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

Pressure, P.S.I.A.	$K = y/x$ Ethane	$K = y/x$ n-Butane
	150° F.	
450	1.791	0.425
500	1.647	0.426
550	1.532	0.431
600	1.438	0.438
650	1.353	0.455
700	1.280	0.479
750	1.203	0.530
800	1.130	0.615
820	1.087	0.706
841[a]	1.000	1.000
	200° F.	
450	2.173	0.613
500	1.972	0.605
550	1.809	0.601
600	1.670	0.606
650	1.546	0.620
700	1.448	0.635
750	1.351	0.663
800	1.243	0.721
820	1.183	0.770
830	1.147	0.805
848[b]	1.000	1.000
	250° F.	
450	2.272	0.854
500	2.022	0.836
550	1.844	0.823
600	1.705	0.813
650	1.585	0.807
700	1.470	0.811
720	1.401	0.827
740	1.292	0.859
750	1.215	0.889
761[c]	1.000	1.000

Critical point: [a] $x_2 = 0.811$. [b] $x_2 = 0.610$. [c] $x_2 = 0.381$.

phases indicated that the estimated critical pressure was approached to within 30 p.s.i. To obtain data nearer the critical pressure becomes not only impractical due to the excessive time needed for the attainment of equilibrium, but in addition demands frequent adjustments in the over-all cell composition.

The equilibrium vapor-liquid phase boundaries of the system at 150° F. are presented in Figure 1. In this figure, the corresponding values reported by Kay (*1*) are also included. Similar curves were also established for 200° and 250° F. For each temperature some disagreement between the two sets of results is evident as shown in Figure 1 for the 150° F. isotherm. These differences are in excess of the 1 mole % tolerance maintained by the analytical equipment. The compositions of the equilibrium vapor and liquid phases obtained experimentally are presented in Table I.

Vapor-liquid equilibrium constants for 150° F. were calculated from the smoothed plot of Figure 1. The data at 200° and 250° F. were treated in a similar manner to obtain equilibrium constants for these temperatures. The resulting K values for the three temperatures are presented in Table II and have been plotted to obtain the K *vs.* pressure relationships shown in Figure 2. When these relationships were extended to $K = 1.00$, a pressure was established which when adjusted for consistency with the corresponding pressure-composition plot, as illustrated in Figure 1, served to define the critical pressure of the particular isotherm. The critical compositions corresponding to each temperature have been included in Table II and have been used to produce the critical temperature–composition and critical pressure–composition relationships presented in Figure 3. The critical values reported by Kay (*1*) for ethane and n-butane, have been used in this figure. Comparisons between the critical values of this study and those reported by Kay show some differences only for the critical pressures.

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Isothermal and Isobaric Vapor-Liquid Equilibrium Data System: Toluene–Isoamyl Alcohol

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Solutions of alcohols and aromatic hydrocarbons exhibit a high degree of nonideality as indicated by the heats of solution (*3*). Vapor-liquid equilibrium data under isobaric conditions for such systems (particularly those with wider boiling ranges) cannot be correlated by the conventional methods (*4*) which do not take into consideration the effect of temperature on the nonideality of the system. The present investigation studied the effect of temperature variation on the activity coefficients of the components of the system toluene–isoamyl alcohol under isobaric conditions. The vapor-liquid equilibrium data were taken at three different temperatures, 107°, 95°, and 80° C. and at a total pressure of 760 mm. of Hg. The activity coefficients under isothermal conditions are computed and correlated employing the Wohl's suffix Margules equations (*13*). The end values of the activity coefficient–composition curves, which are also the constants in the Margules equations, are related to the absolute temperature, and the relationship obtained is used to correlate the activity coefficients under isobaric conditions.

Vapor-liquid equilibrium data of the system toluene–isoamyl alcohol are determined under isothermal conditions at 107°, 95°, and 80° C. and under isobaric conditions at 760 mm. of Hg. The data are correlated in terms of activity coefficients by Margules three suffix equations. Effect of temperature on the Margules constants is established, and it is used in correlating the activity coefficient data under isobaric conditions.

