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

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

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***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 minuscule 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

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Table I. *P-V-T-x* Data for the *n*-Pentane + Pent-1-ene System

type[a]	P, MPa	T, K	ρ, kg m^{-3}
	$x_1 = 0.2489$		
b	0.358	344.6	
b	0.442	354.6	
b	0.564	363.6	
b	0.695	373.4	
b	0.844	382.3	
b	1.045	392.9	
b	1.292	404.2	
b	1.567	415.8	
b	1.778	422.5	
b	2.107	432.4	
b	2.287	437.4	
d	2.249	437.8	71.8
d	2.391	441.6	78.1
b	2.440	441.6	
d	2.779	450.8	118.0
b	2.820	450.8	
d	3.063	456.9	120.6
b	3.101	456.9	
d	3.182	459.2	133.5
b	3.207	459.2	
d	3.262	460.8	137.5
b	3.291	460.8	
d	3.477	464.9	178.2
b	3.494	464.9	
	$x_1 = 0.5019$		
b	0.338	344.0	
b	0.431	353.5	
b	0.534	362.7	
b	0.669	373.1	
b	0.815	382.6	
b	1.000	392.8	
b	1.260	404.1	
b	1.395	410.0	
b	1.715	422.2	
b	2.034	432.2	
b	2.349	441.1	
b	2.817	452.9	
b	2.996	457.0	
b	3.193	461.1	
b	3.263	462.6	
b	3.300	463.5	
b	3.365	464.6	
d	1.983	432.1	59.6
d	2.312	441.5	73.7
d	2.760	452.5	97.8
d	2.977	457.3	112.7
d	3.201	462.2	134.6
d	3.338	464.8	155.1
	$x_1 = 0.7898$		
b	0.313	343.5	
b	0.397	352.9	
b	0.510	364.1	
b	0.638	373.6	
b	0.780	383.4	
b	0.951	393.0	
b	1.183	403.9	
b	1.370	412.3	
b	1.674	423.7	
b	1.961	432.8	
b	2.274	441.4	
b	2.738	453.3	
b	2.993	459.7	
b	3.116	462.3	
b	3.259	465.3	
d	1.902	432.1	
d	2.226	441.3	71.6
d	2.684	453.1	96.2
d	2.947	459.0	114.7
d	3.198	464.4	140.4

[a] b = bubble point, d = dew point.

sample "wetting" the tube wall was avoided.

To determine a bubble point the desired temperature was set as before, the sample pressure being maintained well above the estimated vapor pressure of the mixture to prevent overexpansion of the liquid sample. When the steady-state temperature had been achieved, the pressure was incrementally decreased until an infinitesimal bubble of vapor appeared at the top of the tube. Usually, the bubble disappeared upon vigorous stirring, in which case the pressure was again decreased by a very small increment. The bubble point was taken, then, to be the point at which the infinitesimal vapor bubble just remained in the sample. The sample volume was determined by increasing the pressure slightly until the sample was completely liquid.

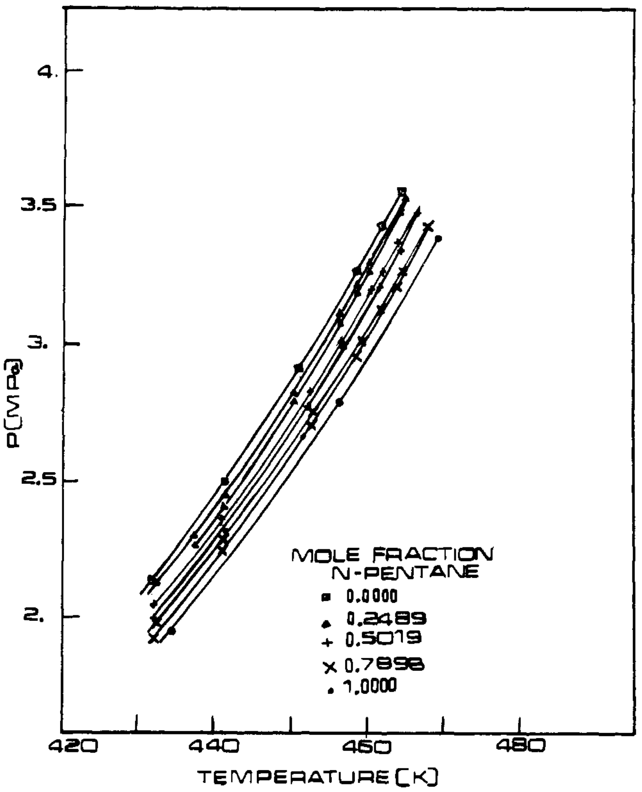

Figure 1. *P-T* diagram for the *n*-pentane + pent-1-ene system.

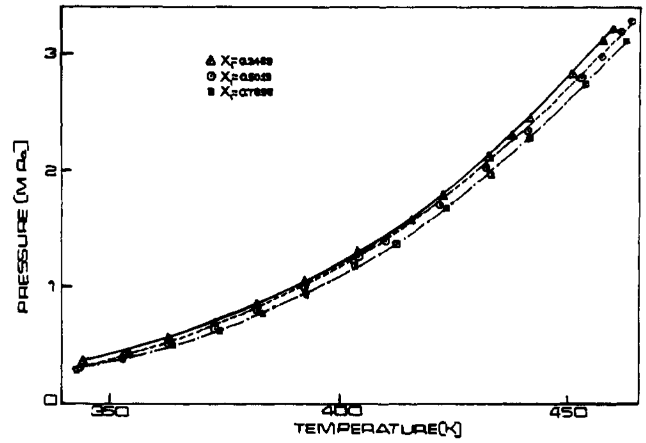

Figure 2. *P-T* projection of the bubble point curves for three *n*-pentane + pent-1-ene mixtures. The lines were calculated by using the Peng-Robinson (*2*) equation.

