J. Chem. Eng. Data 1983, 28, 319-322

Phase Equilibria in the *n*-Pentane + Pent-1-ene System. 1. Critical States

Danley Wolfe and Webster B. Kay*

Department of Chemical Engineering, The Ohio State University, Columbus, Ohio 43210

Amyn S. Teja

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

$P-V-T-x$ data for the binary system composed of *n*-pentane and pent-1-ene have been determined over a range of conditions extending into the critical region. Pure-component properties for pent-1-ene as well as the critical states of the binary system are reported in this work. The critical states have been correlated by using the Peng-Robinson equation of state. As expected, the Peng-Robinson equation does not lead to good predictions of the critical volume vs. composition behavior. However, it is shown that a minor modification leads to significant improvement in these predictions.

Introduction

Components which are similar in size, shape, and chemical nature tend to form nearly ideal solutions. These types of solutions occur frequently in industrial applications and are well-known for the difficulty of their separations. There is consequently a great need for the accurate description of their thermodynamic and phase equilibrium properties over wide ranges of conditions. *n*-Pentane and pent-1-ene form a nearly ideal solution and are found in many hydrocarbon processing operations. Because of this, and the fact that in close boiling nearly ideal systems the errors in sampling and analyzing the coexisting phases may be large, we have studied this system over a range of conditions extending to the critical region and examined the ability of the Peng-Robinson (*1*) equation to correlate and predict the data. Pure-component properties and critical states of the binary system are reported in this paper. Vapor-liquid equilibria and $P-V-T$ data will be reported in a subsequent paper.

Experimental Section

The $P-T$ border curves and $\rho-T$ relationships for a series of mixtures of known composition and for pure pentene were determined experimentally. The relationships between any set of variables were then obtained by appropriate cross plots of these curves.

The apparatus and experimental techniques were the same as those employed in previous studies (*2*, *3*). Mixtures were prepared by deaerating and individually loading predetermined quantities of *n*-pentane and pent-1-ene into a sample tube under conditions of high vacuum. The samples were confined over mercury in the sealed end of a thick-walled precision-bore glass tube of 2-mm i.d. The tube was secured in a mercury-filled compressor with a means provided for controlling the pressure on the sample. Temperature control was provided by a vacuum reflux column surrounding the experimental tube. The sample temperature was kept constant by maintaining constant pressure on a series of pure organic liquids boiling in a side-arm flask attached to the reflux jacket. The temperature was measured with a precision of ±0.01 K by a calibrated iron-constantan thermocouple projecting into the reflux jacket in close proximity to the sample. The thermocouple was calibrated by comparison with a standard platinum rsistance thermometer certified by the National Bureau of Standards. The sample tube was secured in one leg of a mercury in steel U-tube, the other leg of which was connected to a source of high-pressure nitrogen gas to pressurize the sample. The pressure on the sample was indicated by a precision spring gage, read to within 1.38 kPa and calibrated at 138-kPa intervals by means of a dead-weight gage. Corrections were also made to account for the vapor pressure of mercury at the sample temperature and the pressure change across the mercury-sample interface due to capillary effects. The volume of the tube was calibrated and expressed analytically as a function of length from the sealed end. The calibration coefficients were determined by using a least-squares fitting routine. The calibration was made with mercury at room temperature by using a precision cathetometer both for the calibration and for subsequent measurements on the samples. Corrections were then applied to the volume to account for temperature and pressure expansions of the Pyrex sample tube. Equilibrium between the vapor and liquid phases was attained by rapid movement of a small steel ball through the sample with a magnet held outside the vacuum reflux jacket. The pressure and the volume of the sample were then observed at the dew and bubble points at a given temperature.

The $P-V-T$ data were obtained by setting the temperature at a constant value, varying the pressure, and measuring the volume of the sample. Three types of phase boundary points were obtained: bubble points, dew points, and critical points. The bubble point was taken as the pressure at which a tiny bubble of vapor appeared in the liquid phase in the top of the tube. A dew point was observed when the first trace of liquid appeared at the mercury-vapor interface. This was viewed as a black spot at the contact of the ball with the liquid on the inner wall of the tube.

The critical point was determined by following the bubble point line to the temperature and pressure at which the meniscus disappeared and was replaced by a band of opalescent fog. Further details of the apparatus and experimental procedure are given elsewhere (*3*).

