

Phase Behavior of the Butane + Decane Binary System

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ABSTRACT: In this work, a series of bubble-point measurements were carried out on the binary system butane + decane. The experiments were carried out using the Cailletet apparatus, and bubble-point pressures were measured in a temperature range of (323.21 to 482.28) K. The corresponding pressures were predicted using the Peng–Robinson equation of state, and the relative errors were estimated. It is shown that this hydrocarbon mixture can be predicted reasonably well by this equation of state.

■ INTRODUCTION

The production of reservoir fluids is often accompanied with variations in composition, pressure, and temperature. This leads not only to changes in fluid properties but also to the frequent formation of new phases or elimination of one or more existing phase(s).¹ For instance, following the decrease of the initial pressure of an oil reservoir upon oil production, a gas phase appears as soon as the reservoir pressure reaches the bubble-point pressure of the reservoir fluid. Hence, knowledge about the phase behavior of reservoir fluids has a very important role in reservoir management and efficient production of reservoir fluids. Much research has been conducted to acquire a better understanding of the phase behavior of such systems. References 2 to 6, to mention only a few, represent examples of such investigations.

Oil and gas reservoir fluids are mainly composed of hydrocarbons. The behavior of a hydrocarbon mixture at reservoir and surface conditions is determined by its chemical composition and the prevailing temperature and pressure. Although a hydrocarbon reservoir fluid may be composed of hundreds of hydrocarbons, the phase behavior fundamentals can be explained with the help of the behavior of simple multicomponent mixtures of representative key components.

Since changes within the hydrocarbon reservoirs are often quite slow, it is reasonable to assume that all coexisting phases at any point in the reservoirs are in equilibrium.¹ Therefore, by performing phase equilibrium measurements on simple mixtures, it is possible to come to a good understanding of the phase behavior of real reservoir fluids. Normal alkanes and normal alkane mixtures are among the most common representative systems that have been studied by a number of researchers.^{7–10} Reamer et al.¹¹ and Reamer and Sage¹² studied the binary system of butane + decane using a dynamic phase recirculation method for determining the equilibrium compositions.

In this work, the fluid phase equilibria in the binary system of butane + decane have been investigated experimentally using a static synthetic method. In addition, the Peng–Robinson

equation of state (PR EOS) has been used to predict the vapor–liquid equilibrium (VLE) data of this system. To check the predictive ability of the PR EOS for such systems, the binary interaction coefficients have been set equal to zero.

■ EXPERIMENTAL SECTION

The apparatus and techniques employed in this investigation are similar to those used in earlier investigations.^{13–15} All experiments were performed using a so-called Cailletet apparatus.

The desired mixture was prepared by mixing the right proportion of liquid (decane) by weight and the required amount of gas (butane) by regulating the correct pressure on a confined volume of gas at a fixed temperature. This mixture was contained in a thick-walled Pyrex glass equilibrium tube. At a fixed temperature, the pressures at which the last bubble disappears, could be determined visually and identified as the bubble point pressure.

The pressure was measured using a dead-weight pressure gauge with an accuracy within 0.03 % of the reading. A platinum resistance thermometer with an accuracy of ± 0.02 K was used to measure the temperature. During the experiments, the temperature was maintained constant within ± 0.01 K. The total error in mole fractions of the components was within ± 0.002 . Depending on the working temperatures, water or silicone oil was used as the thermostating fluid. A more detailed description of the apparatus and the experimental procedures can be found elsewhere.^{13–15}

The butane used in this study was purchased from Air Products with a specified purity better than 0.9995 on a mole fraction basis. Decane, with a specified purity more than 0.99 on a mole fraction basis, was supplied by Janssen Chimica. All chemicals were used without further purification.

