mentally the same as that used in Example 1. The number of theoretical plates required for this separation, obtained from Figure 3, is 13.1. Therefore, to achieve the separation desired, the required number of plates is the difference between the result obtained in Example 1, $\mathcal{N}$ = 65.3, and 13.1, or 52.2 theoretical plates.

NOMENCLATURE

$\mathcal{N}$ = number of plates in distillation column
P = total pressure, mm. of mercury
P_v = vapor pressure, mm. of mercury
f^0 = fugacity of pure component in standard state at temperature and pressure of system
x = mole fraction in liquid phase
y = mole fraction in vapor phase
α = relative volatility
γ = liquid phase activity coefficient
η = refractive index

Subscripts

av refers to average value of property
d refers to distillate
l refers to liquid
v refers to vapor
w refers to bottoms

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Vapor-Liquid Equilibria at Subatmospheric Pressures

Binary and Ternary Systems Containing Ethyl Alcohol, Benzene, and *n*-Heptane

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Vapor-liquid equilibrium data were determined for the ethyl alcohol-benzene and benzene-*n*-heptane binary systems at pressures of 400 and 180 mm. of mercury. Similar data at a pressure of 760 mm. of mercury had previously been determined for the ethyl alcohol-benzene system by Barbaudy (*1*) and for the benzene-*n*-heptane system by Myers (*10*) and Sieg (*12*). These binary systems have now been investigated at three pressures. As in the case at atmospheric pressure, the ethyl alcohol-benzene system deviated greatly from ideal liquid phase behavior and showed a minimum boiling azeotrope at each reduced pressure. On the other hand, the benzene-*n*-heptane system departed from ideal liquid phase behavior to a lesser extent.

Vapor-liquid equilibrium data for the ethyl alcohol-benzene-*n*-heptane system at a pressure of 400 mm. of mercury supplement the data on this ternary system, determined at atmospheric pressure by Wagner and Weber (*13*). The information reported in this article and by Katz and Newman (*5*) include ternary vapor-liquid equilibrium data and similar data for the three possible binary systems at a pressure of 400 mm. of mercury for the system ethyl alcohol-benzene-*n*-heptane.

The ternary system showed large deviations from ideal liquid phase behavior, but no ternary azeotrope was found.

PURITY OF COMPOUNDS

The benzene and *n*-heptane used in this study were pure grade materials of 99 mole % minimum purity obtained from the Phillips Petroleum Co. The ethyl alcohol was manufactured by the United States Industrial Chemical Co. These chemicals were used without further purification. Physical constants for the materials appear in Table I.

Binary Systems Ethyl Alcohol–Benzene and Benzene–*n*-Heptane

EXPERIMENTAL METHOD

Vapor-liquid equilibrium data were obtained using a Braun still as described by Hipkin and Myers (*4*), and the experimental technique outlined by these authors was followed. Constant subatmospheric pressures were obtained using a manostat and vacuum pump. Jacket and still pressures were measured using absolute manometers. Samples were drawn by reducing the pressure in the sample receivers to 2 or 3 mm. of mercury below the still pressure, the pressure difference being measured with a differential manometer. The pressures could be read to 0.1 mm. of mercury, and the still pressure was kept within 0.5 mm. of mercury of the desired pressure.

Temperatures in the vapor spaces of the still and jacket were obtained by the use of a Leeds & Northrup Type K potentiometer in conjunction with copper-constantan thermocouples. The thermocouples were placed in thermowells provided in the apparatus. This arrangement allowed temperatures to be read to ±0.1° C. The jacket temperature was matched to within 0.05° C. of the still temperature, the jacket temperature being controlled by adjusting the jacket pressure. Pure benzene was used as the jacket fluid.

Table I. Properties of Pure Compounds

	Ethyl alcohol		Benzene		*n*-Heptane	
	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)
Density, 25°C., g/ml.	0.7843	0.78404	0.8732	0.87368	0.6786	0.67947
Refractive index, 25° C.	1.3591	1.35914	1.4976	1.49790	1.3851	1.38517
Boiling point, °C. at 760 mm. Hg	78.3	78.33	80.0	80.103	98.4	98.428
Boiling point, °C. at 400 mm. Hg	62.6	62.91	60.3	60.60	77.9	77.89
Boiling point, °C. at 180 mm. Hg	45.7	45.81	39.5	39.62	56.1	55.98

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The still was allowed to operate for approximately 1 hour before samples were drawn. About 15 minutes previous to sampling, preliminary samples were taken to flush the lines. Constant still temperature was also used as a criterion of equilibrium. Sample receivers were placed in ice baths to minimize evaporation losses during sampling.

Samples were analyzed by refractive index using an Abbe refractometer which allowed refractive indices to be read to within 0.0001 unit. Since the refractive index difference between pure ethyl alcohol and pure benzene is 0.1385 and between pure *n*-heptane and pure benzene is 0.1125, the compositions can be measured to better than ±0.1 of 1 mole %.

VAPOR-LIQUID EQUILIBRIUM DATA

Liquid phase activity coefficients were calculated using the following equation:

$$\gamma = yP/xP_v \qquad (1)$$

The derivation of Equation 1 assumes that the vapor phase forms an ideal solution and that the ratio of $f°_v$ to $f°_l$ equals the ratio of the total pressure, P, to the vapor pressure, P_v, of the component at the equilibrium temperature. The vapor pressure data for the pure components reported by Dreisbach (*3*) were used in the calculations.

