Vapor-Liquid Equilibria at Atmospheric Pressure for the Ternary System Benzene– Ethyl Alcohol – *n* - Heptane

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As part of a continuing study of vapor-liquid equilibrium relationships, vapor-liquid equilibrium data for the ternary system benzene–ethyl alcohol–*n*-heptane at atmospheric pressure were determined. This ternary system was chosen because it could be expected to show large deviations from ideal liquid phase behavior, and the vapor-liquid equilibrium data for the three possible binary systems made up of the components of the ternary system are available (*2*, *5*, *8*). In this latter respect the data reported in this work and those reported in the works cited above should be useful in seeking means of predicting multicomponent equilibrium data from binary equilibrium data. Also, it is of interest to ascertain whether this ternary system exhibits an azeotrope, as do the binary systems benzene–ethyl alcohol and ethyl alcohol–*n*-heptane.

PURITY OF COMPOUNDS

The benzene and *n*-heptane used in the experimental work were pure grade materials obtained from the Phillips Petroleum Co. and had a minimum purity of 99 mole %. The ethyl alcohol was manufactured by United States Industrial Chemical Co. The chemicals were used without further purification. Table I reports the physical constants for these chemicals and, for comparison, similar data on the pure compounds.

EXPERIMENTAL METHOD

The vapor-liquid equilibrium data were determined in a Braun still designed by Hipkin and Myers (*4*), by an operating procedure essentially the same as used by them. The pressure in the distillation unit was maintained at 760 mm. of mercury by bleeding nitrogen into the system. The flow of nitrogen was controlled by a manostat and the pressure difference between the standard and local atmospheric pressures was measured by a mercury manometer. The total pressure on the system was at all times within 0.5 mm. of mercury of standard atmospheric pressure. The minimum time allowed for a run for the determination of vapor-liquid equilibrium data was 45 minutes. In addition to this, the constancy of the temperature of the still was used as a criterion of the attainment of equilibrium conditions.

n-Heptane was used as the jacket fluid and its boiling temperature was maintained at 0.5°C. above the boiling temperature of the sample by adjusting the pressure in the jacket.

Temperatures were measured by copper-constantan thermocouples used in conjunction with a Leeds & Northrup Type K potentiometer and are believed to be accurate within ± 0.1°C. The two thermocouple wells in the still are located in the vapor spaces above the jacket liquid and the liquid sample.

The liquid and vapor samples analyzed chromatographically. A Perkin-Elmer Vapor Fractometer, Model 154-B, was

Table I. Properties of Pure Compounds

	Benzene		Ethyl Alcohol		n-Heptane	
	Exptl.	Lit. (*1*)	Exptl.	Lit. (*3*)	Exptl.	Lit. (*1*)
Density, 25°C., g./ml.	0.8732	0.87368	0.7843	0.78404	0.6786	0.67947
Refractive index, 25°C.	1.4976	1.49790	1.3591	1.35914	1.3851	1.38517
Normal boiling point, °C.	80.0	80.103	78.3	78.33	98.4	98.428

