Part I

Vapor-Liquid Equilibrium in the Ethane–*n*-Heptane System

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The vapor-liquid phase behavior of the ethane–*n*-heptane system has been experimentally investigated at 150, 200, 250, 300, and 350° F. for pressures ranging from 450 p.s.i.a. up to the critical region. The results of this study have been utilized to establish the corresponding critical temperature and critical pressure behavior of this system. Vapor-liquid equilibrium constants and critical values obtained in this study have been compared with values resulting from another investigation reported in the literature for this system.

AN EXPERIMENTAL investigation for the vapor-liquid equilibrium behavior of the ethane–*n*-heptane system has been carried out in a variable volume vapor-liquid equilibrium cell (*3*) at 150, 200, 250, 300, and 350° F. For these temperatures, the pressure of the system was increased from a value of 455 p.s.i.a. to conditions approaching the critical region. Vapor and liquid samples in equilibrium with each other were withdrawn, and their compositions were established using a gas chromatography unit. Experimental vapor-liquid equilibrium studies on this system have been previously reported by Kay (*2*) who utilized a visual observation technique to establish the bubble and dew points of mixtures of known compositions. The results of the present study have been found to agree well with those reported by Kay.

EXPERIMENTAL EQUIPMENT

The equipment used in the present study consisted of a variable volume vapor-liquid equilibrium cell, provided with a movable piston which was actuated with mercury supplied from a positive displacement pump. The pressure of the system was measured with two Heise gages, which were connected to this mercury system. These gages were calibrated periodically against a dead-weight gage and were reproducible to within 3 p.s.i. for the pressure range encountered in this study.

Because of the design of the equipment, ethane was first introduced into the cell as a gas, and then the appropriate amount of *n*-heptane was forced into this cell as a liquid by means of a positive displacement mercury pump. The complete details and construction of the equilibrium cell and auxiliary equipment have been described elsewhere (*3*). To expedite the attainment of equilibrium, agitation within the equilibrium chamber was provided by a stirrer which was magnetically coupled to an external mechanical drive. The equilibrium cell was surrounded by a constant temperature air bath which was capable of maintaining the over-all temperature of the cell to within 0.3° F. of the desired temperature. Under these conditions, the temperature gradient across the cell varied from 0.2° at 150° F. to 0.5° at 350° F.

After equilibrium was attained, microsamples of the vapor and liquid phases were withdrawn by first freezing them with liquid nitrogen into a sample bulb and then allowing them to vaporize and expand into this bulb. These vapors were then analyzed with a gas chromatography unit equipped with a thermal conductivity cell as a detector. This unit was calibrated with ethane–*n*-heptane standard samples whose compositions were established with a mass spectrometer. Analyses made on this gas chromatograph were reproducible to within 1 mole % of a component, based on the assumption that the mass spectrometer results represent the true composition.

MATERIALS

The hydrocarbons used were research grade and were supplied by the Phillips Petroleum Co. As claimed by the supplier, the purity of ethane used was 99.91 mole % and *n*-heptane, 99.78 mole %.

PROCEDURE AND RESULTS

For each temperature, ethane and *n*-heptane were individually charged into the equilibrium cell to produce a binary charge of a desired composition. The composition of each charge was adjusted so that both vapor and liquid phases existed within the cell for pressures up to the critical region.

For each isotherm investigated, the pressure was increased in steps, and the system was allowed to reach equilibrium. The attainment of equilibrium required approximately 2 hours, except for conditions in the vicinity of the critical point, when more time was necessary. After reaching equilibrium, vapor and liquid samples were withdrawn from the equilibrium cell and were analyzed according to the procedure already outlined. The pressure of the system was then increased to the next higher pressure, and this procedure was continued until the withdrawal of samples appreciably disturbed the equilibrium of the vapor and liquid phases in the cell, indicating that the vicinity of the critical point has been reached.

