Vapor-Liquid Equilibrium of *n*-Pentane-Acetone

TEH CHENG LO, HAROLD H. BIEBER, ANDREW E. KARR
Hoffmann-La Roche Inc., Nutley, N. J.

SOLVENT MIXTURES of *n*-pentane and acetone are used in chemical processing and very often these solvents are to be recovered or repurified by distillation. A brief review of the literature indicated no reported vapor-liquid equilibrium data on this system. Since this information would be essential for the design of a distillation unit for carrying out this separation, the present work was undertaken.

EXPERIMENTAL PROCEDURE

Apparatus. The equipment used for obtaining the vapor-liquid equilibrium data was a modification of the Othmer still (*9*, *14*). To ensure adiabatic operation, radiation losses from the vapor sections of the still were eliminated by the addition of a carefully designed heating jacket (*9*). The boiler and vapor sections were covered with 3/8 inch and 1/4 inch, respectively, of magnesia. Three iron-Constantan thermocouples were installed under the insulation and adjacent to the still body. One thermocouple was located about 1 inch above the liquid level, another at the center and the third at the top of the vapor jacket. Wound over the insulation around the vapor space were 8.8 feet of 20 B. and S. gage Nichrome wire having a total measured resistance of 5.66 ohms. The wire spacing near the center of the winding was 3/8 inch and at both ends was about 1/2 inch. Magnesia was used to cover the Nichrome windings. By means of this heating jacket, the temperatures of all three thermocouples were maintained within 2° C. of the indicated boiling points of the mixtures studied in the course of this investigation.

A −5° to 210° C. thermometer, having 0.2° C. scale divisions and calibrated by the National Bureau of Standards, was used. Calibration and stem corrections were applied to all temperature readings. To avoid losses of the low boiling *n*-pentane, cold brine (−1° to −4° C.) was circulated through the condensers. The barometric pressure was recorded after each run and the observed temperature corrected to 760 mm. using the following equation:

$$t_{\text{corr.}} = t_{\text{obs.}} + 0.04\,(760 - P)$$

where

$t_{\text{corr.}}$ = corrected boiling point, ° C.
$t_{\text{obs.}}$ = observed boiling point
P = barometric pressure, mm. Hg
0.04 = slope of vapor pressure curves at the boiling point of the pure components

Materials. The acetone used was Baker's C.P. reagent. As acetone absorbs moisture from the air readily, the material was stored in a tightly stoppered bottle.

Phillips 99% *n*-pentane was fractionated in a 50-plate Oldershaw column at a reflux ratio of 40 to 1. A 50% heart cut was blended for the equilibrium studies.

The physical properties of the materials used in this investigation are given in Table I and are compared to the literature values. Discrepancies among various references were found for almost every property. Therefore, only the values believed to be the most reliable are shown. Boiling points were determined in the modified Othmer apparatus.

Experimental Procedure. A series of vapor-liquid equilibrium determinations was made by adding 300 to 350 ml. of the *n*-pentane–acetone mixture to the still. The immersion electric heater voltage was adjusted to obtain the desired rate of distillation. It usually took 1 hour to heat up the jacket to the equilibrium temperature. To avoid superheating the vapor, the center thermocouple was maintained 1 to 2° C. lower than the still thermometer. The bottom thermocouple usually read 0 to 1° C. lower than the one at the center, while the top thermocouple read 0.5 to 1° higher than the center one. These relative temperatures were found to hold at operating temperatures of 31° to 49° C.

The voltage variation was only two volts over the 18° C. temperature range, and no difficulty was encountered in setting and maintaining the proper conditions. As the temperatures between runs were small, the same voltage setting was used for several consecutive runs.

The usual distillation rate was approximately 10 ml./min. At this rate, the entrainment was assumed to be negligible. This was based on a preliminary experiment in which a 10% potassium chloride solution was boiled in the apparatus for 1 hour at a rate equivalent to a vapor velocity at the surface of approximately 1.4 cm./sec. This was a higher velocity than ever used during the data collecting runs. A sample taken from the condensate receiver contained 0.0018% KCl.