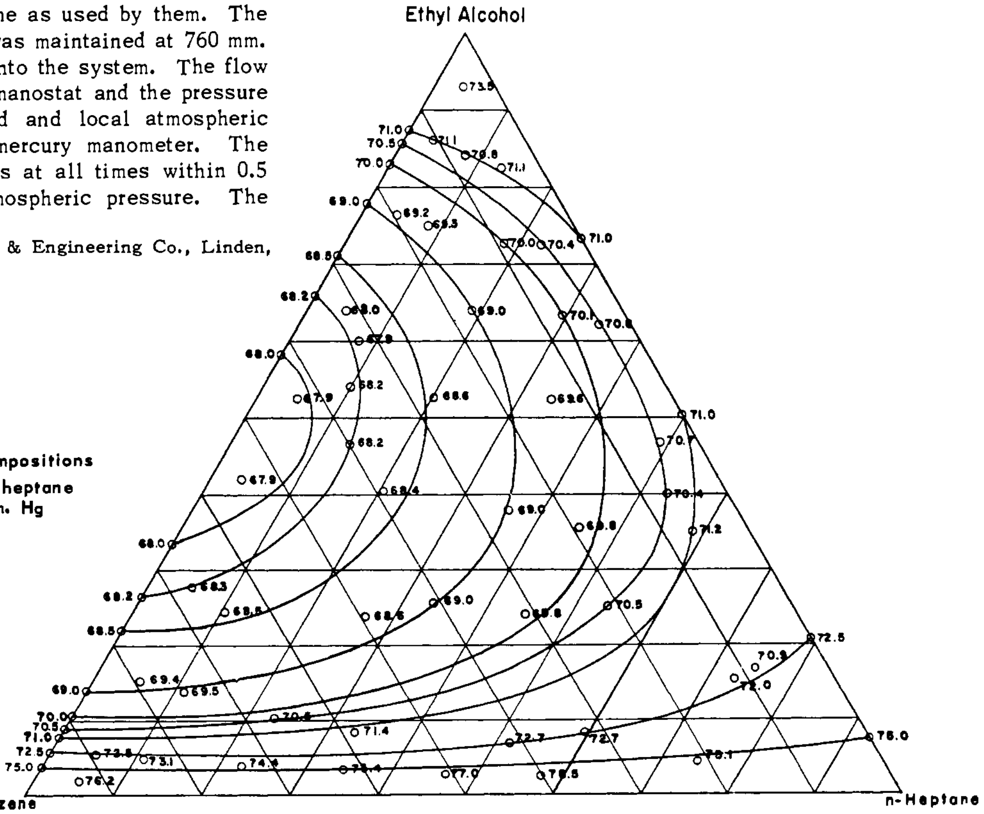

Figure 1. Bubble point compositions
Benzene–ethyl alcohol–*n*-heptane
Absolute pressure 760 mm. Hg
Temperature °C.

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Table II. Vapor-Liquid Equilibrium Data System: Benzene-Ethyl Alcohol-*n*-Heptane Pressure, 760 mm. Hg.

	Vapor, Mole Fraction			Liquid, Mole Fraction			Liquid Phase Activity Coefficients, γ		
Temp., °C.	Ethyl alcohol	Benzene	*n*-Heptane	Ethyl alcohol	Benzene	*n*-Heptane	Ethyl alcohol	Benzene	*n*-Heptane
75.1	0.424	0.212	0.364	0.044	0.213	0.743	10.94	1.16	1.03
72.7	0.426	0.265	0.309	0.084	0.323	0.593	6.38	1.03	1.19
72.7	0.376	0.371	0.253	0.069	0.415	0.516	6.86	1.13	1.12
71.4	0.346	0.478	0.176	0.086	0.584	0.330	5.32	1.08	1.27
70.5	0.359	0.506	0.135	0.103	0.651	0.246	4.78	1.05	1.35
69.5	0.371	0.560	0.069	0.138	0.750	0.112	3.85	1.05	1.56
72.0	0.575	0.091	0.334	0.155	0.115	0.730	4.77	1.02	1.07
70.5	0.518	0.201	0.281	0.252	0.212	0.536	2.82	1.29	1.28
69.8	0.502	0.260	0.238	0.242	0.310	0.448	2.94	1.17	1.34
69.0	0.452	0.364	0.184	0.257	0.407	0.336	2.57	1.27	1.42
68.6	0.468	0.387	0.145	0.238	0.495	0.267	2.92	1.13	1.43
68.5	0.415	0.520	0.065	0.244	0.651	0.105	2.55	1.16	1.64
71.2	0.598	0.065	0.337	0.350	0.065	0.585	2.28	1.27	1.42
70.9	0.587	0.082	0.331	0.168	0.084	0.748	4.71	1.32	1.07
69.8	0.534	0.199	0.267	0.356	0.193	0.451	2.12	1.43	1.49
69.0	0.527	0.255	0.218	0.378	0.261	0.361	2.04	1.39	1.56
68.4	0.485	0.370	0.145	0.406	0.391	0.203	1.79	1.38	1.89
67.9	0.510	0.401	0.089	0.602	0.320	0.078	1.30	1.85	3.08
67.9	0.446	0.520	0.034	0.419	0.544	0.037	1.63	1.42	2.44
70.7	0.614	0.051	0.335	0.467	0.044	0.489	1.79	1.58	1.67
70.4	0.599	0.092	0.309	0.399	0.069	0.532	2.07	1.83	1.43
69.6	0.572	0.179	0.249	0.522	0.139	0.339	1.56	1.80	1.86
68.6	0.511	0.318	0.171	0.527	0.272	0.201	1.44	1.69	2.24
68.2	0.498	0.407	0.095	0.541	0.361	0.098	1.39	1.65	2.58
67.9	0.477	0.471	0.052	0.524	0.428	0.048	1.36	1.63	2.93
70.8	0.632	0.053	0.315	0.622	0.036	0.342	1.38	2.02	2.16
70.1	0.617	0.099	0.284	0.635	0.071	0.294	1.36	1.99	2.40
70.0	0.563	0.240	0.197	0.640	0.172	0.188	1.29	1.99	2.73
68.2	0.524	0.362	0.114	0.467	0.397	0.136	1.70	1.33	2.24
68.0	0.516	0.421	0.063	0.642	0.314	0.044	1.22	1.97	3.83
70.4	0.631	0.083	0.286	0.725	0.050	0.225	1.20	2.26	3.13
70.0	0.622	0.141	0.237	0.727	0.091	0.182	1.20	2.14	3.26
69.3	0.592	0.273	0.135	0.751	0.166	0.083	1.14	2.32	4.17
69.2	0.583	0.344	0.073	0.766	0.196	0.038	1.10	2.48	4.91
71.1	0.669	0.094	0.237	0.825	0.045	0.130	1.08	2.76	4.39
70.8	0.658	0.170	0.172	0.842	0.078	0.080	1.06	2.92	5.24
71.1	0.678	0.237	0.085	0.862	0.105	0.033	1.05	3.00	6.26
73.5	0.791	0.098	0.111	0.932	0.035	0.033	1.03	3.44	7.44
69.4	0.365	0.597	0.038	0.154	0.792	0.054	3.41	1.06	1.78
68.3	0.423	0.538	0.039	0.277	0.673	0.050	2.30	1.17	2.06
72.5	0.251	0.712	0.037	0.054	0.892	0.054	5.90	1.01	1.59
76.2	0.129	0.831	0.040	0.020	0.927	0.053	7.04	1.01	1.53
73.1	0.234	0.693	0.073	0.049	0.841	0.110	5.92	1.03	1.50
78.5	0.240	0.430	0.330	0.024	0.402	0.574	10.00	1.12	1.07
77.0	0.230	0.504	0.266	0.027	0.508	0.465	9.12	1.09	1.12
75.4	0.232	0.570	0.198	0.034	0.622	0.344	7.63	1.06	1.20
74.4	0.229	0.633	0.138	0.038	0.735	0.227	7.14	1.03	1.30

