

Bubble Point Pressures of Some Selected Carbon Dioxide + Synthetic C₆₊ Mixtures

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In this work, the bubble points of some selected synthetic C₆₊ mixtures were measured in the presence of carbon dioxide. In all the systems, the composition of carbon dioxide was kept about 25 mol %. Measurements were carried out in the Cailletet apparatus within a temperature range of 312 K to 470 K. In addition, the ability of the Peng–Robinson equation of state (PR EOS) in correlating the phase behavior of CO₂ + C₆₊ fractions was investigated, by correlating the bubble points of experimented systems using this equation of state. To increase the accuracy of the correlations, suitable binary interaction parameters between each component of the C₆₊ mixture and carbon dioxide were determined, which minimized the difference between correlated and experimental bubble point pressures. Average absolute deviations between experimental and predicted data are less than 2.1% in all the systems.

Introduction

Phase equilibrium computations of mixtures containing C₆₊ fractions are usually regarded as being difficult. Lack of experimental data for these mixtures are one of the main reasons for this difficulty. The accurate correlation of phase behavior of C₆₊ fractions is essential, for example, in reservoir simulation and in the design of transport and separator equipment. As the need for enhanced oil recovery methods such as gas injection increases, the demand for accurate phase behavior prediction increases. The phase behavior model must take into account not only the effects caused by the complicated composition of the reservoir fluids but also the effects caused by the presence of injection gases such as CO₂ or N₂ in significant amounts. Much effort has been given to developing models suitable for the prediction of phase behavior in oil and gas condensate mixtures, but most of the models available in the literature need experimental data to tune one or more of their parameters (Aasberg-Petersen and Stenby, 1991).

Of the approaches for representing complex C₆₊ fractions is the one for instance used by de Leeuw et al. (1992) and Peters et al. (1992, 1993). A mixture of a limited number of well-defined components is used instead of a real fraction. This method allows a thorough experimental investigation that can be used to verify the prediction and adjust the description by equations of state.

In this work, synthetic mixtures made from a number of alkanes, cycloalkanes, and aromatics with known compositions were chosen to represent the C₆₊ fractions. The bubble point pressures of these mixtures were then measured in the presence of carbon dioxide at several temperatures, ranging from 312 K to 470 K. The constituent components of the C₆₊ fractions were chosen in different proportions, such that the resulting C₆₊ fractions had different boiling ranges. The bubble point pressures of these synthetic systems were then correlated by the Peng–

Table 1. Suppliers and Purities of the Substances Used in This Work

substance	supplier	purity (mass %)
carbon dioxide	Air Products	>99.95
methylcyclohexane	Merck	>99
<i>m</i> -xylene	J. T. Baker	>99
ethylbenzene	Fluka	>99
octane	Janssen Chimica	>99
nonane	Merck	>98
naphthalene	Fluka	>99
decane	Merck	>99
undecane	Janssen Chimica	>99
dodecane	Merck	>99

Table 2. Investigated Systems and Their Compositions

component	composition (mol %)					
	system 1	system 2	system 3	system 4	system 5	system 6
carbon dioxide	25.39	25.12	24.96	25.10	25.07	25.00
methylcyclohexane						12.55
<i>m</i> -xylene	7.13					12.84
ethylbenzene		11.13				
octane	37.62	36.16				49.61
nonane	29.86	27.59				
naphthalene					3.30	
decane			51.24			
undecane			23.80	34.04		
dodecane				40.86	71.63	

Robinson equation of state (PR EOS). Suitable binary interaction parameters between carbon dioxide and each of the C₆₊ fraction constituents were determined by minimizing the following objective function

$$\text{OF} = \frac{1}{N} \sum_{i=1}^n \left(\frac{P - P_{\text{calcd}}}{P} \right)_i^2$$

where N is the number of data points and P and P_{calcd} are experimental and calculated bubble point pressures, respectively. The binary interaction parameters between

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Table 3. Experimental (P) and PR-Estimated (P_{calcd}) Bubble Point Pressures for System 1^a