After equilibrium conditions were obtained, as indicated by the constancy of the vapor thermometer reading for at least 20 minutes, the immersion heater was shut off. One hour was the usual recycling time required for a run, after which the liquid and vapor condensate samples were taken quickly. The liquid drain outlet was connected with a small condenser which was cooled with −3° C. brine. The drain lines were first flushed and then dried with nitrogen. Samples then were run into chilled test tubes immersed in a dry ice–acetone bath at approximately −50° C. The drain outlets extended, about 1 to 1½ inches into the chilled test tubes and were provided with vented rubber stoppers which fitted tightly into the test tubes. The test tubes were quickly stoppered after the samples were taken and left in the dry ice–actone bath until they were analyzed.

Method of Analysis. Accuracy for this work required more than a simple physical property determination of the

Table I. Physical Properties of Material Used

	B. P., ° C.		Refractive Index n_D^{25}	
	Obsd.	Lit.	Obsd.	Lit.
Acetone	56.07	56.1 (*1*) 56.15(*5*) 56.20(*23*) 56.30(*8*)	1.3558	1.35662(*18*) 1.3556 (*7*)
n-Pentane	36.05	36.0 (*4*) 36.06(*11*) 36.10(*22*) 36.15(*10*)	1.3546	1.35470(*11*) 1.35480(*6*)

unkown mixture. Therefore, it was decided to determine acetone directly by a modification of Marasco's method (*12*). Acetone was condensed with hydroxylamine hydrochloride, and the liberated HCl was titrated with standard base.

Samples to be analyzed were removed from the acetone-dry ice bath and warmed up to −25° C. to ensure complete miscibility of the solvents. A siphoning device was used to transfer the sample from the test tube to the weighted volumetric flask.

Analytical Procedure. Fill a 50 ml. volumetric flask with 20 to 30 ml. of pure ethyl alcohol and weigh. Immerse the flask in the dry ice-acetone bath and transfer 2 to 5 grams of sample from the test tube into the flask. Maintain the temperature of the bath in which the test tube and flask are immersed between −20° and −30° C. Weigh the flask again to obtain the weight of the sample. Dilute with ethyl alcohol to 50 ml. (Make all weighings on an analytical balance.) Place 400 ml. of reagent solution (12 grams hydroxylamine hydrochloride per 6 liters, pH = 3.75) in a 600 ml. beaker. Immerse the electrodes into the solution and measure the pH. Pipet 5 or 10 ml. (containing 0.1 to 0.2 grams acetone) of sample into the beaker below the surface. Wait 5 minutes. Titrate with 0.1*N* NaOH until nearly neutral, stir, and wait 20 seconds. Repeat two to three times until the pH meter shows that the neutral point is reached. Run blank.

Synthetic solutions were used to determine the precision of the analytical method. A summary of the results is given in Table II.

RESULTS AND DISCUSSION

The vapor-liquid equilibrium data obtained using the equipment and procedures described above are summarized in Table III. The data are also shown on an *X*−*Y* plot (Figure 1).

Table II. Precision of *n*-Pentane–Acetone Analysis

Acetone, Wt. %	Obsd.	Deviation	% Deviation
5.94	6.09 5.90 Av. 5.995	+0.06	1.01
13.9	13.7 13.8 Av. 13.75	−0.15	1.08
90.8	91.7 91.3 Av. 91.5	+0.70	0.77
95.6	96.0 96.3 Av. 96.15	+0.55	0.58

