of methane have been measured with a DMA-type densitometer, which allows simultaneously a saturated liquid density measurement.

Discussion

The results presented in this paper are in very good agreement with those obtained by various authors using different methods. This clearly shows the ability of the infrared absorption method to investigate the equilibrium properties of systems involving heavy hydrocarbons. Furthermore, as it has been already emphasized, the infrared method has many advantages compared to some others: (i) the concentrations of each component are directly measured without any sampling nor any weighing; (ii) measurements are done at thermodynamic equilibrium so that investigation very close to the critical region is possible; (iii) the whole phase diagram can be described by using only one mixture, provided its initial composition is close to the critical one; (iv) systems under high pressure, up to 200 MPa in the present case, are easily investigated.

List of Symbols

T = temperature, K
P = pressure, MPa
C_1 = concentration of the heavy component (hexatriacontane or squalane)

C_2 = concentration of methane
w = mass fraction
x = mole fraction in the liquid phase
y = mole fraction in the gas phase

Acknowledgment

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