***Materials and Preparation of Mixtures*.** The *n*-pentane and pent-1-ene used in this study were supplied by the Phillips Petroleum Co. and had a purity of better than 99.9 mol %. Before use, the chemicals were further purified by contacting with activated molecular sieves to eliminate any traces of moisture. The components were then deaerated by freezing with liquid nitrogen and pumping off the residual noncondensable gas to a pressure of 10^{-4} Pa, followed by melting and freezing. This process was repeated 10-12 times to ensure complete degassing of the hydrocarbons. The individual components were then stored as liquids in closed flasks attached to the vacuum train using acetone-dry ice baths. The purity of the components was checked by determining the isothermal pressure

0021-9568/83/1728-0319$01.50/0 © 1983 American Chemical Society

Table I. Critical Constants of the Pure Components

T_c, K	P_c, MPa	ρ_c, kg m^{-3}	ref
		n-Pentane	
469.8	3.38	231.0	this work
470.4	3.41	229.1	7
469.8	3.37	244.0	8
470.4	3.35	232.3	2
		Pent-1-ene	
465.1	3.55	233.0	this work
464.7			9

change between the dew and bubble points. The purity was considered satisfactory if this pressure change was no greater than 10 kPa.

The *n*-pentane + pent-1-ene mixtures were prepared by transferring predetermined amounts of each deaerated component by molecular distillation to the experimental tube which was attached to the vacuum train. A quantity of *n*-pentane was allowed to vaporize from the storage flask to the evacuated vacuum train until a certain pressure was reached. A portion of this gas was sealed from the system in a special loading flask at room temperature, the volume of which was measured prior to use. The mass of that component was then calculated from the measured pressure, volume, and temperature by using the ideal gas law.

Precision and Accuracy of Experimental Data. Temperature measurements were made with an iron-constantan thermocouple which was calibrated against a platinum resistance thermometer with an accuracy of ±0.05 K. The estimated accuracy of the calibration was ±0.07 K in the range 330-520 K. Sources of temperature variation were minimized during observations. A pure organic boiling liquid was used to avoid temperature gradients in the vacuum vapor column. The temperature measurements were estimated to be precise within ±0.01 K.

The primary source of error in determining the sample pressure was the calibration and reading of the Heise gauge. The calibration was performed with a Ruska dead-weight gauge at intervals of 138 kPa (with linear interpolation made between calibration points). The Heise gauge could only be read to within ±1.38 kPa, so that the estimated accuracy of the pressure is approximately ±3.4 kPa. Errors associated with other sources are small compared with the former and do not affect the esimated accuracy.

The volume of the sample was determined by measuring the sample height and using a calibration equation. The precision was estimated to be ±0.001 cm^3 with an accuracy of ±0.01 cm^3.

The composition and mass of the samples were determined as described above. The samples were loaded in the gas phase and the ideal gas law was used to calculate the number of moles and the mole fraction. The mass of the samples was determined with the samples under high vacuum and at room temperature. Under these conditions, the compressibility factor is greater than 0.999 and the assumption of ideality did not introduce significant error. The main source of error was the measurement of the pressure in the gaseous phase. It was estimated that errors from this source correspond to an accuracy of ±0.0003 g in the determination of the mass of the sample. The estimated error in the composition was approximately ±0.6 mol %.

Experimental Data

The following experimental data are reported in this work: (i) the critical properties of the pure substances, (ii) the experimental $P-V-T$ data at saturation for pure pent-1-ene, and (iii) the critical states of binary *n*-pentane + pent-1-ene mixtures. Measurements along the saturation boundaries of the mixtures are presented in part 2 of this study.