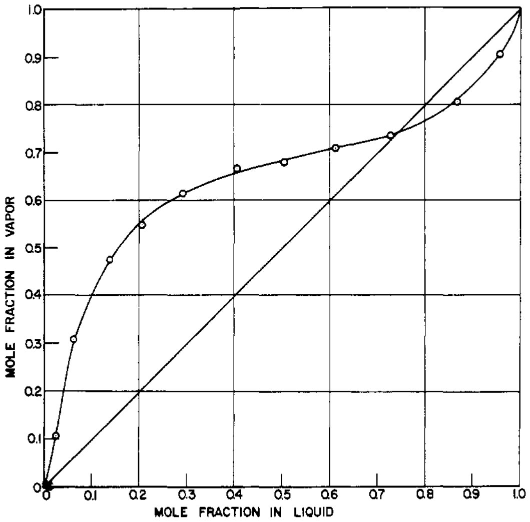

Figure 1. Vapor-liquid equilibrium curve calculated from Redlich and Kister constants for *n*-pentane–acetone at 760 mm. Hg

O Observed points

Calculation Methods. The correlation of vapor-liquid equilibrium data according to thermodynamic relations requires a correction for liquid density and the deviation of the saturated vapors from the ideal gas laws (*2, 13, 17, 19*). This correction is appreciable when the components have widely different boiling points. The correction factor as applied to the activity coefficient has been expressed by Benedict and others (*2*) as follows:

$$\gamma_1 = \frac{Z_1 P y_1}{P_1^\circ X_1} \qquad (1)$$

$$\gamma_2 = \frac{Z_2 P y_2}{P_2^\circ X_2} \qquad (2)$$

in which the correction factor, Z_1, is expressed as

$$Z_1 = e^{[(P_1^\circ - P)(v_1 - \beta_1)/RT]} \qquad (3)$$

where v_1 is the molar volume and β_1 is the second coefficient of the following virial equation of state, in which higher coefficients have been neglected

$$PV = RT + \beta_1 P$$

The determination of the *Z* factor requires an involved calculation of the second virial coefficient for the gas law deviation (according to generalized charts or an empirical

Table III. Vapor Liquid Equilibrium Data and Calculated Activity Coefficients

						Vapor Temp., ° C.							
Run No.	X_1	X_2	Y_1	Y_2	Press., Mm. Hg	Actual	Cor. to 760 mm.	P_1°	P_2°	Z_1	Z_2	γ_1	γ_2
1	0.021	0.979	0.108	0.892	766.5	49.38	49.15	1170	602.5	1.028	0.990	3.465	1.148
2	0.061	0.939	0.307	0.693	760.0	45.76	45.76	1048	527	1.017	0.985	3.715	1.048
3	0.134	0.866	0.475	0.525	758.6	39.52	39.58	860	413.5	1.006	0.979	3.150	1.088
4	0.2105	0.7895	0.550	0.450	758.6	36.61	36.67	777	370	1.003	0.980	2.558	1.145
5	0.292	0.708	0.6145	0.3855	761.0	34.39	34.35	720	340	0.996	0.972	2.216	1.184
6	0.405	0.595	0.664	0.336	760.8	32.88	32.85	685	318.5	0.995	0.970	1.812	1.323
7	0.503	0.497	0.678	0.322	768.8	32.68	32.35	677	316	0.993	0.970	1.520	1.530
8	0.611	0.389	0.711	0.289	765.8	32.18	31.97	665	310	0.992	0.970	1.328	1.780
9	0.728	0.272	0.739	0.261	761.8	32.00	31.93	660	307.5	0.990	0.970	1.160	2.303
10	0.869	0.131	0.810	0.190	765.5	32.48	32.27	672	314	0.993	0.970	1.055	3.426
11	0.953	0.047	0.9065	0.0935	761.3	33.94	33.89	709	334	0.996	0.970	1.017	4.405

equation) and a calculation of the density of the pure liquid at the temperature of the mixture. This rarely is available and usually must be determined from general correlations. A convenient method was proposed by Scheibel (*20*) in which the equation for the activity coefficient correction factor has been reduced to an equation in terms of critical pressure, reduced temperature, and the difference between the vapor pressure of the pure component and the total pressure on the system. It was used for the calculation of the Z factor in this investigation, using the following critical constants:

	Crit. Temp., ° K.	Crit. Press., Atm.
n-Pentane	470.2	33.0
Acetone	508	47.0

Vapor pressure data of Young (*24*) for *n*-pentane and of Schmidt (*21*) for acetone were smoothed by the method of Othmer (*14*) before being used.