EXPERIMENTAL

In the present investigation, an equilibrium still of the Jones, Schoenborn, and Colburn type (*2*) with the modifications made by Ward (*10*) and cited by Satyanarayana Murti (*8*) was employed. The still had a capacity of 45 ml. For the isobaric conditions, the pressure was maintained at 760 ± 1 mm. of Hg using air supply. For the isothermal runs, the necessary vacuum was manually controlled within 1 mm. of Hg. In all the runs, when the equilibrium temperature was constant, two additional hours were allowed to attain thermodynamic equilibrium before collecting the samples. The temperature was measured with a mercury thermometer calibrated to 0.1° C.

MATERIALS AND METHODS OF ANALYSIS

Toluene. Analar grade toluene of May and Baker Co., was directly fractionated in a laboratory fractionating column, and the fraction boiling at 110.7° C. was collected and used.

Isoamyl Alcohol. Isoamyl alcohol of the guaranteed reagent quality supplied by E. Merck Ltd., was purified by digesting over unslaked lime and fractionating in a glass column. The middle portion of the distillate from this operation was purified by further digesting and redistilling to give the fraction employed for the present study (*12*).

The physical properties of the chemicals used in this investigation are compared with values in the literature (Table I). Refractive index was measured at 30 ± 0.01° C. for sodium light with Abbe's precision refractometer calibrated up to 0.001.

Mixtures of toluene and isoamyl alcohol were analyzed by means of the refractive index.

DISCUSSION OF RESULTS

The vapor-liquid equilibrium data are given in Table II, and they are shown in the form of equilibrium diagrams in Figure 1. The data are interpreted in terms of activity coefficients computed from the experimental points using the relation

$$\gamma_i = C_i P y_i / P_i^0 x_i \qquad (1)$$

where

γ_i = activity coefficient
P = total pressure
P_i^0 = vapor pressure of the pure component i

Table II. Experimental Vapor-Liquid Equilibrium Data System Toluene (1)–Isoamyl Alcohol (2)

(Composition on mole per cent basis)

Run No.	Total Pressure, Mm. of Hg	x_1	y_1	log γ_1	log γ_2
		At 107° C.			
1	320	0.0	0.0	...	...
2	415	11.0	30.0	0.2183	0.0111
3	470	19.1	43.6	0.1951	0.0136
4	525	25.1	51.2	0.1942	0.0265
5	536	28.9	55.1	0.1738	0.0278
6	547	29.6	56.1	0.1801	0.0311
7	594	39.8	64.4	0.1483	0.0437
8	643	51.1	70.9	0.1149	0.0806
9	669	62.9	76.3	0.0738	0.1290
10	680	69.4	79.3	0.0546	0.1608
11	690	96.4	96.4	$\bar{1}.9969$	0.3306
12	683	98.0	97.6	$\bar{1}.9969$	0.4118
13	686	100.0	100.0	...	...
		At 95° C.			
1	196	0.0	0.0	...	...
2	250	6.5	28.0	0.3537	$\bar{1}.9961$
3	282	12.0	37.5	0.2667	0.0149
4	289	12.9	40.5	0.2792	0.0068
5	315	17.0	46.0	0.2526	0.0233
6	331	20.5	50.4	0.2319	0.0265
7	354	27.3	57.2	0.1917	0.0306
8	378	32.1	61.6	0.1821	0.0414
9	380	32.3	62.5	0.1881	0.0342
10	408	39.5	66.9	0.1611	0.0603
11	432	45.7	68.9	0.1354	0.1048
12	456	59.0	75.1	0.0852	0.1538
13	465	62.9	76.9	0.0763	0.1732
14	469	67.2	78.2	0.0584	0.2052
15	477	77.0	82.0	0.0274	0.2835
16	482	87.0	88.0	0.0094	0.3598
17	477	100.0	100.0	...	...
		At 80° C.			
1	98	0.0	0.0	...	...
2	135	5.5	31.2	0.4198	0.0051
3	143	7.4	34.5	0.3596	0.0178
4	162	11.2	45.5	0.3541	0.0103
5	201	23.6	60.5	0.2480	0.0294
6	210	24.1	61.0	0.2613	0.0457
7	212	25.6	63.0	0.2534	0.0359
8	246	43.2	72.1	0.1492	0.0948
9	258	52.0	75.5	0.1093	0.1322
10	264	56.6	78.6	0.1000	0.1274
11	268	57.8	77.8	0.0930	0.1620
12	280	73.0	83.2	0.0399	0.2539
13	282	81.3	86.4	0.0123	0.3245
14	285	82.0	87.2	0.0174	0.3196
15	295	91.4	92.8	0.0123	0.4072
16	293	100.0	100.0	...	...