T/K	P/MPa	$P_{\text{calcd}}/\text{MPa}$	$100\delta^b$
313.45	2.5267	2.5525	-1.02
321.91	2.7668	2.8073	-1.46
331.72	3.0420	3.1024	-1.99
341.55	3.3122	3.3943	-2.48
351.44	3.5822	3.6806	-2.75
361.38	3.8474	3.9584	-2.89
371.30	4.0975	4.2230	-3.06
381.19	4.3375	4.4725	-3.11
391.08	4.5677	4.7062	-3.03
400.96	4.7878	4.9225	-2.81
410.88	4.9929	5.1220	-2.59
420.78	5.1928	5.3028	-2.12
430.72	5.3779	5.4650	-1.62
440.62	5.5479	5.6079	-1.08
450.51	5.7083	5.7315	-0.41
460.45	5.8536	5.8364	0.29
470.36	5.9887	5.9216	1.12
	AAD % ^c		1.99

^a Binary interaction parameters: $k_{\text{CO}_2-\text{C}_8} = 0.13$; $k_{\text{CO}_2-\text{xy}} = 0.11$; $k_{\text{CO}_2-\text{C}_9} = 0.13$. ^b $100\delta = (P - P_{\text{calcd}})/P \times 100$. ^c AAD % = $(\sum |\text{error}|)/\text{number of data points}$.

Table 4. Experimental (P) and PR-Estimated (P_{calcd}) Bubble Point Pressures for System 2^a

T/K	P/MPa	$P_{\text{calcd}}/\text{MPa}$	100δ
312.10	2.4826	2.4898	-0.29
321.82	2.7576	2.7818	-0.88
331.65	3.0327	3.0773	-1.47
341.49	3.3078	3.3696	-1.87
351.41	3.5779	3.6574	-2.22
361.34	3.8429	3.9359	-2.42
371.25	4.0929	4.2017	-2.66
381.16	4.3376	4.4535	-2.67
391.03	4.5677	4.6889	-2.65
400.91	4.7879	4.9079	-2.51
410.81	4.9930	5.1099	-2.34
420.72	5.1932	5.2940	-1.94
430.66	5.3780	5.4600	-1.52
440.58	5.5531	5.6070	-0.97
450.45	5.7231	5.7343	-0.20
460.42	5.8720	5.8441	0.48
470.35	6.0122	5.9340	1.30
	AAD %		1.67

^a Binary interaction parameters: $k_{\text{CO}_2-\text{C}_8} = 0.13$; $k_{\text{CO}_2-\text{EB}} = 0.11$; $k_{\text{CO}_2-\text{C}_9} = 0.13$.

Table 5. Experimental (P) and PR-Estimated (P_{calcd}) Bubble Point Pressures of System 3^a

T/K	P/MPa	$P_{\text{calcd}}/\text{MPa}$	100δ
314.10	2.4860	2.3143	6.91
321.85	2.6911	2.5526	5.15
331.68	2.9511	2.8052	4.95
341.52	3.2012	3.0784	3.84
351.39	3.4513	3.3474	3.01
361.30	3.6913	3.6095	2.22
371.20	3.9209	3.8609	1.53
381.15	4.1411	4.1010	0.97
391.05	4.3512	4.3256	0.59
400.96	4.5412	4.5351	0.14
410.89	4.7262	4.7284	-0.05
420.76	4.8963	4.9036	-0.15
430.72	5.0557	5.0627	-0.14
440.59	5.2008	5.2026	-0.03
450.45	5.3308	5.3247	-0.11
460.37	5.4510	5.4299	0.39
470.37	5.5611	5.5178	0.78
	AAD %		1.82

^a Binary interaction parameters: $k_{\text{CO}_2-\text{C}_{10}} = 0.11$; $k_{\text{CO}_2-\text{C}_{11}} = 0.11$.