The equilibrium vapor-liquid phase boundaries of the system at 300° F. are presented in Figure 1. In this figure, values obtained from the work of Kay (2) are also presented and indicate that some small differences exist between these two studies. Similar curves were also established at 150, 200, 250, and 350° F. The equilibrium compositions of the vapor and liquid phases obtained in this investigation are presented in Table I for all the five temperatures studied.

The bubble and dew point curves, such as those presented in Figure 1, were smoothed for each temperature and were used to calculate the vapor-liquid equilibrium constants for each component of this system. The resulting K values for all temperatures studied are presented in Table II. These

Table I. Experimental Vapor-Liquid Equilibrium Data for the Ethane–*n*-Heptane System at 150, 200, 250, 300, and 350° F.

Pressure, P.S.I.A.	Vapor, Mole Fraction		Liquid, Mole Fraction		$K = y/x$	
	Ethane	*n*-Heptane	Ethane	*n*-Heptane	Ethane	*n*-Heptane
			150° F.			
455	0.982	0.018	0.517	0.483	1.899	0.0373
569	0.983	0.017	0.616	0.384	1.596	0.0443
669	0.983	0.017	0.699	0.301	1.406	0.0565
783	0.982	0.018	0.776	0.224	1.265	0.0804
887	0.977	0.023	0.848	0.152	1.152	0.151
947	0.972	0.028	0.887	0.113	1.096	0.248
968	0.967	0.033	0.903	0.097	1.071	0.340
			200° F.			
524	0.961	0.039	0.452	0.548	2.126	0.0712
623	0.960	0.040	0.517	0.483	1.857	0.0828
725	0.961	0.039	0.580	0.420	1.657	0.0929
867	0.959	0.041	0.662	0.338	1.449	0.121
975	0.953	0.047	0.738	0.262	1.291	0.179
1083	0.944	0.056	0.798	0.202	1.183	0.277
1127	0.938	0.062	0.829	0.171	1.131	0.363
			250° F.			
577	0.919	0.081	0.410	0.590	2.241	0.137
718	0.925	0.075	0.476	0.524	1.943	0.143
874	0.923	0.077	0.563	0.437	1.639	0.176
1020	0.917	0.083	0.631	0.369	1.453	0.225
1142	0.904	0.096	0.700	0.300	1.291	0.320
1215	0.888	0.112	0.738	0.262	1.203	0.427
			300° F.			
590	0.859	0.141	0.340	0.660	2.526	0.214
746	0.869	0.131	0.425	0.575	2.045	0.228
920	0.862	0.138	0.512	0.488	1.684	0.283
1081	0.859	0.141	0.593	0.407	1.449	0.346
1182	0.840	0.160	0.658	0.342	1.276	0.468
1235	0.821	0.179	0.690	0.310	1.190	0.577
			350° F.			
586	0.767	0.233	0.296	0.704	2.591	0.331
717	0.783	0.217	0.333	0.667	2.351	0.325
855	0.792	0.208	0.407	0.593	1.946	0.351
993	0.783	0.217	0.473	0.527	1.655	0.412
1102	0.772	0.228	0.536	0.464	1.440	0.491
1156	0.756	0.244	0.569	0.431	1.329	0.566

Table II. Final *K*-Values for the Ethane–*n*-Heptane System at 150, 200, 250, 300, and 350° F.