For the ethyl alcohol-benzene system, data were smoothed using the four-constant form of the equation proposed by Redlich, Kister, and Turnquist (*11*) as the van Laar equations were found to be inadequate.

$$\log(\gamma_1/\gamma_2) = B'(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_1 - x_2)(8x_1x_2 - 1) + E(x_1 - x_2)^2(10x_1x_2 - 1) \qquad (2)$$

The technique outlined by these authors for fitting this equation to experimental data was followed. Similar equations describe the individual activity coefficient data.

$$\log \gamma_1 = x^2_2\ B' + C(3x_1 - x_2) + D(x_1 - x_2)(5x_1 - x_2) + E(x_1\ x_2)^2(7x_1 - x_2) \qquad (3)$$

Table II. Vapor-Liquid Equilibrium Data for Ethyl Alcohol-Benzene System

P = 180 mm. Hg

Redlich, Kister, and Turnquist Equation Constants

B' = 0.77 C = -0.12 D = 0.12 E = -0.06

Temp., °C.	$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	$\gamma_{C_2H_5OH}$	$\gamma_{C_6H_6}$
39.5	0.000	0.000	11.75	1.00
33.6	0.100	0.277	5.24	1.04
32.8	0.200	0.314	3.10	1.14
32.5	0.300	0.331	2.19	1.28
32.5	0.338	0.338	1.99	1.34
32.6	0.400	0.349	1.73	1.45
32.9	0.500	0.370	1.45	1.68
33.3	0.600	0.399	1.27	1.96
34.0	0.700	0.434	1.15	2.38
35.5	0.800	0.500	1.06	3.00
39.3	0.900	0.652	1.02	3.89
45.7	1.000	1.000	1.00	5.13

P = 400 mm. Hg

Redlich, Kister, and Turnquist Equation Constants

B' = 0.74 C = -0.10 D = 0.10 E = -0.05

Temp., °C.	$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	$\gamma_{C_2H_5OH}$	$\gamma_{C_6H_6}$
60.3	0.000	0.000	9.77	1.00
52.8	0.100	0.301	4.78	1.03
51.6	0.200	0.353	2.96	1.13
51.3	0.300	0.377	2.15	1.25
51.2	0.399	0.399	1.71	1.41
51.2	0.400	0.399	1.71	1.42
51.3	0.500	0.424	1.45	1.59
51.6	0.600	0.453	1.27	1.90
52.2	0.700	0.491	1.14	2.30
54.1	0.800	0.554	1.06	2.88
56.3	0.900	0.680	1.02	3.73
62.5	1.000	1.000	1.000	4.90

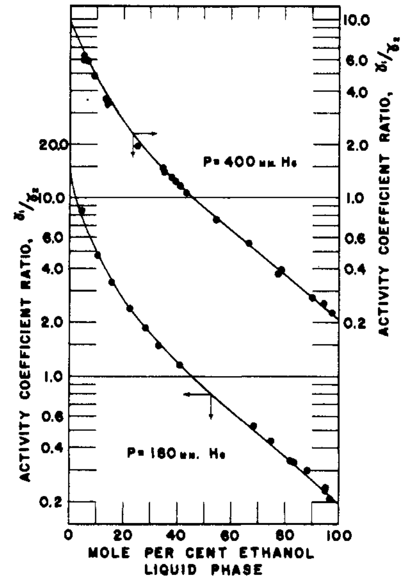

Figure 1. Logarithm of ratios of activity coefficients of ethyl alcohol-benzene vs. composition (smoothed curves)

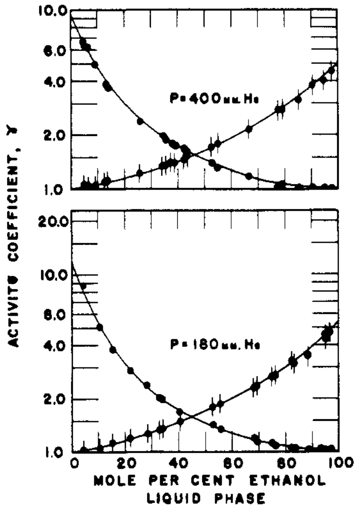

Figure 2. Logarithm of activity coefficients vs. composition for ethyl alcohol-benzene system (smoothed curves)

$$\log \gamma_2 = x^2_1\ B' + C(3x_1 - x_2) + D(x_1 - x_2)(x_1 - 5x_2) + E(x_1 - x_2)^2(x_1 - 7x_2) \qquad (4)$$

Redlich, Kister and Turnquist (*11*) show that the relationship

$$\int_0^1 \log\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0 \qquad (5)$$

must be satisfied in order for the experimental data to be consistent. Equation 5 means if $\log(\gamma_1/\gamma_2)$ is plotted against x_1, the total area under the curve is equal to zero. Or, the area above the abscissa axis is equal to the area below that axis. This is the so-called "area condition" and is strictly valid for isothermal conditions only, but may be applied to cases in which the range of boiling temperatures is not great. The curves drawn in Figure 1 meet the area condition.