Table II. Pressure, Temperature, and Density Relationship of Pent-1-ene

		density, kg m^{-3}	
press., MPa	temp, K	liquid	vapor
0.551	362.4	556.9	
0.689	372.6	543.0	
0.862	383.0	527.8	
1.034	391.8	514.0	
1.207	399.6	501.8	
1.379	406.8	489.8	
1.551	413.6	477.6	
1.724	419.6	465.2	
1.896	425.2	453.1	
2.068	430.2	441.9	59.5
2.241	435.0	431.3	66.9
2.413	439.6	420.6	74.3
2.586	444.0	408.9	83.0
2.758	448.2	395.6	92.9
2.930	452.2	380.8	103.8
3.103	455.8	362.8	117.0
3.275	459.4	341.1	133.0
3.447	463.0	310.8	158.7
3.553	465.1	233.0	233.0

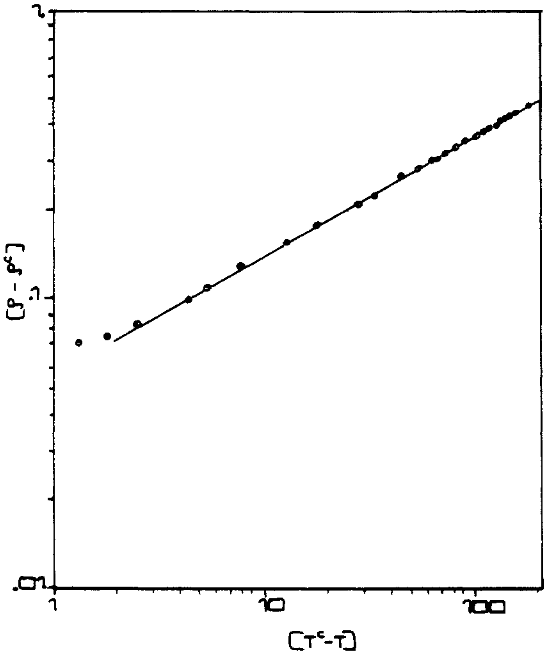

Figure 1. Plot of log ($\rho - \rho^c$) vs. log ($T_c - T$) for pent-1-ene.

Critical Properties of the Pure Substances. Table I presents the experimentally determined critical constants of *n*-pentane and pent-1-ene, together with values obtained from the literature. Values of the critical volume were determined by using the law of rectilinear diameters. As can be seen, the experimental critical properties determined in this work are in good agreement with values found in the literature, although the literature values do show a considerable amount of scatter. No data were available for comparison of the critical volume of pent-1-ene.

Pure-Component Data for Pent-1-ene. Table II summarizes the pressure, temperature, and density data obtained for pent-1-ene.

The consistency of the density-temperature data was determined as described by Rowlinson (*4*). The experimental density-temperature data for pent-1-ene was plotted as $|\rho_c - \rho|$ vs. $T_c - T$ on log-log coordinates. It has been shown that the quantity $\rho^c - \rho$ has a dependence on a leading term proportional to $T^c - T$ and is nearly linear over limited ranges of data (Figure 1). The slope of the experimental data for liquid pent-1-ene was 0.40, while that of the saturated vapor was

Table III. Comparison of Experimental and Literature Values of the Density of Liquid Pent-1-ene

density, kg m^{-3}			
293.2 K	298.2 K	303.2 K	ref
640.0	635.5	631.3	this work
640.5	635.3		*10*
642.3	637.2	631.9	*11*

0.29. Data for *n*-pentane vapor nearly coincided with that for pent-1-ene over the range of experimental measurements.

A comparison between measured and literature values of liquid densities of pent-1-ene at various temperatures is made in Table III. As the table indicates, excellent agreement with the limited data available was obtained.

Critical States of the Binary Mixtures. Table IV represents a summary of the experimental critical properties of *n*-pentane + pent-1-ene mixtures and therefore defines the critical locus curve of the system. Because the system is very nearly ideal and the densities of the two components are also nearly identical, the data indicate that the density does not change very much with composition.

Correlation of Critical States

The critical states measured in this investigation have been used to test the Peng–Robinson (*7*) equation of state. This method has been used previously (*5*) for the calculation of the critical states of hydrocarbon mixtures. It is shown here that the method is able to correlate the T_c vs. x_c and P_c vs. x_c behavior of the *n*-pentane + pent-1-ene system but fails to correlate the V_c vs. x_c behavior. This is not unexpected and is a result of the constant value of Z_c (=0.3074) which is implied by the equation of state.

The Peng–Robinson equation is given by

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

where, for a pure component *i*, the constants a_{ii} and b_{ii} are given by

$$a_{ii} = 0.45724(R^2T_{ci}^{\ 2}/P_{ci})\{1 + k_i(1 - T^{1/2}/T_{ci}^{\ 1/2})\}^2 \tag{2}$$

$$b_{ii} = 0.07780RT_{ci}/P_{ci} \tag{3}$$

$$k_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^{\ 2} \tag{4}$$

Equation 1 implies a universal critical compressibility factor of 0.3074 for pure substances. This is large compared with our measured values of 0.267 for *n*-pentane and 0.279 for pent-1-ene.