Table I. Physical Properties of Materials

	Boiling Point		Ref. Index at 30° C.		Density at 30° C.	
	Present investigation	Literature	Present investigation[a]	Literature	Present investigation	Literature
Toluene	110.7	110.6 to 110.8 (*9*)	1.4912	1.4912 (*9*)	0.8573	0.8577 (*9*)
Isoamyl alcohol	132.0	132.0 (*11*)	1.4026	1.40298 (*11*)[b]	0.8017	0.80175 (*11*)

[a] Fourth decimal place obtained by visual interpolation. [b] Obtained using temperature correction.

x_i, y_i = mole fractions of the ith component in the liquid and vapor phases, respectively

C_i = vapor phase nonideality correction factor

$$= \exp 10 \frac{(P_i^0 - P)(V_i - \beta_{ii})}{2.303\,RT}$$

V_i = liquid molal volume

β_{ii} = second virial coefficient

R = gas constant

T = absolute boiling temperature

Vapor pressure data for isoamyl alcohol and toluene was taken from Timmermans (*9*). The data were verified at a few temperatures by the use of the still employed in this investigation, and they corresponded with the reported values (*9*, *11*). The vapor phase nonideality correction factor was calculated using the second virial coefficients, computed from Wohl's generalized equation of state (*1*, *14*), and the other properties were computed by the methods given by Reid and Sherwood (*7*).

The data were tested for thermodynamic consistency by the method of Redlich and Kister (*6*). The isothermal data are thermodynamically consistent, but the isobaric data exhibited a wide deviation from the equal area condition—the difference in areas being about 50%.

The activity coefficient data for the isothermal runs could be satisfactorily correlated by Wohl's three suffix Margules equations, Equations 3 and 4, with the constants shown below:

$$\log \gamma_1 = (2A_{21} - A_{12})\, x_2^2 + 2(A_{12} - A_{21})x_2^3 \tag{3}$$

$$\log \gamma_2 = (2A_{12} - A_{21})\, x_1^2 + 2(A_{21} - A_{12})x_1^3 \tag{4}$$

Constants in Margules equations	Temperature, ° C.		
	107	95	80
A_{12}	0.29	0.37	0.48
A_{21}	0.44	0.47	0.51

where component 1 is toluene and component 2 is isoamyl alcohol.

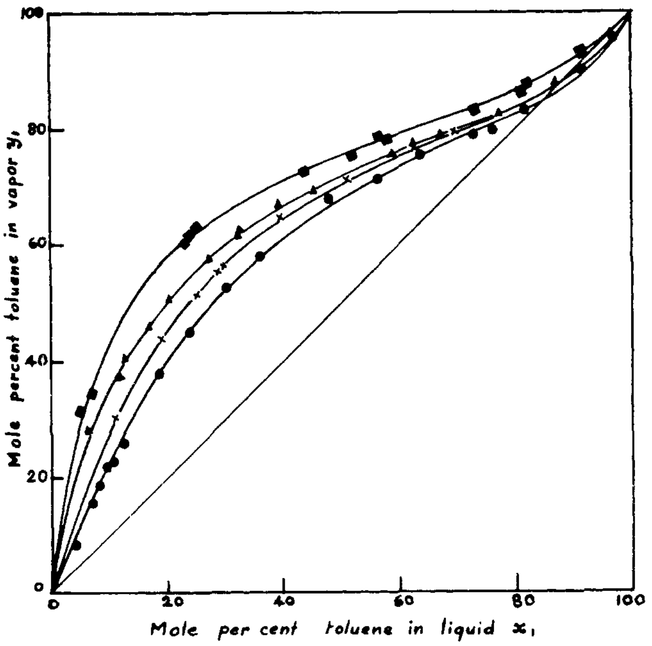

Figure 1. Equilibrium diagram for the system toluene (1)–isoamyl alcohol (2) under different conditions of restraint

● 760 mm. of Hg ▲ 95° C.

x 107° C. ■ 80° C.