The constants for these equations and the smoothed data are presented for each pressure in Table II. Activity coefficient ratio, smoothed activity coefficient, and $x - y$ data are presented graphically in Figures 1, 2, and 3, respectively. The experimental points are included to show the accuracy of the fit of the above equations. Figure 4 is a temperature *vs.* composition diagram for the system at each pressure; the deviation from ideal liquid phase behavior increased as the pressure decreased. These data are consistent with those of Barbaudy (*1*) in this respect, because the liquid phase activity coefficients are greater at a pressure of 400 than at 760 mm. of mercury.

For the benzene-*n*-heptane system, the van Laar equations (*8, 9*) as solved by Carlson and Colburn (*2*) were found to fit the experimental data well.

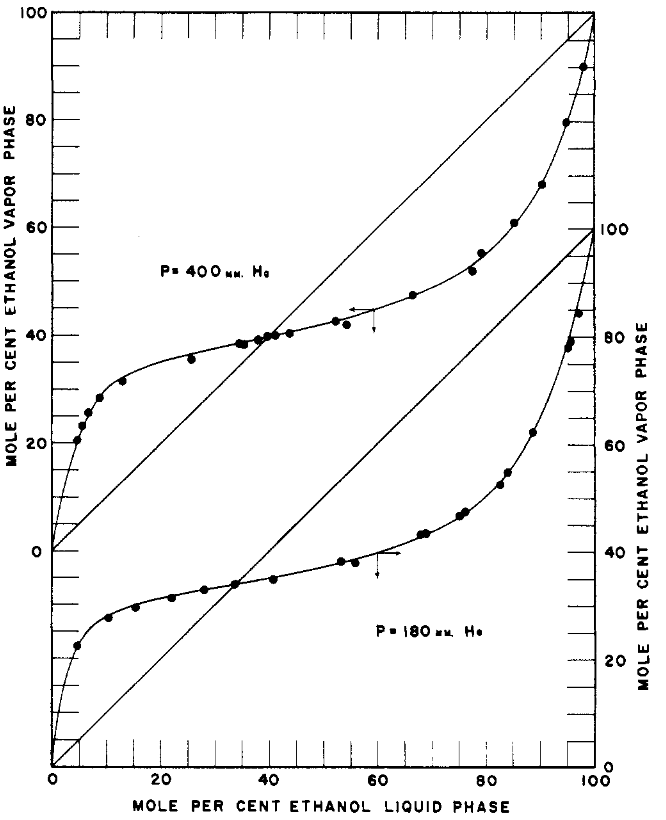

Figure 3. $x - y$ diagrams for ethyl alcohol–benzene system (smoothed curves)

$$\log \gamma_1 = \frac{Ax_2^2}{(A/Bx_1 + x_2)^2} \tag{6}$$

$$\log \gamma_2 = \frac{Bx_1^2}{(B/Ax_2 + x_1)^2} \tag{7}$$

The constants for Equations 6 and 7 were obtained by extrapolating the activity coefficient data to the values at zero concentration. A trial and error procedure was used to determine the best values of the van Laar constants, *A* and *B*. Because the van Laar equation (*8*, *9*) is a solution for the Gibbs-Duhem relationship and the experimental data fit the former relationship, one can conclude that the experimental data are internally consistent. The constants and smoothed data for each pressure are presented in Table III. Smoothed data are presented in the form of log γ *vs.* x and $x - y$ diagrams as Figures 5 and 6, respectively. The experimental points are included to show the accuracy of the fit of the above equations. Figure 7 is a temperature-composition diagram for the system at each pressure; the deviation from ideal liquid phase behavior increased as the pressure decreased. In this respect, the data reported in this work are consistent with those of Myers (*10*) and Sieg (*12*).

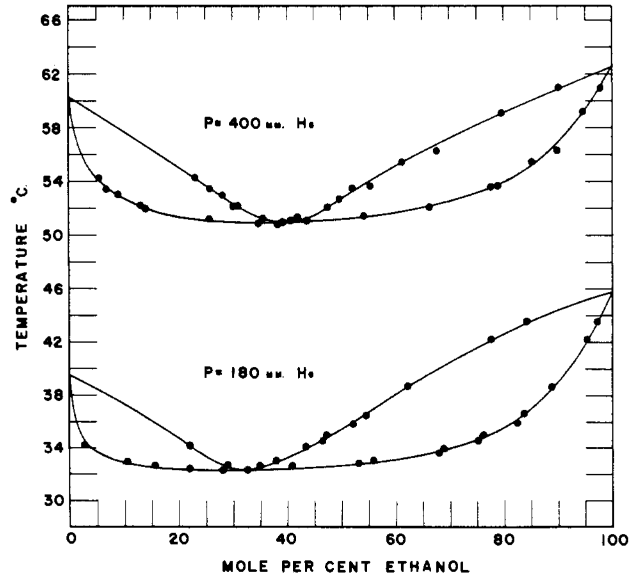

Figure 4. Temperature-composition diagrams for ethyl alcohol–benzene system (smoothed curves)

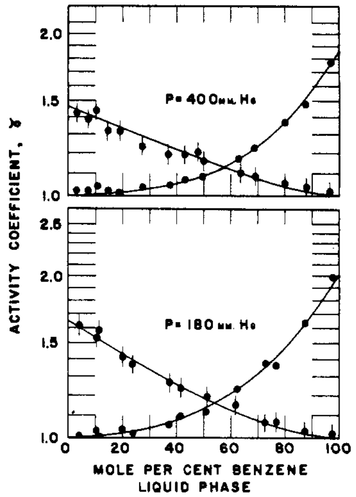

Figure 5. Logarithm of activity coefficients *vs.* compositions for benzene–*n*-heptane system (smoothed curves)

Ternary System Ethyl Alcohol–Benzene–*n*-Heptane

EXPERIMENTAL METHOD

The vapor-liquid equilibrium data were obtained using the same apparatus and experimental technique as for the binary systems.