For mixtures, the parameters *a* and *b* are defined by the mixing rules

$$a = \sum_i \sum_j (1 - \delta_{ij})x_ix_ja_i^{\ 1/2}a_j^{\ 1/2} \tag{5}$$

$$b = \sum_i x_ib_i \tag{6}$$

where δ_{ij} is a binary interaction coefficient characteristic of the binary system composed of components *i* and *j*.

Critical states of binary mixtures satisfy the following equations (*6*):

$$A_{2x}A_{2v} - A_{xv}^{\ 2} = 0 \tag{7}$$

$$A_{3x}A_{2v}^{\ 3} - 3A_{2xv}A_{xv}A_{2v}^{\ 2} + 3A_{x2v}A_{xv}^{\ 2}A_{2v} - A_{3x}A_{xv}^{\ 3} = 0 \tag{8}$$

where the subscripts denote derivatives, e.g., $A_{2xv} = \partial^3A/\partial x^2\partial v$. If the Helmholtz energy and its derivatives are available, then the two equations may be solved for any two of the three variables T_c, V_c, and x_c. In the calculations presented here, the Helmholtz energy and its derivatives were obtained from the Peng–Robinson equation using standard thermodynamic relationships.

Results of our calculations are shown in Table IV. As expected, the system is very nearly ideal, as evidenced by the approximately linear critical locus curve. The Peng–Robinson equation (with $\delta_{ij} = 0$) correlates the T_c vs. x_c behavior well but, not surprisingly, fails to correlate the V_c vs. x_c behavior. The latter is due to the unrealistic critical compressibility inherent in the use of the equation.

The critical volume was also calculated with

$$V_c' = Z_{cm}RT_c/P_c \tag{9}$$

where

$$Z_{cm} = \sum_i x_iZ_{ci} \tag{10}$$

Here T_c and P_c are the critical temperatures and pressure calculated by using the method described above and Z_{ci} is the experimental critical compressibility of component *i*. In this case, agreement with experimental critical volumes is much better as shown in Table IV. The average absolute deviation between calculated and experimental critical volume is reduced from 13.6% to 0.37% if eq 9 and 10 are used for this system.

Glossary

A	Helmholtz energy
a	constant in eq 1
b	constant in eq 1
k	constant in eq 2
P	pressure
R	gas constant
T	thermodynamic temperature
V	volume
x	mole fraction
Z	compressibility factor
δ	binary interaction coefficient
ρ	density

Subscripts

1, 2	component 1, 2
c	critical
i, *j*	component *i*, *j*
x, *v*	differentiation with respect to *x*, *v*

Table IV. Experimental and Calculated Critical States of *n*-Pentane + Pent-1-ene Mixtures

	exptl			calcd			
x_1	T_c, K	P_c, MPa	V_c, m^3 kmol^{-1}	T_c, K	P_c, MPa	V_c, m^3 kmol^{-1}	V_c', m^3 kmol^{-1}
0.0000	465.1	3.55	0.3010				
0.2489	465.6	3.53	0.3030	466.3	3.416	0.3399	0.3010
0.5010	467.2	3.47	0.3055	467.5	3.375	0.3450	0.3056
0.7898	468.5	3.42	0.3076	468.8	3.327	0.3509	0.3089
1.0000	469.8	3.38	0.3123				
AAD,[a] %				0.09	1.57	13.61	0.37

[a] AAD (%) = $(100/n)\Sigma_1^{\ n}\,|1 - (\text{calculated value/experimental value})|$.

Registry No. *n*-Pentane, 109-66-0; pent-1-ene, 109-67-1.