Correlation of Data. It has been demonstrated (*2, 3, 17*) that isobaric vapor-liquid equilibria data can be satisfactorily correlated using thermodynamically consistent equations having empirical constants. This assumes that the boiling range is not large, so that the effect of temperature on the activity coefficients can be neglected. These data were correlated using the method of Redlich and Kister (*17*).

In a binary system, by definition

$$Q = X_1 \log \gamma_1 + (1 - X_1) \log \gamma_2 \tag{4}$$

and

$$\frac{dQ}{dX_1} = \log \frac{\gamma_1}{\gamma_2} \tag{5}$$

log γ_1 and log γ_2 are then expressed by following equations:

$$\log \gamma_1 = Q + (1 - X_1)\frac{dQ}{dX_1} \tag{6}$$

$$\log \gamma_2 = Q - X_1\frac{dQ}{dX_1} \tag{7}$$

Redlich and Kister proposed for the Q function the expansion

$$Q = X_1 (1 - X_1) [B + C(2X - 1) + D (2X - 1)^2] \tag{8}$$

By using the method proposed by Redlich and Kister, the best fit of the data were found for the following values of the constants:

$$B = 0.624$$
$$C = 0$$
$$D = 0$$

The experimental values of log γ_1/γ_2 given in Table IV were plotted against X_1 in Figure 2. These data fit a straight line drawn through $X = 0.5$ at $\log(\gamma_1/\gamma_2) = 0$, so that the areas under the curve above and below the abscissa are equal. The agreement of the experimental points with this line is good and indicates thermodynamic constancy of these data.

When $C=D=0$, Equatio 8 becomes

$$Q = X_1 (1 - X_1)B \tag{9}$$

and

Table IV. Comparison of Observed and Calculated Vapor-Liquid Equilibrium Data System *n*-Pentane–Acetone

Run No.	*n*-Pentane X_1	Obsd. γ_1	Obsd. γ_2	Obsd. Log γ_1/γ_2	Calcd. γ_1	Calcd. γ_2	Calcd. Log γ_1/γ_2	Temp., ° C. Obsd.	Temp., ° C. Calcd.	Temp., ° C. Δt	Y_1 Obsd.	Y_1 Calcd.	ΔY_1
1	0.021	3.465	1.148	0.4800	4.153	1.0015	0.5975	49.15	51.90	2.52	0.108	0.142	+0.034
2	0.061	3.715	1.048	0.5495	3.552	1.006	0.548	45.76	46.90	1.14	0.307	0.304	−0.003
3	0.134	3.150	1.088	0.4616	2.938	1.026	0.457	39.58	41.69	2.11	0.4775	0.475	−0.0025
4	0.2105	2.558	1.145	0.3490	2.450	1.064	0.361	36.67	38.40	1.73	0.550	0.558	+0.008
5	0.292	2.216	1.184	0.2724	2.055	1.131	0.2598	34.35	36.30	1.95	0.6145	0.611	−0.0035
6	0.405	1.812	1.323	0.1365	1.664	1.266	0.1186	32.85	35.00	2.15	0.664	0.655	−0.009
7	0.503	1.520	1.530	−0.0025	1.4265	1.438	−0.0036	32.35	33.89	1.54	0.678	0.675	−0.003
8	0.611	1.328	1.780	−0.1270	1.243	1.710	−0.1385	31.97	33.89	1.92	0.711	0.709	−0.002
9	0.728	1.160	2.303	−0.2974	1.112	2.142	−0.2845	31.93	33.30	1.37	0.739	0.744	+0.005
10	0.869	1.055	3.426	−0.5115	1.025	2.960	−0.460	32.27	33.60	1.33	0.810	0.826	+0.016
11	0.953	1.017	4.405	−0.6363	1.005	3.690	−0.566	33.89	34.70	0.81	0.9065	0.919	+0.0125

$$\frac{dQ}{dX} = B(1 - 2X_1) \qquad (10)$$

therefore,

$$\log \gamma_1 = (1 - X_1)^2 B \qquad (11)$$

and

$$\log \gamma_2 = X_1^2 B \qquad (12)$$

Equations 11 and 12 are the same as would have been obtained by the Van Laar equations or the three suffix Margules equation for a symmetrical system. These equations were used to calculate the activity coefficient curves shown in Figure 3. The observed and calculated activity coefficients are compared in Table IV.