Samples were analyzed with a Perkin-Elmer Vapor Fractometer, Model 154-B. Three 1-meter columns packed with

Table III. Vapor–Liquid Equilibrium Data for Benzene–*n*-Heptane System

Temp., °C.	$x_{C_6H_6}$	$y_{C_6H_6}$	$\gamma_{C_6H_6}$	$\gamma_{n\text{-}C_7H_{16}}$
	van Laar Constants $A = 0.2162$ $B = 0.3022$ $P = 180$ mm. Hg			
56.1	0.000	0.000	1.65	1.00
51.5	0.100	0.245	1.53	1.00
48.3	0.200	0.404	1.43	1.02
45.9	0.300	0.516	1.34	1.04
44.2	0.400	0.603	1.26	1.08
42.8	0.500	0.672	1.18	1.13
41.7	0.600	0.734	1.12	1.21
40.9	0.700	0.790	1.07	1.31
40.4	0.800	0.848	1.03	1.47
39.8	0.900	0.914	1.01	1.68
39.5	1.000	1.000	1.00	2.01
	van Laar Constants $A = 0.1644$ $B = 0.2676$ $P = 400$ mm. Hg			
77.9	0.000	0.000	1.46	1.00
73.9	0.100	0.218	1.39	1.00
70.5	0.200	0.373	1.33	1.01
68.0	0.300	0.490	1.27	1.03
66.0	0.400	0.583	1.21	1.05
64.4	0.500	0.660	1.16	1.09
63.3	0.600	0.727	1.11	1.15
62.1	0.700	0.788	1.07	1.24
61.4	0.800	0.849	1.03	1.37
60.8	0.900	0.916	1.01	1.56
60.3	1.000	1.000	1.00	1.85

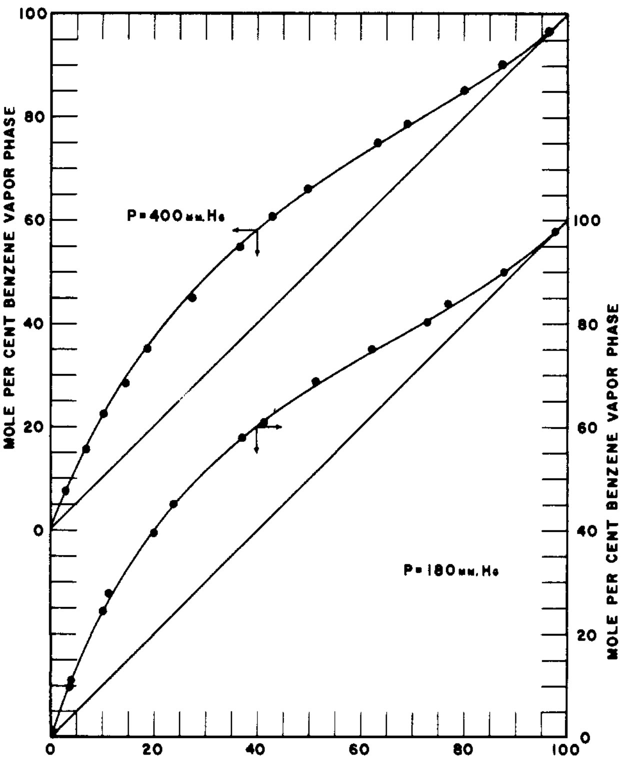

Figure 6. *x* – *y* diagrams for benzene–*n*-heptane system (smoothed curves)

Perkin-Elmer's Type B packing material were used to effect separation. Operating conditions of 90° C., and an inlet pressure of 12 p.s.i.g. allowed complete analysis of a sample in approximately 28 minutes.

Calibration of the instrument was found to be necessary to convert peak area fractions to mole fractions. The calibration changed somewhat when the matched thermistors were replaced in the detecting element of the fractometer. Calibration test analysis showed that a precision of about 0.3 mole % could be expected. Thus, it is felt that all concentrations are accurate to within ±0.5 mole %. However, for components present in relatively small quantities, the analysis is more accurate, as the peaks are traced at a high sensitivity. Some of the error in the compositions is due to the error in the measurement of the area under the curves. A planimeter was used to measure these areas.