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Table 1. Bubble-Point Pressures of the Butane + Decane System at Several Temperatures for Various Concentrations of *n*-Butane

T/K	<i>p</i> /MPa	T/K	<i>p</i> /MPa	T/K	<i>p</i> /MPa
$x_{n-C4} = 1.000$		403.17	2.237	$x_{n-C4} = 0.407$	
313.10	0.387	418.11	2.796	323.24	0.198
332.96	0.650	433.02	3.420	333.30	0.250
333.27	0.648	447.90	4.082	343.24	0.309
352.78	1.024	462.69	4.624	358.16	0.416
353.28	1.023	466.49	4.692	373.27	0.544
373.39	1.542	466.61	4.694	373.32	0.590
393.26	2.226	467.46	4.707	388.28	0.697
413.23	3.125	$x_{n-C4} = 0.801$		403.28	0.871
418.15	3.389	323.23	0.406	418.19	1.067
425.07 ^a	3.791 ^a	333.32	0.523	433.06	1.287
$x_{n-C4} = 0.954$		343.42	0.656	447.93	1.530
323.31	0.531	358.27	0.892	462.74	1.795
333.45	0.673	373.25	1.183	477.53	2.065
348.39	0.925	388.22	1.531	477.86	2.086
363.19	1.240	403.17	1.940	$x_{n-C4} = 0.202$	
373.28	1.498	418.17	2.410	343.19	0.160
388.23	1.947	433.18	2.930	358.19	0.212
403.20	2.488	448.14	3.496	373.27	0.277
418.11	3.118	463.11	4.081	388.23	0.351
425.74	3.475	478.07	4.625	403.25	0.437
433.02	3.831	$x_{n-C4} = 0.600$		418.17	0.536
436.07	3.976	313.26	0.228	433.18	0.651
439.00	4.113	328.28	0.332	447.96	0.778
441.99	4.228	343.65	0.468	462.77	0.927
444.15	4.303	358.22	0.630	477.46	1.088
444.21	4.287	373.29	0.831		
444.83	4.299	388.18	1.068		
445.04	4.303	403.32	1.347		
$x_{n-C4} = 0.891$		418.18	1.658		
323.21	0.454	433.28	2.011		
333.20	0.586	448.06	2.390		
343.18	0.736	462.69	2.795		
358.19	1.009	477.30	3.223		
373.25	1.347				
388.23	1.754				

^a Critical point.

DATA PREDICTION

The PR EOS¹⁶ was used to predict the phase behavior of the binary system of butane + decane. The PR EOS can adequately predict the phase behavior of hydrocarbon mixtures, when these mixtures are not very close to their critical points. The original mixing rules of the PR EOS (a quadratic mixing rule for its attractive term and a linear mixing rule for its repulsive term) was used to predict the phase behavior of the binary system of butane + decane. The original temperature dependency of the attractive parameter of the PR EOS was kept for calculations. Readers are referred to ref 16 for further details of this EOS.

RESULTS AND DISCUSSION

The experimentally measured vapor pressures of pure butane and the bubble-point pressures of the binary system of butane +

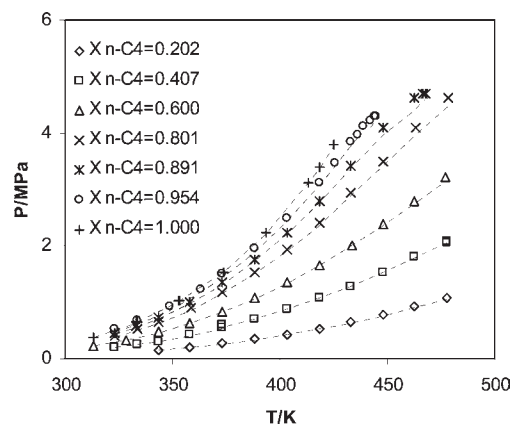


Figure 1. Experimental vapor pressures of pure butane and the bubble-point pressures of the binary system of butane + decane at different compositions (the points are experimental data, and the dashed lines are the PR EOS predictions).