Pressure, P.S.I.A.	$K = y/x$	
	Ethane	*n*-Heptane
	150° F.	
450	1.932	0.0340
500	1.774	0.0373
550	1.650	0.0391
600	1.540	0.0443
650	1.451	0.0498
700	1.372	0.0595
750	1.307	0.0685
800	1.247	0.0849
850	1.191	0.113
900	1.140	0.161
920	1.122	0.191
950	1.092	0.255
970[a]	1.064	0.376
991[a]	1.000	1.000
	200° F.	
450	2.435	0.0708
500	2.225	0.0721
550	2.056	0.0750
600	1.922	0.0780
650	1.803	0.0835
700	1.700	0.0876
750	1.610	0.0968
800	1.531	0.107
850	1.457	0.120
900	1.392	0.135
950	1.329	0.161
1000	1.273	0.194
1050	1.222	0.233
1100	1.166	0.302
1120	1.140	0.354
1140	1.104	0.456
1165[b]	1.000	1.000
	250° F.	
450	2.755	0.135
500	2.550	0.135
550	2.378	0.134
600	2.217	0.137
650	2.074	0.139
700	1.958	0.144
750	1.850	0.150
800	1.755	0.159
850	1.674	0.170
900	1.598	0.184
950	1.533	0.200
1000	1.471	0.218
	250° F. (*continued*)	
1050	1.410	0.244
1100	1.349	0.279
1150	1.285	0.329
1200	1.212	0.422
1220	1.172	0.488
1250[c]	1.000	1.000
	300° F.	
450	3.118	0.220
500	2.861	0.217
550	2.644	0.216
600	2.478	0.215
650	2.314	0.219
700	2.165	0.223
750	2.030	0.232
800	1.914	0.243
850	1.810	0.259
900	1.718	0.274
950	1.633	0.292
1000	1.555	0.313
1050	1.484	0.336
1100	1.414	0.369
1150	1.338	0.415
1200	1.255	0.489
1230	1.188	0.581
1250	1.136	0.671
1275[d]	1.000	1.000
	350° F.	
450	3.474	0.330
500	3.182	0.325
550	2.931	0.322
600	2.721	0.321
650	2.529	0.319
700	2.376	0.322
750	2.229	0.327
800	2.093	0.336
850	1.973	0.346
900	1.857	0.361
950	1.750	0.381
1000	1.651	0.404
1050	1.549	0.440
1100	1.448	0.487
1150	1.336	0.563
1170	1.288	0.602
1190	1.218	0.673
1219[e]	1.000	1.000

Critical point: [a] $x_2 = 0.939$. [b] $x_2 = 0.883$. [c] $x_2 = 0.825$. [d] $x_2 = 0.760$. [e] $x_2 = 0.681$.

values have been plotted to obtain the *K vs.* pressure relationships as shown in Figure 2. In this figure, the ordinate of the equilibrium constant of ethane is linear, while that of *n*-heptane is logarithmic. The *K* values resulting from this study and those obtained from the work of Kay (*2*) are in good agreement. These relationships, when extended to $K = 1.00$ produce an estimate for the critical pressure corresponding to each temperature. These pressures were then used to approximate the corresponding critical compositions at the point where the bubble and dew point curves meet, as shown in Figure 1 for 300° F. For each temperature, the critical compositions corresponding to these critical pressures are also included in Table II. These critical values, when compared with those resulting from the work of Kay, show the following differences:

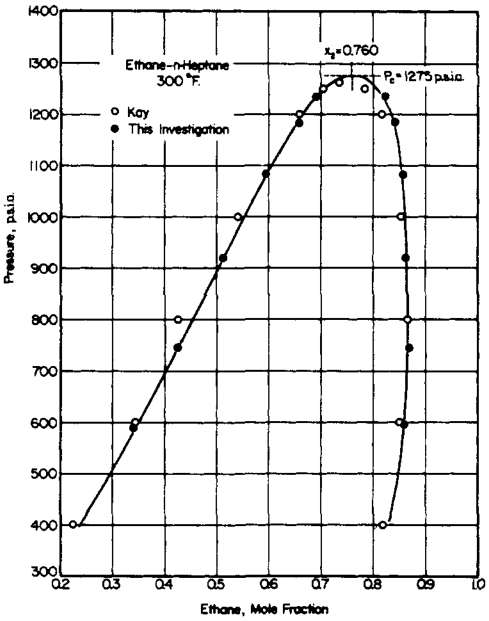

Figure 1. Vapor-liquid equilibrium behavior for the ethane–*n*-heptane system at 300° F.