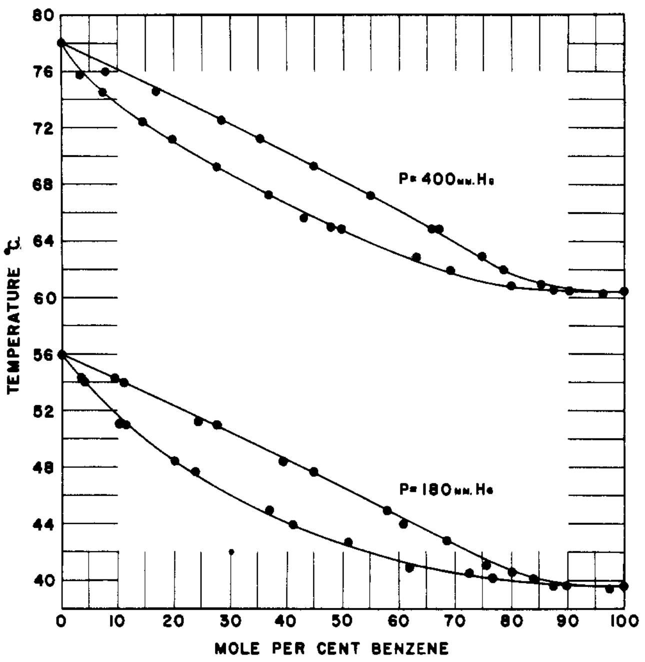

Figure 7. Temperature vs. composition diagrams for benzene–*n*-heptane system (smoothed curves)

VAPOR-LIQUID EQUILIBRIUM DATA

Liquid phase activity coefficients were calculated using Equation 1. Experimental data and calculated activity coefficients are presented in Table IV. Figure 8 shows experimental bubble point data, while Figures 9, 10, and 11 show experimental activity coefficient data. Binary data on these

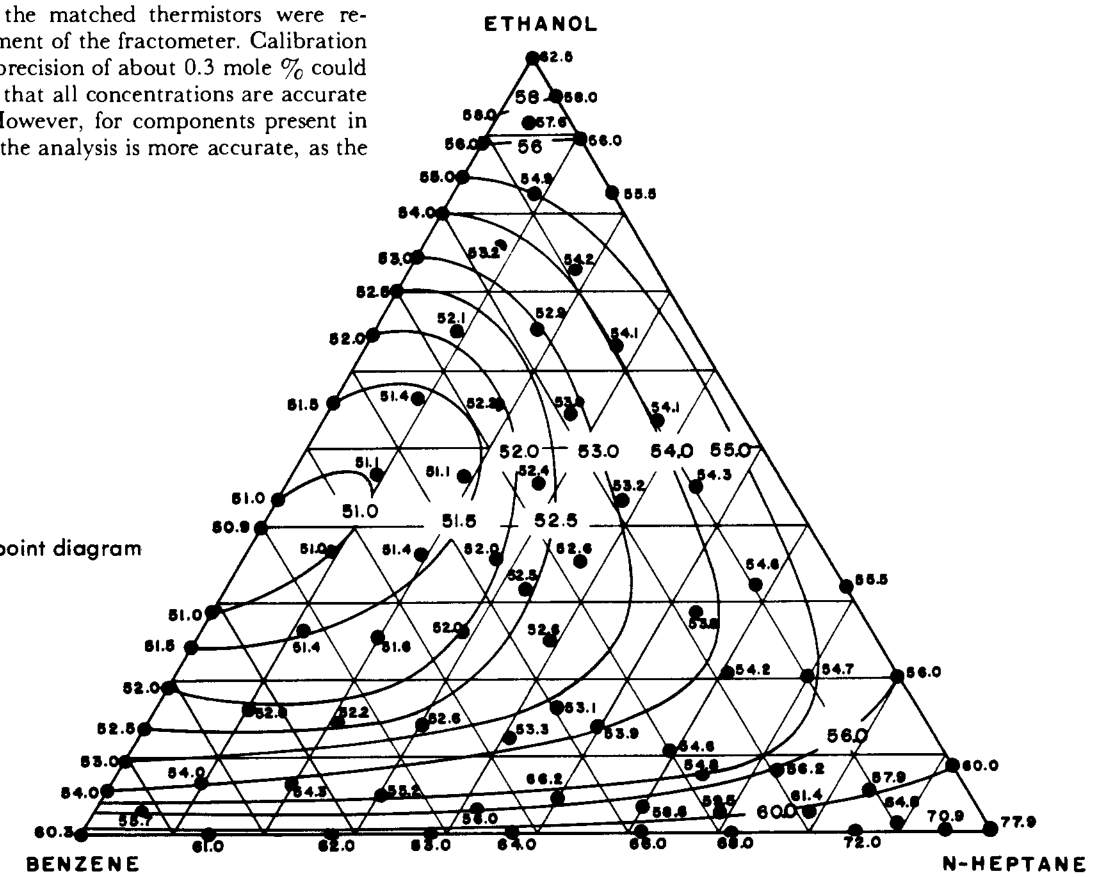

Figure 8. Bubble point diagram

Table IV. Vapor-Liquid Equilibrium Data Ethyl Alcohol-Benzene-*n*-Heptane System at 400 Mm. of Mercury

(Experimental data)

