Bubble-Point Pressures of Some Selected Methane + Synthetic C$_{6+}$ Mixtures

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In this work, a series of bubble-point measurements were carried out on some synthetic C$_{6+}$ mixtures in the presence of methane. These synthetic mixtures included alkanes, cycloalkanes, and aromatics. The experiments were carried out using the Cailletet apparatus, and bubble-point pressures were measured in a temperature range of 311−470 K. The corresponding pressures were predicted using the Peng−Robinson equation of state, and the relative errors were estimated. It is shown that such synthetic C$_{6+}$ mixtures can be simulated reasonably well by this equation of state.

Introduction

Knowledge of hydrocarbon-mixture phase equilibria is needed for modeling of separation processes such as distillation and flash vaporization, just to name a few. These equilibrium states are usually predicted using equations of state, but for developing and checking these equations of state, experimental data are required.

Laborious experiments must be carried out for obtaining phase-equilibrium data of multicomponent hydrocarbon mixtures. Consequently, such experimental data are not abundantly reported in the literature. Among the available data, those of White and Brown (1942) stand out as some of the best and most complete. They carried out equilibrium vaporization measurements on mixtures of light naphtha and furnace oil. But since the exact composition of such naturally occurring oils are unknown, data on synthetic multicomponent mixtures are required for the purpose of simulating equilibrium states of hydrocarbon mixtures. For this purpose, some synthetic C$_{6+}$ fractions with different boiling ranges were considered in this work. They consisted of alkanes, cycloalkanes, and aromatics. The bubble-point pressures of methane and these synthetic C$_{6+}$ mixtures were measured at temperatures between 311 K and 470 K. To investigate the ability of an equation of state to predict the phase behavior of such multicomponent systems, the bubble-point pressures were also estimated using the Peng−Robinson (PR) equation of state (Peng and Robinson, 1976a,b).

In this work, the mixing rules presented by Peng and Robinson (1976b) were used, and in order to bring about better agreement between experimental data and predictions for each system, the binary interaction parameters were adjusted.

Experimental Work

All experiments were performed using a so-called Cailletet apparatus. The desired mixture was prepared by mixing the right proportion of solid and liquid substances

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Table 1. Suppliers and Purities of the Chemicals

substance	supplier	purity (mass %)
methane	Air Products	>99.99
benzene	J. T. Baker	>99
cyclohexane	J. T. Baker	>99
3-methylpentane	Janssen Chimica	>99
hexane	J. T. Baker	>99
toluene	Janssen Chimica	>99.5
methylcyclohexane	Merck	>99
heptane	J. T. Baker	>99
m-xylene	J. T. Baker	>99
ethylbenzene	Fluka	>99
cyclooctane	Fluka	>99
octane	Janssen Chimica	>99
nonane	Merck	>98
naphthalene	Fluka	>99
decane	Fluka	>98

by weight and the required amount of gas by achieving the correct pressure on a confined volume of gas at a fixed temperature. This mixture was contained in a thick-walled Pyrex glass measuring tube. At a fixed temperature, the pressures 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 was maintained constant within ±0.03 K. The total error in mole fractions of the components were within ±0.002. Silicone oil was used as the heating fluid. A more detailed description of the apparatus and the experimental procedure can be found elsewhere (de Loos et al., 1986; Peters et al., 1987a,b, 1993; Coorens et al., 1988).

Table 1 summarizes the names of the suppliers of the chemicals used in this work and the purities that they claimed for these chemicals. All substances were used without further purification.

Table 2 shows the seven different systems used for experimentation, indicating the components and their compositions in mole percent. The first three systems have the same components but differ in composition.

Table 2. Investigated Systems and Their Compositions

	composition (mol %)						
component	system 1	system 2	system 3	system 4	system 5	system 6	system 7
methane	25.06	30.38	25.25	26.75	24.83	24.53	25.44
3-methylpentane						4.98	
hexane						40.29	
benzene						5.08	
cyclohexane				4.07		5.01	
methylcyclohexane				2.66			4.96
heptane				62.65		20.11	39.68
toluene				3.87			
octane					60.20		20.07
ethylbenzene							9.85
m-xylene					1.98		
cyclooctane	5.32	4.94	10.58		3.01		
nonane					9.98		
decane	64.75	60.15	58.97				
naphthalene	4.87	4.53	5.20				
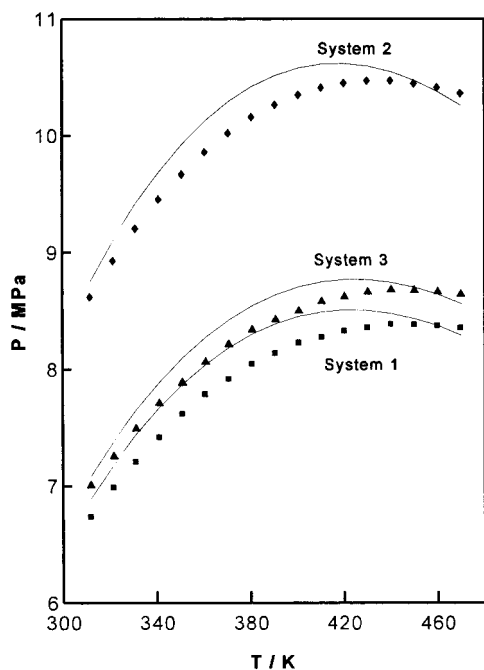
Figure 1. Experimental bubble-point pressures of systems 1, 2, and 3 (solid lines are predicted, and points are experimental).