Literature Cited

(1) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(2) Kay, W. B. *J. Am. Chem. Soc.* **1947**, *69*, 1273.
(3) Genco, J. M.; Teja, A. S.; Kay, W. B. *J. Chem. Eng. Data* **1980**, *25*, 350.
(4) Rowlinson, J. S. "Liquids and Liquid Mixtures", 2nd ed.; Butterworths: Oxford, 1969.
(5) Peng, D. Y.; Robinson, D. B. *AIChE J.* **1977**, *23*, 137.
(6) Teja, A. S.; Rowlinson, J. S. *Chem. Eng. Sci.* **1973**, *28*, 529.
(7) Ambrose, D.; Cox, J. D.; Townsend, T. *Trans. Faraday Soc.* **1960**, *56*, 1452.
(8) Beattie, J. A.; Levine, S. W.; Douslin, D. R. *J. Am. Chem. Soc.* **1951**, *73*, 4431.
(9) Guggenheim, E. A. *J. Chem. Phys.* **1945**, *13*, 253.
(10) Forziatti, A. F.; Kamin, D. L.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1950**, *45*, 406.
(11) Hill, P. L. Ph.D. Thesis, The Ohio State University, Columbus, OH, 1950.

Received for review August 26, 1982. Accepted March 14, 1983.

Phase Equilibria in the *n*-Pentane + Pent-1-ene System. 2. Dew and Bubble Points

Danley Wolfe and Webster B. Kay*
Department of Chemical Engineering, The Ohio State University, Columbus, Ohio 43210

Amyn S. Teja
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

$P-V-T-x$ data for the binary system composed of *n*-pentane and pent-1-ene have been measured over a range of conditions extending into the critical region. Dew and bubble points of the binary system are reported in this work as well as their correlation using the Peng–Robinson equation.

Introduction

n-Pentane and pent-1-ene form a nearly ideal solution. Because of the frequency of occurrence of such solutions in hydrocarbon processing operations and the difficulty of separation of the components, it was decided to study the *n*-pentane + pent-1-ene system over a wide range of conditions extending into the critical region. Critical states of *n*-pentane + pent-1-ene mixtures and their correlation using the Peng–Robinson equation have been reported in part 1 of this work (*1*). Dew and bubble points are reported in this paper. Vapor–liquid equilibria have been correlated by using the Peng–Robinson equation and this is described below.

Experimental Section

Experimental details have been reported fully in part 1 and are not repeated here. At a given temperature, bubble and dew points were measured as well as the densities of the phases.

The densities of saturated liquid *n*-pentane and pent-1-ene are very close to one another and, moreover, the density–temperature plots of the pure liquids cross each other at approximately 402 K. Because of this fact and because the volume change on mixing is extremely small for this nearly ideal system, consistent data for excess volumes could not be obtained in this study. Moreover, considerable experimental difficulties which are described below were encountered with the measurement of liquid densities at the bubble point. Only vapor densities of mixtures are therefore reported below.

During a run, the procedure used was to determine a series of bubble points from about 320 K to near the critical point. The pressure and the temperature of the sample were then carefully lowered to the point where the volume of the saturated vapor was just within the range of the tube calibration. Dew points were now determined until the critical region was approached. The critical temperature, pressure, and volume were then obtained. It was found that significant errors were introduced if dew points and bubble points were determined alternately as the temperature and pressure increased to those at the critical point. At a dew point, the sample was fully vaporized and occupied a volume about 3 times that at the bubble point. When the pressure was raised slightly to condense the sample, the column of mercury rose and the condensing liquid inevitably "wetted" the wall of the tube. This was apparent by the appearance of the mercury along the wall. Because of the small sample size, this loss of sample along the tube wall could cause considerable error in the volume of the saturated liquid as measured by the sample height.

Dew Point Determinations

The desired temperature of the sample was fixed by setting the pressure of the organic vapors in the vacuum column. The sample pressure was then lowered and the sample was expanded until it was completely vaporized and in the superheated region. The pressure was incrementally increased until the first trace of liquid appeared, characterized by the appearance of a black dot at the point of contact between the stirring ball and the wall of the experimental tube. Near the critical region, however, the dew point was taken as the point at which miniscule droplets of liquid were seen condensing throughout the vapor sample. After each incremental increase in pressure, equilibrium was assured by moving the steel ball vigorously through the sample via a permanent magnet.

Bubble Point Determinations

Since the saturated volume of a liquid increases with increasing temperature, the series of bubble points of the sample was determined beginning at low temperatures and increasing to higher temperatures. In this manner, the problem of liquid

0021-9568/83/1728-0322$01.50/0 © 1983 American Chemical Society