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

T/K	P/MPa	$P_{\text{calcd}}/\text{MPa}$	100δ
312.03	2.4294	2.2699	6.57
321.84	2.6844	2.5438	5.24
331.69	2.9395	2.8205	4.05
341.52	3.1897	3.0950	2.97
351.42	3.4398	3.3666	2.13
361.26	3.6800	3.6289	1.39
371.20	3.9051	3.8836	0.55
381.21	4.1251	4.1277	-0.06
391.09	4.3300	4.3544	-0.56
401.00	4.5250	4.5666	-0.92
410.88	4.7101	4.7617	-1.10
420.81	4.8852	4.9407	-1.14
430.72	5.0354	5.1015	-1.31
440.62	5.1804	5.2446	-1.24
450.50	5.3105	5.3690	-1.10
460.41	5.4306	5.4762	-0.84
470.33	5.5357	5.5657	-0.54
	AAD %		1.87

^a Binary interaction parameters: $k_{\text{CO}_2-\text{C}_{11}} = 0.11$; $k_{\text{CO}_2-\text{C}_{12}} = 0.11$.

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

T/K	P/MPa	$P_{\text{calcd}}/\text{MPa}$	100δ
311.92	2.4670	2.3056	6.54
321.77	2.7271	2.5848	5.22
331.60	2.9822	2.8653	3.92
341.44	3.2373	3.1445	2.87
351.29	3.4873	3.4193	1.95
361.22	3.7275	3.6886	1.04
371.16	3.9625	3.9478	0.37
381.08	4.1827	4.1942	-0.27
390.97	4.3878	4.4258	-0.87
400.85	4.5828	4.6417	-1.29
410.77	4.7629	4.8419	-1.66
420.71	4.9332	5.0251	-1.86
430.64	5.0933	5.1903	-1.90
440.56	5.2383	5.3370	-1.88
450.47	5.3684	5.4655	-1.81
460.36	5.4834	5.5755	-1.68
470.37	5.5886	5.6688	-1.44
	AAD %		2.15

^a Binary interaction parameters: $k_{\text{CO}_2-\text{naphthalene}} = 0.2$; $k_{\text{CO}_2-\text{C}_{12}} = 0.11$.

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

T/K	P/MPa	$P_{\text{calcd}}/\text{MPa}$	100δ
313.83	2.5734	2.5608	0.49
321.79	2.8033	2.8060	-0.10
331.63	3.0883	3.1099	-0.70
341.47	3.3734	3.4111	-1.12
351.34	3.6534	3.7075	-1.48
361.27	3.9236	3.9966	-1.86
371.20	4.1887	4.2743	-2.04
381.06	4.4439	4.5367	-2.09
390.99	4.6893	4.7861	-2.06
400.88	4.9245	5.0179	-1.90
410.80	5.1446	5.2334	-1.73
420.72	5.3600	5.4307	-1.32
430.64	5.5600	5.6097	-0.89
440.52	5.7502	5.7690	-0.33
450.44	5.9304	5.9106	0.33
460.38	6.0955	6.0324	1.04
470.31	6.2457	6.1340	1.79
	AAD %		1.25

^a Binary interaction parameters: $k_{\text{CO}_2-\text{xylene}} = 0.11$; $k_{\text{CO}_2-\text{C}_8} = 0.13$; $k_{\text{CO}_2-\text{methylcyclohexane}} = 0.13$.

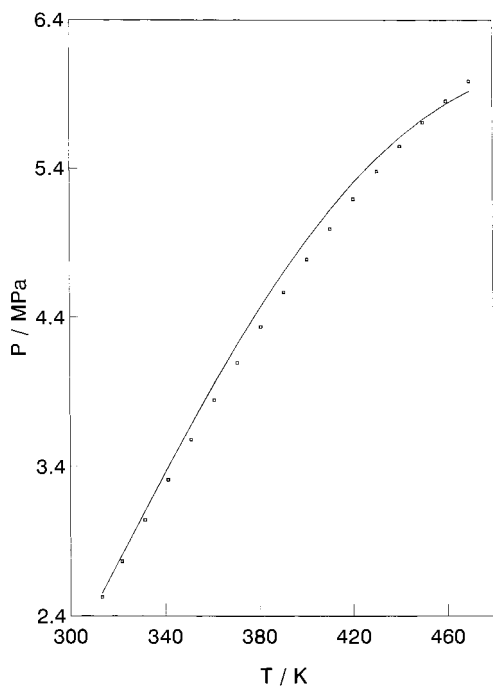


Figure 1. Experimental and correlated bubble point pressures of system 1 (solid line is correlated, and points are experimental).