	Liquid Mole Fractions			Vapor Mole Fractions			Activity Coefficients		
Temp., °C.	Ethyl Alcohol	Benzene	*n*-Heptane	Ethyl Alcohol	Benzene	*n*-Heptane	Ethyl Alcohol	Benzene	*n*-Heptane
64.84	0.011	0.096	0.893	0.303	0.128	0.569	26.7	1.16	1.01
57.94	0.054	0.107	0.839	0.461	0.120	0.419	10.6	1.23	1.03
54.70	0.204	0.098	0.698	0.513	0.120	0.367	3.66	1.52	1.23
54.60	0.323	0.095	0.582	0.529	0.119	0.352	2.39	1.55	1.42
54.32	0.450	0.096	0.455	0.538	0.125	0.337	1.77	1.63	1.76
54.13	0.533	0.098	0.369	0.534	0.141	0.325	1.49	1.81	2.11
54.13	0.630	0.092	0.277	0.548	0.149	0.303	1.30	2.03	2.62
54.17	0.729	0.089	0.183	0.569	0.166	0.265	1.16	2.37	3.47
54.92	0.824	0.085	0.091	0.619	0.191	0.190	1.08	2.76	4.82
61.36	0.27	0.185	0.789	0.322	0.227	0.451	13.0	1.20	1.03
56.18	0.080	0.192	0.728	0.432	0.205	0.363	7.29	1.25	1.10
54.24	0.209	0.184	0.607	0.477	0.210	0.314	3.38	1.44	1.23
53.78	0.285	0.179	0.535	0.488	0.216	0.296	2.59	1.55	1.34
53.24	0.433	0.185	0.383	0.491	0.230	0.279	1.76	1.63	1.81
53.02	0.543	0.188	0.269	0.501	0.246	0.252	1.45	1.73	2.34
52.88	0.650	0.171	0.179	0.513	0.273	0.214	1.25	2.12	3.01
53.23	0.757	0.159	0.084	0.543	0.308	0.149	1.11	2.53	4.43
59.46	0.028	0.282	0.690	0.303	0.317	0.380	12.4	1.17	1.07
54.79	0.076	0.279	0.646	0.413	0.286	0.302	7.82	1.27	1.10
54.62	0.107	0.298	0.594	0.414	0.298	0.288	5.63	1.24	1.14
52.57	0.353	0.272	0.375	0.439	0.313	0.248	2.00	1.54	1.69
52.37	0.453	0.268	0.279	0.471	0.314	0.214	1.69	1.59	1.98
52.19	0.556	0.260	0.184	0.479	0.340	0.182	1.41	1.78	2.57
52.10	0.651	0.260	0.089	0.483	0.391	0.126	1.22	2.06	3.68
58.62	0.031	0.367	0.603	0.293	0.388	0.319	11.6	1.13	1.06
53.94	0.135	0.364	0.501	0.397	0.352	0.251	4.44	1.23	1.21
52.58	0.251	0.359	0.390	0.435	0.348	0.217	2.78	1.30	1.42
51.96	0.356	0.365	0.279	0.438	0.370	0.192	2.03	1.39	1.75
51.08	0.465	0.347	0.188	0.441	0.400	0.159	1.64	1.64	2.29
51.43	0.561	0.346	0.093	0.425	0.476	0.100	1.28	1.93	2.87
56.15	0.043	0.456	0.501	0.306	0.442	0.253	9.58	1.14	1.12
53.27	0.125	0.468	0.408	0.379	0.413	0.208	4.72	1.16	1.26
52.01	0.264	0.448	0.289	0.411	0.414	0.175	2.57	1.27	1.58
51.45	0.363	0.443	0.194	0.412	0.445	0.143	1.93	1.41	1.97
51.06	0.466	0.441	0.093	0.429	0.479	0.092	1.59	1.54	2.68
55.97	0.043	0.549	0.408	0.274	0.525	0.201	8.70	1.13	1.10
52.63	0.141	0.557	0.303	0.362	0.471	0.167	4.12	1.13	1.41
51.59	0.259	0.544	0.198	0.384	0.486	0.130	2.50	1.25	1.74
51.04	0.367	0.542	0.092	0.398	0.518	0.084	1.87	1.36	2.48
55.20	0.050	0.642	0.309	0.269	0.561	0.170	7.68	1.06	1.27
52.19	0.148	0.645	0.208	0.352	0.526	0.122	3.90	1.11	1.53
51.40	0.266	0.633	0.101	0.380	0.544	0.076	2.37	1.21	2.01
54.26	0.060	0.736	0.204	0.273	0.607	0.120	6.70	1.04	1.40
52.01	0.163	0.735	0.102	0.350	0.581	0.069	3.54	1.08	1.77
54.02	0.065	0.835	0.100	0.264	0.671	0.065	6.09	1.02	1.57
55.67	0.027	0.920	0.053	0.157	0.802	0.041	8.10	1.08	1.74
57.64	0.915	0.047	0.038	0.733	0.135	0.132	1.01	3.18	7.17
70.87	0.002	0.050	0.948	0.165	0.091	0.745	62.0	1.29	1.00
52.46	0.318	0.350	0.332	0.448	0.333	0.220	2.27	1.28	1.70
53.10	0.164	0.396	0.440	0.413	0.363	0.225	3.94	1.20	1.28