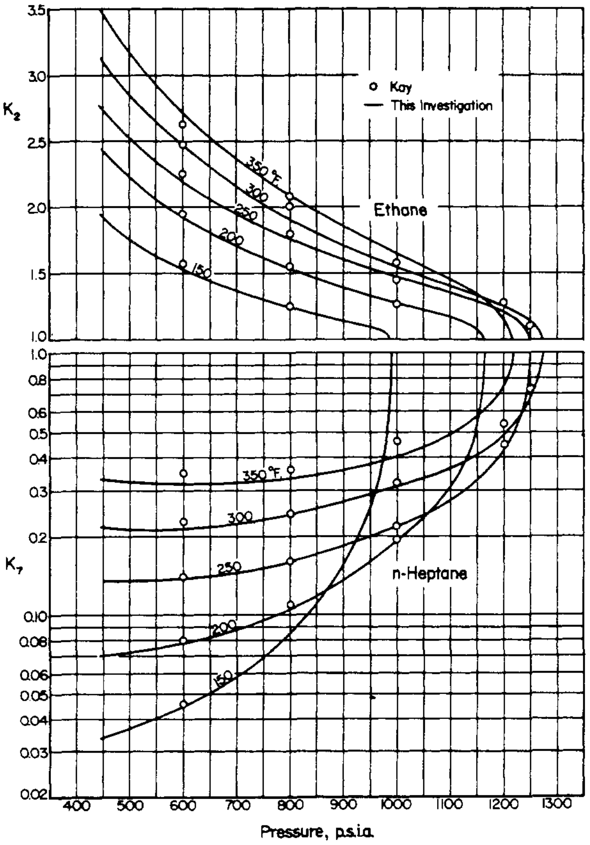

Figure 2. Relationships between K and pressure for the ethane–*n*-heptane system at 150, 200, 250, 300, and 350° F.

	Critical Temperature, ° F.		Critical Pressure, P.S.I.A.	
x_2	Kay (*2*)	This investigation	Kay (*2*)	This investigation
0.939	148	150	980	991
0.883	192	200	1140	1165
0.825	238	250	1225	1250
0.760	283	300	1266	1275
0.681	330	350	1227	1219

Because of the experimental limitations of the equipment, it was not possible to operate much below 150° F., and consequently no evaluations of the critical state for the system could be made below mole fractions of ethane less than approximately 0.68.

The critical values resulting from this study are related to composition in Figure 3 and are also compared with the corresponding critical values obtained from the work of Kay (*2*). The critical values of ethane and *n*-heptane reported by Kay (*2*) have been used in Figure 3.

For ethane mole fraction compositions of less than 0.68, the critical temperature relationship was extrapolated to