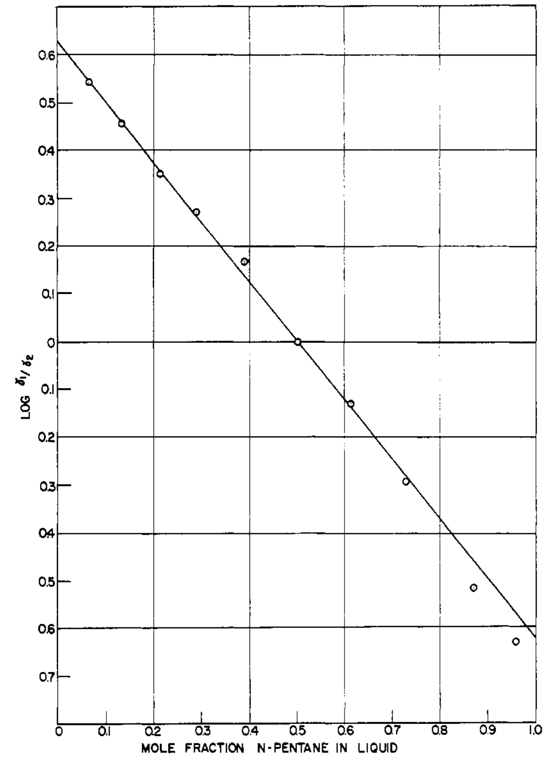

Figure 2. Redlich and Kister plot for *n*-pentane–acetone at 760 mm. Hg

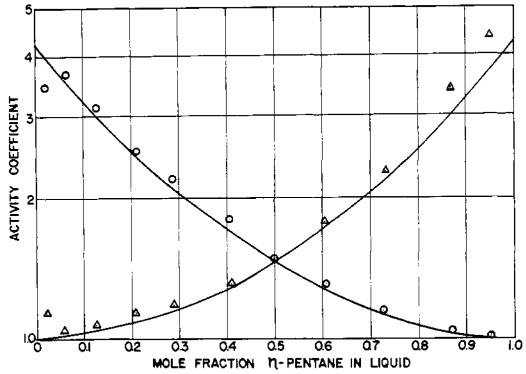

Figure 3. Activity coefficients–composition curves calculated from Redlich and Kister constants for *n*-pentane–acetone at 760 mm. Hg

○ Observed points of *n*-pentane

△ Observed points of acetone

Vapor compositions and temperature were calculated from the correlated activity coefficients by assuming temperatures that resulted in a summation of Y_1 and Y_2 equal to one. Observed and calculated vapor compositions are compared in Table IV and Figure 1. There is good agreement between the observed and calculated values of vapor compositions. The over-all average absolute deviation between observed and calculated vapor compositions is 0.9 mole %.

From Figure 3, the values of γ_1 and γ_2 at infinite dilution are 4.2 and 4.3, respectively. This compares favorably with the value given by Pierotti (*16*) of 4.4 for γ_1 and a value of somewhat greater than 4.9 for γ_2.

As indicated in Table IV, the boiling points of the mixture calculated with the smoothed data were consistently 1 to 2° C. higher than the observed temperatures. The reasons for this were probably a combination of experimental errors and errors inherent in the correlation method. The observed and calculated temperature data are given in Table IV. The plot of observed temperature *vs.* composition is shown in Figure 4.