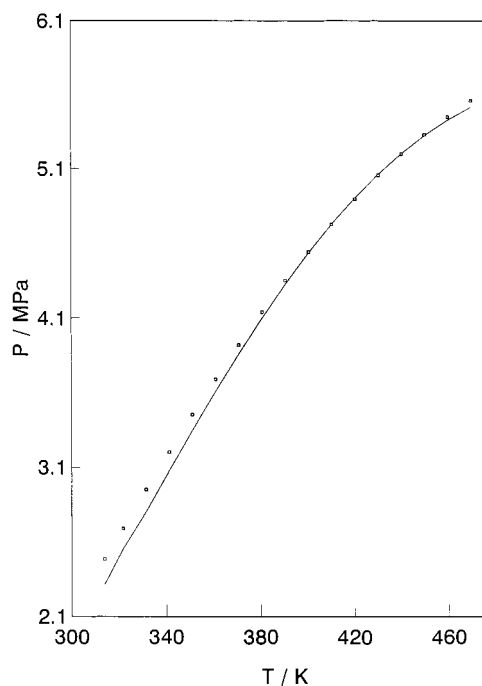


Figure 3. Experimental and correlated bubble point pressures of system 3 (solid line is correlated, and points are experimental).

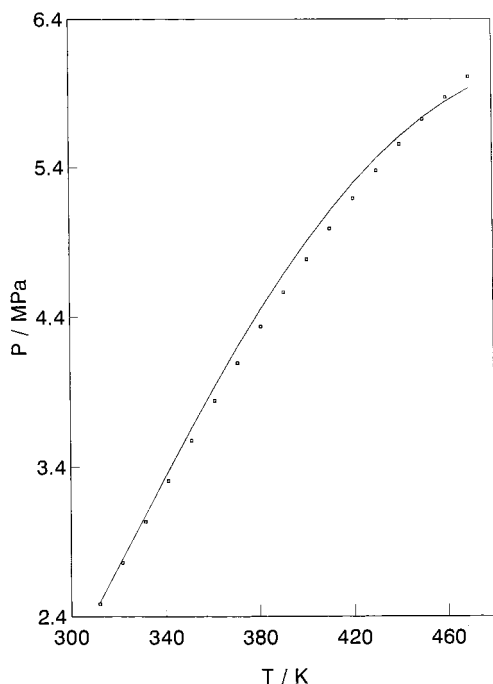


Figure 2. Experimental and correlated bubble point pressures of system 2 (solid line is correlated, and points are experimental).

pairs of molecules other than the ones containing CO_2 were neglected (appointed a zero value).

Experimental Section

The experimental work was carried out in a so-called high-pressure Cailletet apparatus. In this apparatus, pressures up to approximately 15 MPa can be handled and the temperature can range from 250 K to 470 K. An advantage of this apparatus is that the phase transitions can be observed visually; in our opinion this is still the most accurate way to determine various types of phase transitions.

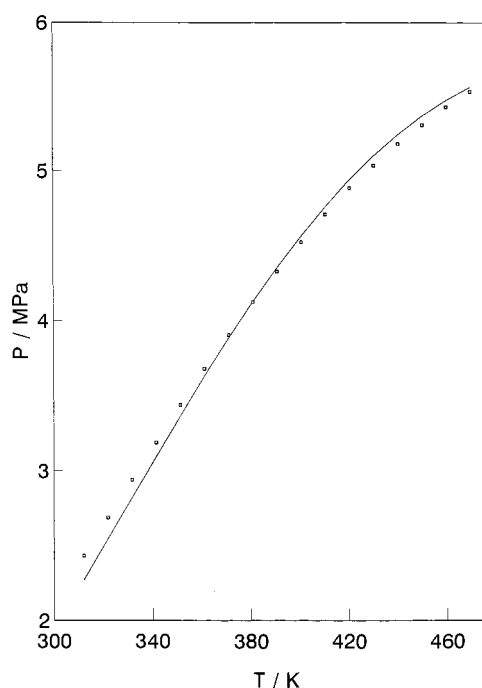


Figure 4. Experimental and correlated bubble point pressures of system 4 (solid line is correlated, and points are experimental).