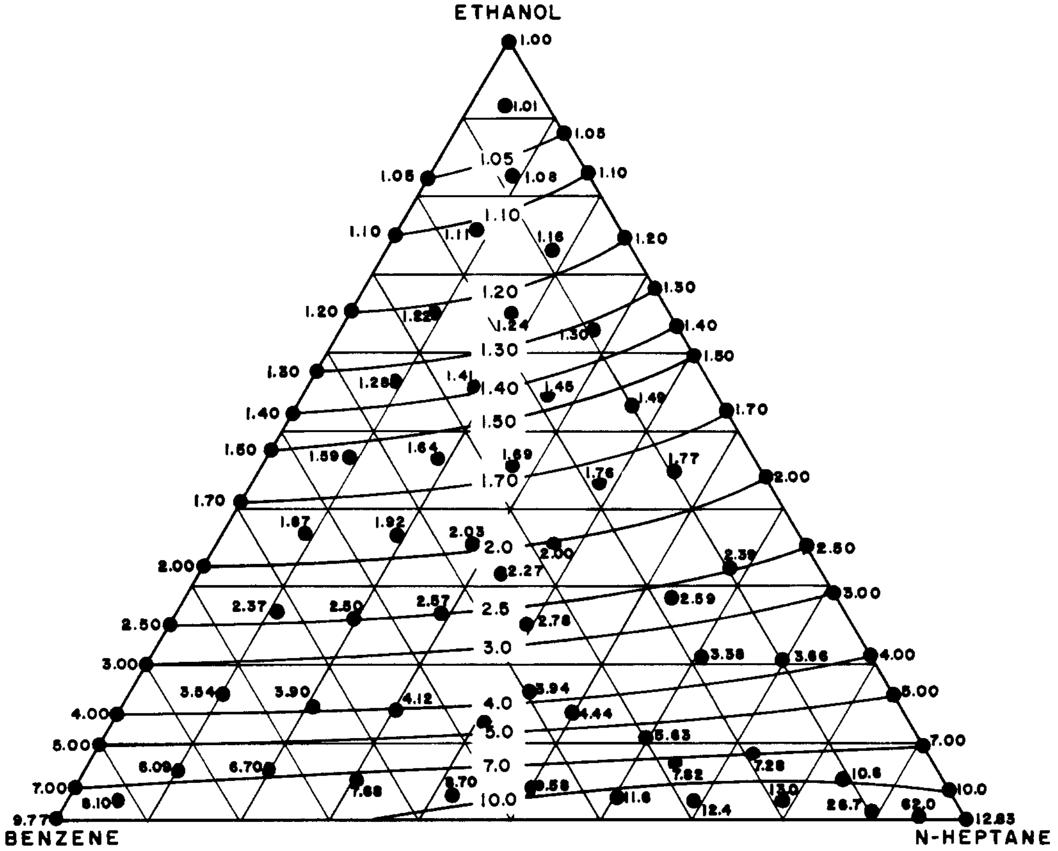

Figure 9. Ethyl alcohol activity coefficients vs. liquid phase composition

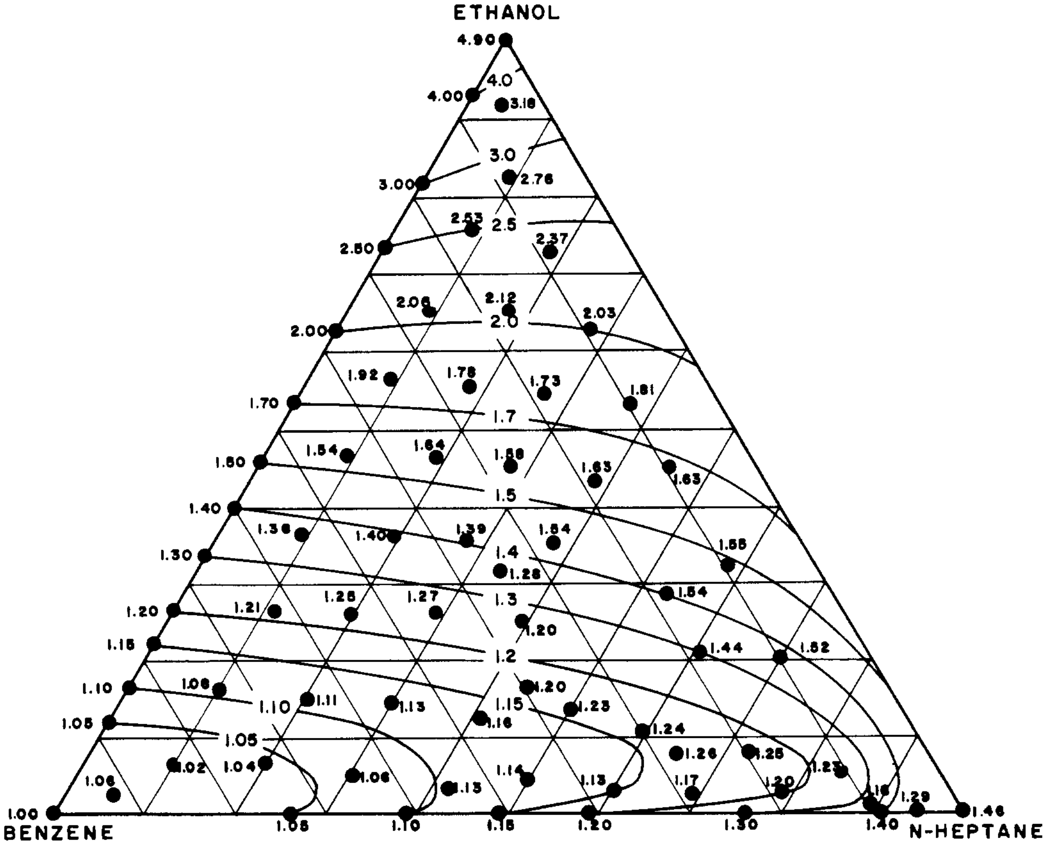

Figure 10. Benzene activity coefficients vs. liquid phase composition

figures were determined by Katz and Newman (*5*) and the authors. Isotherms and parameters of constant activity coefficient were established by constructing cross plots of the experimental data.