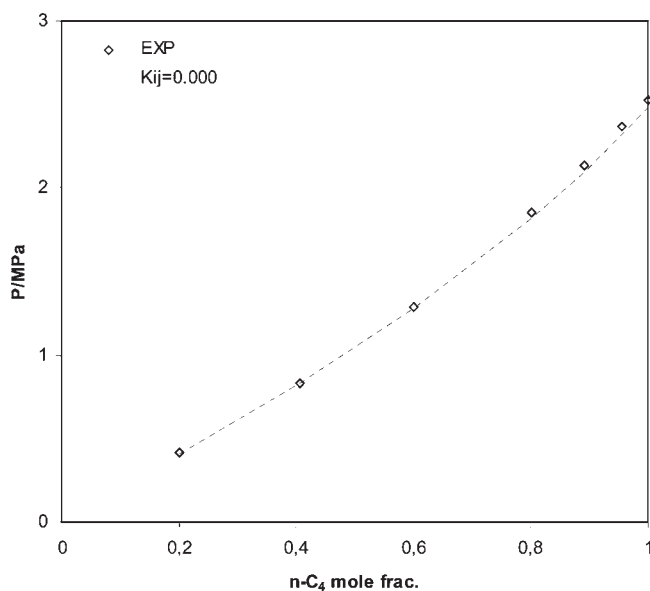


Figure 2. *P*-*x* diagram of the binary system of butane + decane at 400 K (the points are experimental data, and the dashed lines are the PR EOS predictions).

decane at different compositions in the temperature range of 323.21 K up to 482.28 K are shown in Table 1. Figure 1 shows the experimental results graphically, along with the predicted results, determined by the PR EOS. To check the predictive ability of the PR EOS, the binary interaction parameter between butane and decane were set equal to zero. Considering that no interaction parameters were used, and hence absolutely no fitting to data, the results of the PR EOS show that it is extremely suitable for accurately describing, even in a purely predictive manner, the phase behavior of hydrocarbon systems, up to decane. The average absolute error (AAD %) of the predictions in Figure 1 is 2.39 %.

The PR EOS had difficulty representing the experimental data of only two isopleths ($x_{n-C4} = 0.891$ and $x_{n-C4} = 0.954$), which showed a maximum in pressure (cricondenbars) on the *PT* diagram. This can be because of the higher pressures in

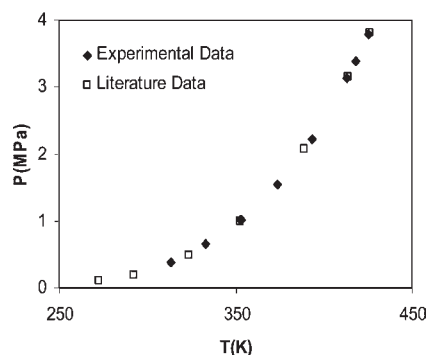


Figure 3. Comparison between the measured vapor pressures of butane in this work and literature vapor pressures (ref 17).

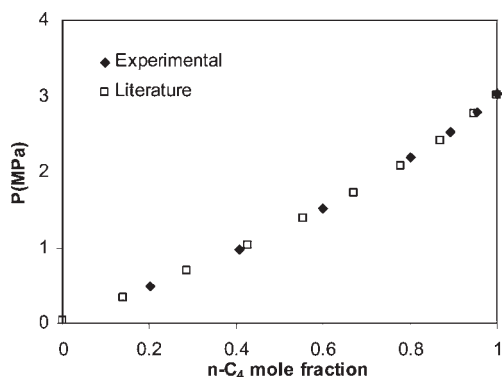


Figure 4. Comparison between the measured bubble-point data and Reamer and Sage's data for the isotherm of 410.9 K.

this part of the system and also because of not having used binary interaction parameters. Even so, the predictions even in this area do not deviate alarmingly from the experimental data.

Figure 2 shows the $P-x$ diagram of the binary system of butane + decane at 400 K. The $P-x$ data for this isotherm have been determined by interpolating the $P-T$ experimental data at different compositions. This figure also includes the PR EOS predictions. Not surprisingly, the PR EOS can accurately predicts the bubble-point curve on $P-x$ coordinates as well (the AAD % for these predictions is 1.74 %), although as the case with most of EOS, the predictions show more deviations at higher gas concentrations where the binary mixtures approach criticality.

The vapor pressures of pure butane at different temperatures are widely available in literature. To compare our results for the vapor pressures of pure butane with literature data, we used the data of Perry's Chemical Engineers' Handbook¹⁷ and presented our comparison in Figure 3. The excellent agreement between these data is clear in Figure 3.

Also, we compared our results with the bubble-point data of Reamer and Sage¹² for the binary system of butane + decane for the isotherm of 410.9 K (280 °F). Again, the agreement between these two results is excellent (Figure 4).

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