A dead-weight pressure balance with a maximum pressure of 100 MPa was used to measure bubble point pressures. The maximum inaccuracy of the pressure balance plus the pressure gauge was ± 0.003 MPa. Temperatures were determined using a platinum resistance thermometer with an accuracy of ± 0.01 K. During the experiments, the temperature was maintained constant within ± 0.03 K. Silicon oil was used as the heating fluid, and mercury had the role of sealing and pressure-transmitting fluid. The Cailletet apparatus and the experimental procedure have been discussed in more detail in the literature (Peters et al., 1993).

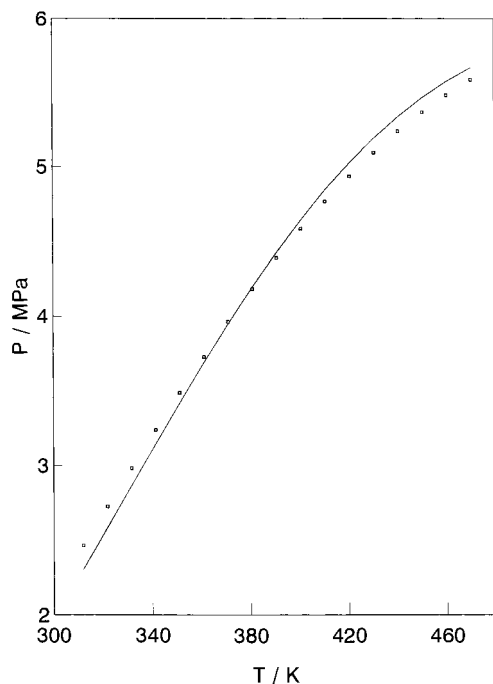


Figure 5. Experimental and correlated bubble point pressures of system 5 (solid line is correlated, and points are experimental).

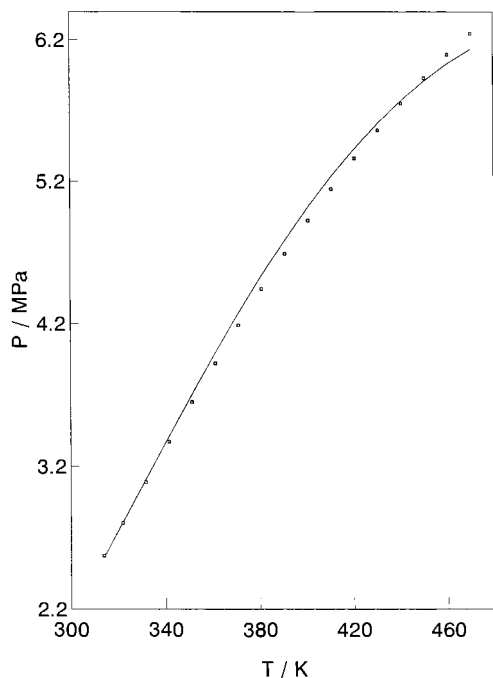


Figure 6. Experimental and correlated bubble point pressures of system 6 (solid line is correlated, and points are experimental).

The suppliers and the purity of the chemicals used in this study are summarized in Table 1. All substances were

used without further purification. Table 2 shows the six systems studied, indicating the components and their compositions in mole percent.

Results and Discussion

The experimental bubble point pressures for systems 1 to 6 are given in Tables 3–8, and Figures 1–6. The bubble point pressures, correlated by the PR EOS, are also shown in these tables. The chosen values of the binary interaction parameters between carbon dioxide and the other components making up the C_{6+} fraction are given at the bottom of each table. For each measured point, the relative error between experimental and predicted values are given in these tables and average absolute deviation of each system is determined. It can be seen that the average absolute deviations (AAD %) is less than or equal to 2.1% in all the systems.

Comparison of the percentages of error and average absolute deviation between the experimental and predicted data shows that the capability of the PR EOS is reasonably good in predicting the phase behavior of hydrocarbon mixtures heavier than hexane.

Acknowledgment

A.S. would like to thank the Delft University of Technology and Shiraz University for giving him the opportunity to perform this research. Thanks are also due to Mr. L. J. Florusse for his help in the experimental work.

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Received for review November 5, 1997. Accepted May 23, 1998.

JE970261X