Table 3. Experimental (*P*) and PR-Estimated (*P*calcd) Bubble-Point Pressures for System 1[a]

T/K	*P*/MPa	*P*calcd/MPa	$100(P - P_{calcd})/P$
311.78	6.7413	6.8908	−2.22
321.55	6.9912	7.1807	−2.71
331.37	7.1213	7.4412	−4.49
341.18	7.4171	7.6707	−3.42
351.03	7.6174	7.8709	−3.33
360.89	7.7923	8.0417	−3.20
370.90	7.9200	8.1859	−3.36
380.82	8.0482	8.3009	−3.14
390.69	8.1432	8.3890	−3.02
400.60	8.2282	8.4522	−2.72
410.50	8.2799	8.4913	−2.55
420.38	8.3300	8.5078	−2.13
430.33	8.3601	8.5028	−1.71
440.24	8.3800	8.4776	−1.16
450.16	8.3854	8.4333	−0.57
460.12	8.3755	8.3728	0.03
470.09	8.3555	8.2912	0.77
		AAD%[b]	2.38

[a] Binary interaction parameters: $k_{C1-CYCC8} = 0.05$, $k_{C1-C10} = 0.048$, $k_{C1-NAPH} = 0.077$. [b] AAD% = (Σ|error %|)/number of data points.

Table 4. Experimental (*P*) and PR-Estimated (*P*calcd) Bubble-Point Pressures for System 2[a]

T/K	*P*/MPa	*P*calcd/MPa	$100(P - P_{calcd})/P$
311.77	8.6174	8.7507	−1.55
321.57	8.9275	9.1039	−1.98
331.39	9.2025	9.4175	−2.34
340.23	9.4527	9.6920	−2.53
351.05	9.6677	9.9274	−2.69
360.89	9.8577	10.1260	−2.72
370.86	10.0178	10.2905	−2.72
380.83	10.1577	10.4198	−2.58
390.72	10.2629	10.5148	−2.45
400.65	10.3480	10.5783	−2.22
410.53	10.4079	10.6114	−1.95
420.44	10.4481	10.6160	−1.60
430.33	10.4682	10.5935	−1.20
440.27	10.4696	10.5449	−0.72
450.24	10.4448	10.4714	−0.25
460.16	10.4104	10.3748	0.34
470.08	10.3604	10.2560	1.01
		AAD%	1.82

[a] Binary interaction parameters: $k_{C1-CYCC8} = 0.05$, $k_{C1-C10} = 0.048$, $k_{C1-NAPH} = 0.077$.

Table 5. Experimental (*P*) and PR-Estimated (*P*calcd) Bubble-Point Pressures for System 3[a]

T/K	*P*/MPa	*P*calcd/MPa	$100(P - P_{calcd})/P$
312.04	7.0160	7.0879	−1.02
321.85	7.2660	7.3882	−1.68
331.66	7.5009	7.6568	−2.08
341.50	7.7208	7.8946	−2.25
351.34	7.9010	8.1014	−2.54
361.22	8.0957	8.2787	−2.26
371.16	8.2166	8.4275	−2.57
381.10	8.3450	8.5478	−2.43
390.97	8.4360	8.6402	−2.42
400.86	8.5107	8.7071	−2.31
410.70	8.5912	8.7495	−1.84
420.69	8.6208	8.7690	−1.72
430.62	8.6712	8.7663	−1.10
440.54	8.6950	8.7429	−0.55
450.44	8.6864	8.7000	−0.16
460.40	8.6712	8.6384	0.38
470.30	8.6515	8.5598	1.06
		AAD%	1.67

[a] Binary interaction parameters: $k_{C1-CYCC8} = 0.05$, $k_{C1-C10} = 0.048$, $k_{C1-NAPH} = 0.077$.