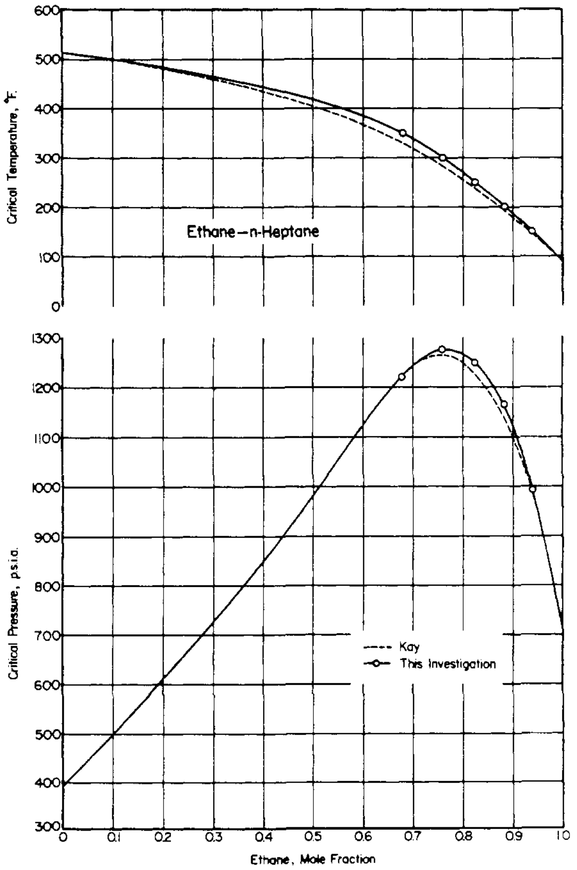

Figure 3. Relationships between composition and critical temperature and pressure for the ethane–*n*-heptane system

pure n-heptane, while the critical pressure relationship below this composition was made the same to that produced from the critical values reported by Kay (2). In this comparison, the agreement appears to be close despite the fact that completely different procedures were used to establish these critical values. The recent direct measurements of Ekiner and Thodos (*1*) of the critical temperatures and critical pressures of the ethane-n-heptane system yielded relationships that were in closer agreement to those resulting in this study. These slight differences between this study, the work of Kay (2), and that of Ekiner and Thodos (*1*) are not serious but point to the experimental difficulty encountered in establishing values in the vicinity of the critical point.

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Vapor-Liquid Equilibria at 760 Mm. of Mercury for the System Vinyl Acetate–2,4-Dimethyl Pentane

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Vapor-liquid equilibrium data at 760 mm. of mercury pressure are reported for the system vinyl acetate–2,4-dimethyl pentane. An azeotrope is formed at 67.2° C. at a composition of 60.6 mole % vinyl acetate.

THE behavior of monomeric materials in hydrocarbon solvents with regard to separability is of interest to the polymer industry. Since it appears that vinyl acetate forms azeotropes with some of the normal paraffins containing seven carbon atoms or less, the vapor-liquid equilibrium of the branched chain compound, 2,4-dimethyl pentane–vinyl acetate system was investigated at 760 mm. of mercury pressure.

An azeotrope at 67.2° C. at the composition 60.6 mole % vinyl acetate was found. The data were correlated by the van Laar equation and were thermodynamically consistent based on the Redlich and Kister (7) consistency test.

The values of the van Laar constants, Carlson and Colburn modification (*1*), were: $A_{12} = 0.490$, $B_{12} = 0.495$ (subscript 1 refers to vinyl acetate).

MATERIALS

The vinyl acetate used in this investigation was obtained from Union Carbide Chemicals Co., and it was purified by fractionation in a packed column. The 2,4-dimethyl pentane obtained from the Phillips Petroleum Co. as 99% minimum purity material was not further purified.

Table I compares the experimental properties of the materials determined in this investigation with those reported in the literature.

EXPERIMENTAL PROCEDURE

A modified (6) Colburn equilibrium still (4) of the vapor-recirculation type was used to determine the vapor-

Table I. Physical Properties of Materials

	Vinyl Acetate		2,4-Dimethyl Pentane	
	Exptl.	Lit.	Exptl.	Lit.
760 Mm. boiling point, ° C.	72.5	72.5(5)	80.5	80.5(2)
Density, d 20/4	0.934	0.9343(5)	0.6676(25/4)	0.6683(2)
Ref. index, n_D 25°	1.3955	1.3956(5)	1.37886	1.37882(2)

Antoine constants for 2,4-DMP (2): $A = 6.8262$, $B = 1192.041$, $C = 221.634$; $\log p = A - [B/(C+t)]$
where p = mm. Hg, t = ° C.

Experimental Vapor Pressure–Temperature Relations for Vinyl Acetate

Temp., ° C.	Vapor Press., Mm. Hg	Temp., ° C.	Vapor Press., Mm. Hg
67	633.1	76	866.7
69	679.9	78	927.4
70	704.3	80	991.5
72	755.4	82	1059.2
74	809.5		