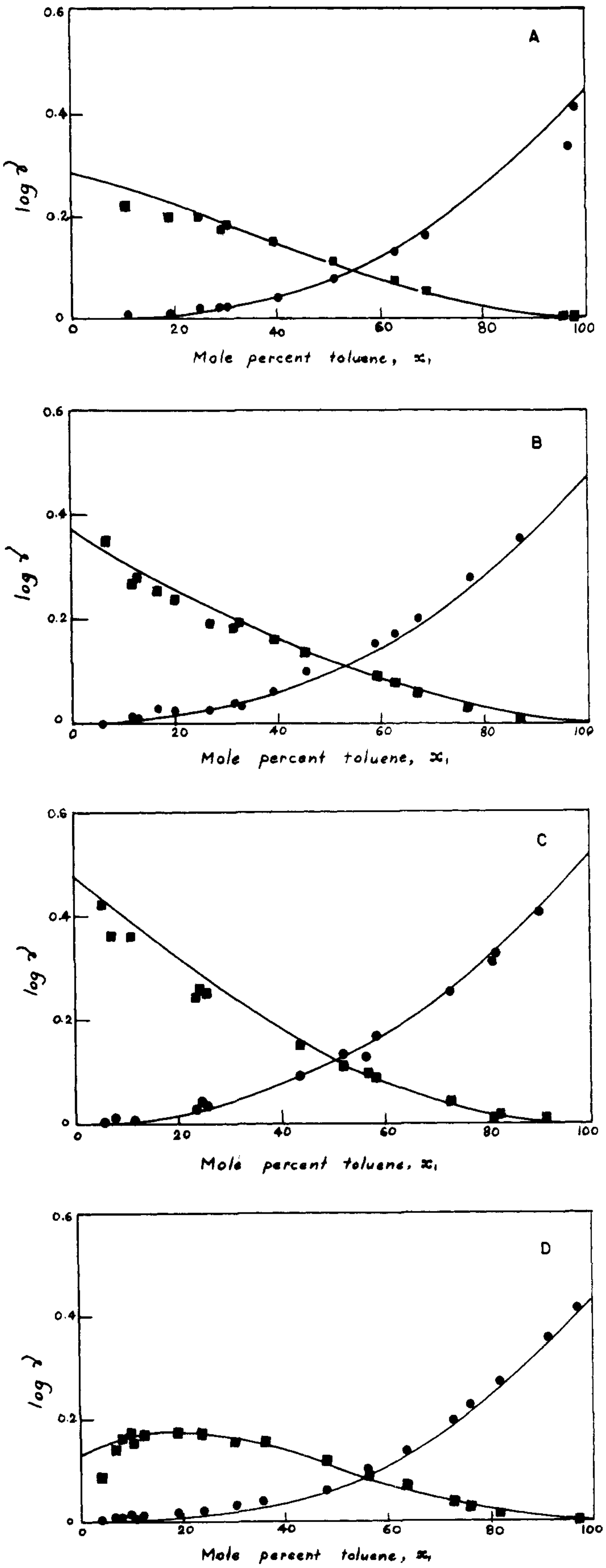

Figure 2. Activity coefficient–composition diagram for the system toluene (1)–isoamyl alcohol (2)