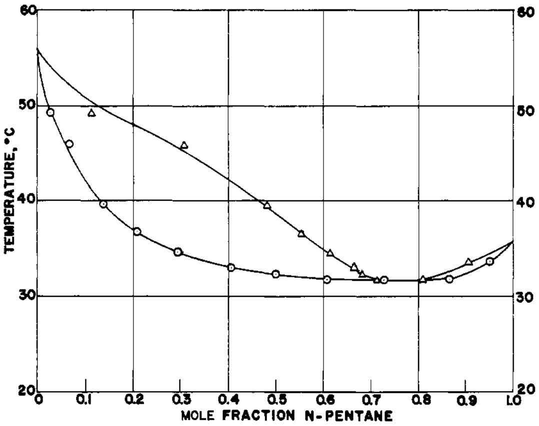

Figure 4. Temperature-composition diagram for *n*-pentane–acetone at 760 mm. Hg

△ Observed points of *n*-pentane in vapor

○ Observed points of *n*-pentane in liquid

The experimentally determined composition of the azeotrope was 74.2 mole % *n*-pentane and the observed boiling point was 31.86° C. at 760 mm. The calculated values are 75.0 mole % and 33.10° C. respectively.

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NOMENCLATURE

B, C, D = constants in Redlich Kister equation
P = barometric or total pressure, mm. Hg
P° = vapor pressure of pure component, mm. Hg
Q = $X_1 \log \gamma_1 + X_2 \log \gamma_2$
t = temperature, ° C.
T = absolute temperature, ° K.
v = liquid molar volume, ml. per gram mole
V = molar vapor volume, ml. per gram mole
X = mole fraction of component in liquid
Y = mole fraction of component in vapor
Z = correction factor for liquid pressure and perfect gas law deviation
γ = activity coefficient of component
β_1 = second virial coefficient in equation of state, ml. per gram mole

Subscripts

1 = component 1, *n*-pentane
2 = component 2, acetone

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Phase Behavior in a Six-Component Hydrocarbon System

L. T. CARMICHAEL, K. C. HWANG, V. M. BERRY, and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

IN DESIGNING EQUIPMENT for the separation of hydrocarbons of similar molecular weight and volatility, information on phase behavior of the system is important. Because hydrocarbons deviate significantly from ideal solutions (*14*), it is difficult to predict the contribution of each of several components to the phase behavior of the system as a whole. Experimental investigation of the phase behavior of the hydrocarbon system is usually necessary if a detailed knowledge of the composition of the coexisting phases is required.

The basis for this study was an industrial interest in the phase behavior of a six-component system made up of hydrocarbons containing four carbon atoms per molecule. Little information appears to be available involving more than binary systems of such hydrocarbons, although the phase behavior of the 1-butene-*n*-butane system has been studied (*22*), and Gerster and coworkers (*9*) investigated the phase behavior of the *n*-butane-1-butene-furfural and isobutane-1-butene-furfural systems.

Ten different mixtures of isobutane, isobutene, *n*-butane, 1-butene, *trans*-2-butene, and *cis*-2-butene were investigated. Experimental work was carried out at temperatures from 126° F. to 220° F., and samples of each of the coexisting phases were obtained at more than one temperature for most of the mixtures.

Raoult's law was used as a frame of reference in depicting the phase behavior of the six-component hydrocarbon system. Only a knowledge of the vapor pressure of each of the components is required in predicting the behavior described by this relation. The deviations from Raoult's law were treated as systematic and simple functions of temperature, pressure, and composition. Results are pre-

Table I. Purity of Components

Component	Composition							Purity[a] Mole Fraction
	Isobutane	Isobutene	n-Butane	1-Butene	trans-2-Butene	cis-2-Butene	Butadiene	
			(Mole Fraction of Component)					
Isobutane	0.998	...	0.002	...	...	...	...	0.9994
Isobutene	...	0.995	0.001	0.004	...	...	...	0.9952
n-Butane	0.001	...	0.999	...	...	...	...	0.9991
1-Butene	0.005	0.003	0.003	0.987	...	...	0.002	0.999+
trans-2-Butene	...	...	0.004	...	0.992	0.004	...	0.9937
cis-2-Butene	...	...	...	...	...	0.999	0.001	0.9933

[a]Reported by Phillips Petroleum Co.