The smoothed data of Figures 9, 10, and 11 were checked for internal consistency by the method outlined by Krishnamurty and Rao (*6*, *7*). This method is rigorous only for constant pressure-constant temperature conditions as a form of the Gibbs-Duhem equation is used in its development.

These authors define a Q term in the following manner

$$Q = \frac{\Delta G^E}{2.3RT} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \tag{8}$$

Differentiating at constant x_3 and substituting the constant pressure-constant temperature form of the Gibbs-Duhem equation results in

$$\frac{dQ}{dx_1} = \log \gamma_1/\gamma_2 \tag{9}$$

Integrating

$$\int_{Q'}^{Q''} dQ = \int_{x_1 \geq 0 = x_1'}^{x_1 \leq (1-x_3) = x_1''} \log \gamma_1/\gamma_2 \, dx_1 \tag{10}$$

The consistency check is accomplished by graphically integrating between the proper limits at constant x_3. If this quantity equals the value of the left hand member of the equation, the data are internally consistent.

The smoothed data were checked by this method at constant *n*-heptane concentrations of 20, 40, and 70 mole %. The differences between the two members of Equation 10 were 0, 1, and 8%, respectively. As the temperature changes over the range of compositions involved in the last case from 55.5° to 68° C. and passes through a minimum of 54.8° C., the lack of agreement in this instance is not unexpected.

Smoothed data are presented in tabular and graphical form, while experimental data are presented in graphical form only. In both binary and ternary systems, the experimental data appear to be internally consistent.

NOMENCLATURE

A,B = constants of van Laar equation
B',C,D,E = constants of Redlich= Kister, Turnquist equation
ΔG^E = excess molal free energy at mixing
P = total pressure, mm. of mercury
P_v = vapor pressure, mm. of mercury
Q = defined by Equation 2
f° = fugacity of a pure component in standard state at temperature and pressure of system
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = liquid phase activity coefficient

Subscripts

l refers to liquid phase
v refers to vapor phase
1,2,3 refer to components in mixture

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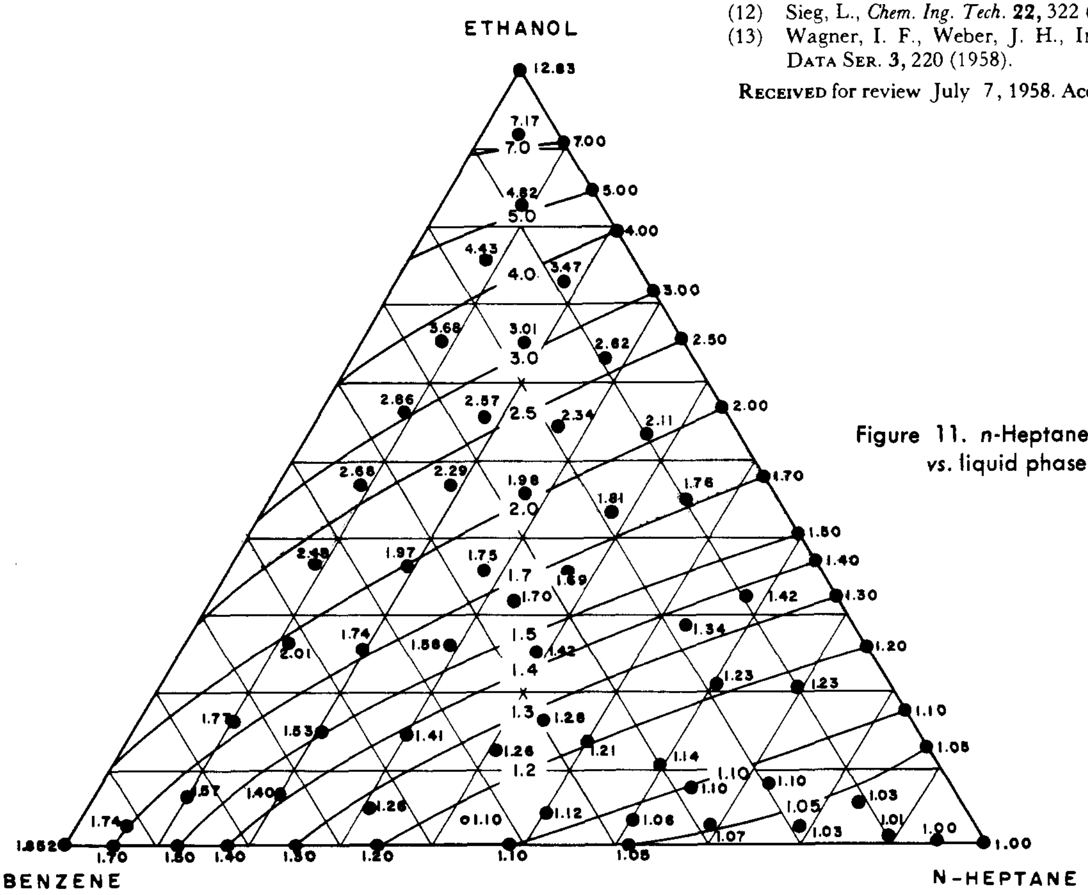

Figure 11. *n*-Heptane activity coefficients vs. liquid phase composition