■ Toluene ● Isoamyl alcohol

A. At 107° C. C. At 80° C.

B. At 95° C. D. At 760 mm. of Hg

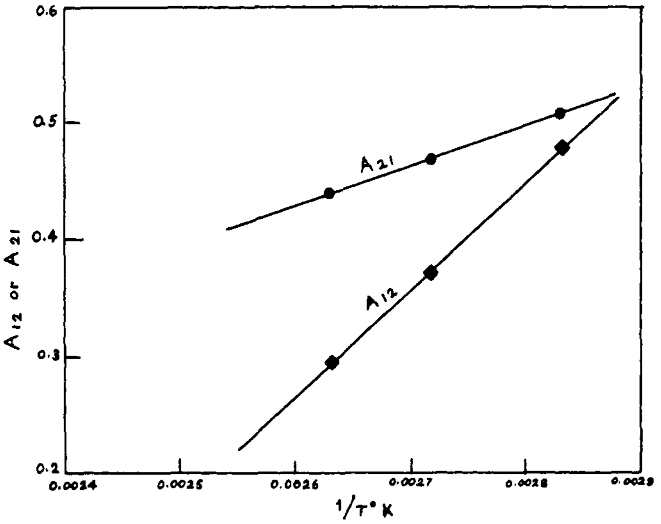

Figure 3. Effect of temperature on the constants in Margules three suffix equation for the system toluene (1)–isoamyl alcohol (2)

The effect of temperature on A_{12} and A_{21} is given by the relations (Figure 3):

$$A_{12} = 950/T - 2.215 \tag{5}$$

$$A_{21} = 360/T - 0.510 \tag{6}$$

The log γ *vs.* x curves, calculated using the constants listed above, are shown as solid lines in Figure 2*A*, *B*, and *C*. The isobaric activity coefficient data shown in Figure 2*D* exhibit a peculiarity in that the activity coefficient values for toluene pass through a maximum while those for isoamyl alcohol do not pass through a minimum at the corresponding composition in accordance with the Gibbs-Duhem equation. This discrepancy may be attributed to the effect of temperature—i.e., indirectly to the heat of solution—on the activity coefficients. The isobaric data could not be correlated by the Wohl's three suffix Margules equations in the usual way employing the end values of the log γ *vs.* x curves as constants in the equations. However, the trend of the data could be represented fairly satisfactorily by these equations when the effect of temperature on the constants is taken into consideration by means of Equations 5 and 6, as shown by the solid lines on Figure 2*D*.

The nonideality of the system toluene-isoamyl alcohol decreases with increase in temperature. An azeotrope is exhibited at 84.2 mole % toluene and 109.6° C. under isobaric conditions.

To obtain information about the association effects in the present system, the function $(x_1 \log \gamma_1 + x_2 \log \gamma_2)/(x_1x_2)$ is plotted against x_1 for the three isothermal conditions in Figure 4. The data do not show systematic deviations from a straight line. Hence, in conformity with the work of Philippe (*5*), the tendency to association in the system investigated is only moderate.

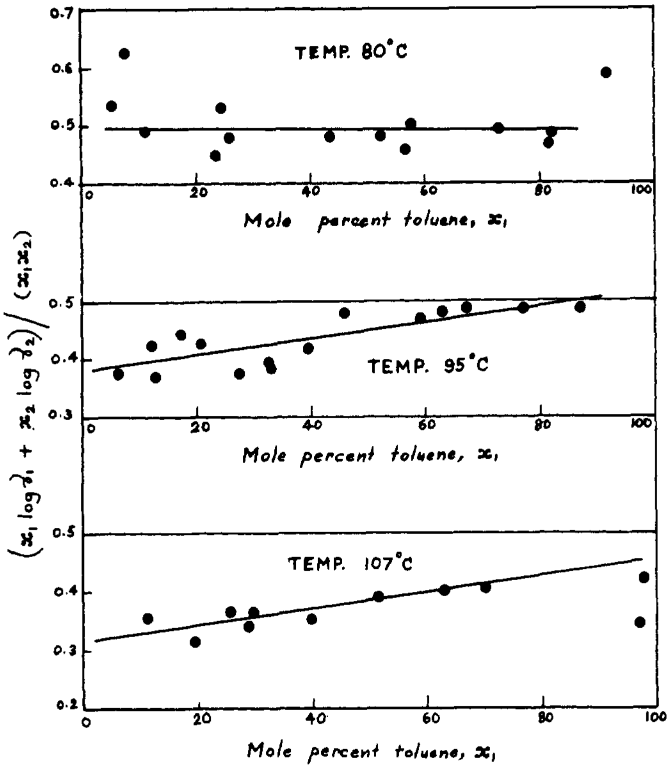

Figure 4. Plot of $(x_1 \log \gamma_1 + x_2 \log \gamma_2)/x_1x_2$ vs. x_1 for the system toluene (1)–isoamyl alcohol (2) under different isothermal conditions

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