Results and Discussion

The experimentally measured bubble-point curves of the three systems having the same components but with different compositions are shown in Figure 1, along with

Table 6. Experimental (P) and PR-Estimated (P_{calcd}) Bubble-Point Pressures for System 4[a]

T/K	P/MPa	P_{calcd}/MPa	$100(P - P_{calcd})/P$
311.97	6.9612	7.1293	−2.41
321.74	7.1917	7.3940	−2.81
331.60	7.4470	7.6273	−2.42
341.44	7.6571	7.8274	−2.22
351.28	7.9123	7.9960	−1.06
371.08	8.2457	8.2450	0.01
381.03	8.3657	8.3275	0.46
390.95	8.4708	8.3834	1.03
400.84	8.5507	8.4141	1.60
410.75	8.6158	8.4209	2.26
420.69	8.6662	8.4048	3.02
430.62	8.7013	8.3663	3.85
440.51	8.7066	8.3060	4.60
450.43	8.6966	8.2234	5.44
460.33	8.6521	8.1178	6.18
465.29	8.6320	8.0555	6.68
470.32	8.6024	7.9855	7.17
		AAD%	3.13

[a] Binary interaction parameters: $k_{C1-CYCC6} = 0.041$, $k_{C1-MCYCC6} = 0.055$, $k_{C1-C7} = 0.45$, $k_{C1-TOL} = 0.041$.

Table 7. Experimental (P) and PR-Estimated (P_{calcd}) Bubble-Point Pressures for System 5[a]

T/K	P/MPa	P_{calcd}/MPa	$100(P - P_{calcd})/P$
312.03	6.3478	6.6003	−3.98
332.06	6.8288	7.0969	−3.93
351.38	7.2052	7.4573	−3.50
371.21	7.4953	7.7139	−2.92
381.12	7.6104	7.8023	−2.52
391.01	7.7104	7.8658	−2.02
400.86	7.7855	7.9058	−1.55
410.81	7.8506	7.9240	−0.93
420.71	7.8907	7.9213	−0.39
430.60	7.9258	7.8990	0.34
440.51	7.9457	7.8582	1.10
460.37	7.9357	7.7241	2.67
470.29	7.9012	7.6322	3.40
		AAD%	2.25

[a] Binary interaction parameters: $k_{C1-C8} = 0.047$, $k_{C1-MXYL} = 0.053$, $k_{C1-CYCC8} = 0.05$, $k_{C1-C9} = 0.048$.

Table 8. Experimental (P) and PR-Estimated (P_{calcd}) Bubble-Point Pressures for System 6[a]

T/K	P/MPa	P_{calcd}/MPa	$100(P - P_{calcd})/P$
312.02	6.0538	6.3166	−4.34
341.52	6.7440	6.9540	−3.11
371.19	7.2543	7.3566	−1.14
381.10	7.3894	7.4435	−0.73
390.99	7.5097	7.5084	0.02
400.91	7.6096	7.5526	0.75
410.82	7.6999	7.5757	1.60
420.78	7.7699	7.5810	2.43
430.68	7.8252	7.5655	3.32
440.60	7.8654	7.5291	4.28
450.49	7.8755	7.4701	5.14
460.46	7.8558	7.3837	6.01
470.38	7.7862	7.2636	6.71
		AAD%	3.07

[a] Binary interaction parameters: $k_{C1-3MC5} = 0.045$, $k_{C1-C6} = 0.041$, $k_{C1-BZ} = 0.027$, $k_{C1-CYCC6} = 0.041$, $k_{C1-C7} = 0.045$.

the bubble-point pressures predicted by the PR equation of state. In Tables 3−9, in addition to the experimental bubble-point pressures, the bubble points predicted by the PR equation of state are also given for the systems 1 to 7.

Table 9. Experimental (P) and PR-Estimated (P_{calcd}) Bubble-Point Pressures for System 7[a]

T/K	P/MPa	P_{calcd}/MPa	$100(P - P_{calcd})/P$
312.02	6.6590	7.0104	−5.28
341.52	7.3742	7.7097	−4.55
371.18	7.8693	8.1369	−3.40
381.10	7.9846	8.2244	−3.0
391.02	8.0898	8.2864	−2.43
400.91	8.1751	8.3244	−1.83
410.81	8.2502	8.3399	−1.09
420.74	8.2954	8.3339	−0.46
430.65	8.3356	8.3076	0.34
440.59	8.3654	8.2615	1.24
450.49	8.3706	8.1966	2.08
460.41	8.3708	8.1127	3.08
470.36	8.3459	8.0092	4.03
		AAD%	2.52

[a] Binary interaction parameters: $k_{C1-MCYCC6} = 0.055$, $k_{C1-C7} = 0.045$, $k_{C1-C8} = 0.047$, $k_{C1-EB} = 0.059$.

The suitable values of the binary intraction parameters between methane and the other C_{6+} components are determined in order to obtain better fits with experimental data. These values are given at the bottom of each table. As can be seen in Tables 3−9, all these systems have a maximum bubble-point pressure (cricondenbar), after which the bubble-point pressure decreases with increasing temperature.

The percentages of error and average absolute deviation between the experimental and simulated data are also given in these tables. Comparison of these values shows that the capability of the PR equation of state is reasonably good in predicting the phase behavior of hydrocarbon mixtures heavier than hexane, even near the critical region.

Acknowledgment

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