Results

Experimental *P-V-T-x* data for the *n*-pentane + pent-1-ene system are given in Table I. Three mixtures containing approximately 25, 50, and 75 mol % *n*-pentane were studied. Together with the data for pure pent-1-ene presented in part 1 of this work and the data for pure *n*-pentane from the literature, the complete system can be described up to the critical point.

Figure 1 illustrates the *P*–*T* relations for the system. The solid line for *n*-pentane was drawn by using literature data while the points on that line correspond to experimental check data on that component.

Figure 2 illustrates the *P*–*T* projections of the bubble points of the three mixtures calculated with the Peng–Robinson (*2*) equation and experimental measurements from this study. As can be seen, the Peng–Robinson equation is able to predict bubble points of this system satisfactorily. No binary interaction coefficients were used in this study.

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Viscosities and Densities of Binary Mixtures of 1-Alkanols from 15 to 55 °C

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Viscosities of binary mixtures of 1-decanol, 1-nonanol, 1-octanol, and 1-heptanol with 1-butanol, 1-propanol, ethanol, and methanol were measured at 15, 25, 35, 45, and 55 °C. Viscosities η are presented as a polynomial in mole fraction X_1 of the low molecular weight component of binary mixture: $\eta = A + BX_1 + CX_1^2 + DX_1^3 + EX_1^4$. Molar volumes of binary mixtures are given by the sums of the products of molar volume and mole fraction of components involved. Viscous heats and preexponential factors are also reported. These data were also fitted to the empirical equation of McAllister, Herric, Auslander, and two additional polynomials.

Introduction

The literature dealing with the viscosity of mixtures of 1-alkanols is rather limited. While a number of empirical relations (*1*–*6*) have been proposed to predict the viscosity of a mixture from that of pure components, we did not trust the extrapolation to higher alkanols. In the present work, we have measured the viscosity of 16 binary mixtures comprising 1-decanol, 1-nonanol, 1-octanol, 1-heptanol, 1-butanol, 1-propanol, ethanol, and methanol. These data were fitted to a five-parameter polynomial with a goodness of fit approximating experimental error. In addition, these binary data were fitted to the empirical relations of McAllister (*1*), Herric (*2*), and Auslander (*3*) and also to two additional polynomial equations using a multiparametric curve-fitting program. In order to obtain viscosity from kinematic viscosity, densities of all mixtures were also determined. The viscous heat and the preexponential factor of the mixtures were also calculated.

Models and Equations

Several equations have been put forward to calculate the viscosities of binary mixtures.

***McAllister's Formula* (*1*).** McAllister derived the following relation for a liquid mixture on the basis of the absolute reaction rate theory of Eyring:

$$\ln \eta = X_1^3 \ln \eta_1 + 3X_1^2X_2 \ln \eta_{12} + 3X_1X_2^2 \ln \eta_{21} + X_2^3 \ln \eta_2 + D' \quad (1)$$

where

$$D' = -\ln (X_1 + X_2M_2/M_1) + 3X_1^2X_2 \ln (\tfrac{2}{3} + M_2/3M_1) + 3X_1X_2^2 \ln (\tfrac{1}{3} + 2M_2/3M_1) + X_2^3 \ln (M_2/M_1)$$

The equation contains two adjustable parameters, $\ln \eta_{12}$ and $\ln \eta_{21}$.

***Herric's Formula* (*2*).** The following relation was proposed by Herric to correlate viscosities of binary mixture:

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 \ln M_1 + X_2 \ln M_2 - \ln (X_1M_1 + X_2M_2) + \Delta 12 \quad (2)$$

where $\Delta 12 = \alpha_{12}X_1X_2$ is a function representing molecular interaction and $\alpha_{12} = \alpha_{21}$ is the interaction parameter. Herric expressed α_{12} or α_{21} as a linear function of composition

$$\alpha_{12} = \beta_{12} + \beta_{21}(X - X_2) \quad (3)$$

The coefficients β_{12} and β_{21} may be determined from a least-squares method.

***Auslander's* Formula (*3*).** Auslander's equation has the following three-parameter form:

$$X_1(X_1 + B_{12}X_2)(\eta - \eta_1) + A_{21}X_2(B_{21}X_1 + X_2)(\eta - \eta_2) = 0 \quad (4)$$

Here, A_{21}, B_{12}, and B_{21} are the parameters representing binary interactions.

***Polynomial Functions*.** Viscosity data were fitted to three different polynomials of the following form, the first of which was chosen as the form of data presentation in this paper; note that polynomial I is the only equation which does not require fixed values of the viscosities of the pure components and allow them to share in the goodness of fit:

polynomial I

$$\eta = A + BX_1 + CX_1^2 + DX_1^3 + EX_1^4 \quad (5)$$

where *A*, *B*, *C*, *D*, and *E* are adjustable parameters.

polynomial II

$$\eta = \eta_1X_1 + \eta_2X_2 + AX_1 + BX_2 + X_1X_2A + B(X_1 - X_2) + C(X_1 - X_2)^2 \quad (6)$$

polynomial III

$$\eta = \eta_1X_1 + \eta_2X_2 + X_1X_2A + B(X_1 - X_2) + C(X_1 - X_2)^2 \quad (7)$$

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