used for this purpose. A 2-meter W-type column filled with Perkin-Elmer's Type A packing was used to separate the three components. Because calibration of the vapor phase chromatographic equipment is necessary, numerous binary and ternary samples of known compositions were separated. It was determined that the ratio between the mole fractions of two components as they actually existed in the mixture, symbolized by r_a, and the mole fractions of the same components as determined by the areas under the curves obtained by vapor phase chromatography, symbolized by r_m, was a constant—e.g.

$$\frac{\left(\dfrac{x_{C_2H_5OH}}{x_{C_6H_6}}\right)_{\text{actual}}}{\left(\dfrac{x_{C_2H_5OH}}{x_{C_6H_6}}\right)_{\text{as determined by the ratio of areas}}} = \frac{r_a}{r_m} = 1.414$$

The other ratios are:

C_6H_6 to n-C_7H_{16}

$$r_a/r_m = 1.356$$

C_2H_5OH to n-C_7H_{16}

$$r_a/r_m = 1.917$$

These constants and the fact that the sum of the mole fractions of any sample must be one were used to calculate the compositions.

The expected error in the majority of the analytical results is ± 0.1 mole %. This was the error obtained when samples of known composition were run. In a few cases, the error may be as much as ± 0.5 mole %. Errors in composition of this magnitude may have resulted when a relatively large percentage of *n*-heptane was present in the sample and a relatively small amount of benzene. In this case, the benzene and *n*-heptane peaks were not entirely separated and extrapolations of the curves were necessary.

The vapor phase chromatography unit was operated at a temperature of 40°C. and an inlet pressure of 15 pounds per square inch gage. The time for one complete analysis was about 55 minutes.

VAPOR-LIQUID EQUILIBRIUM DATA

From the experimental data, liquid phase activity coefficients were calculated by the equation:

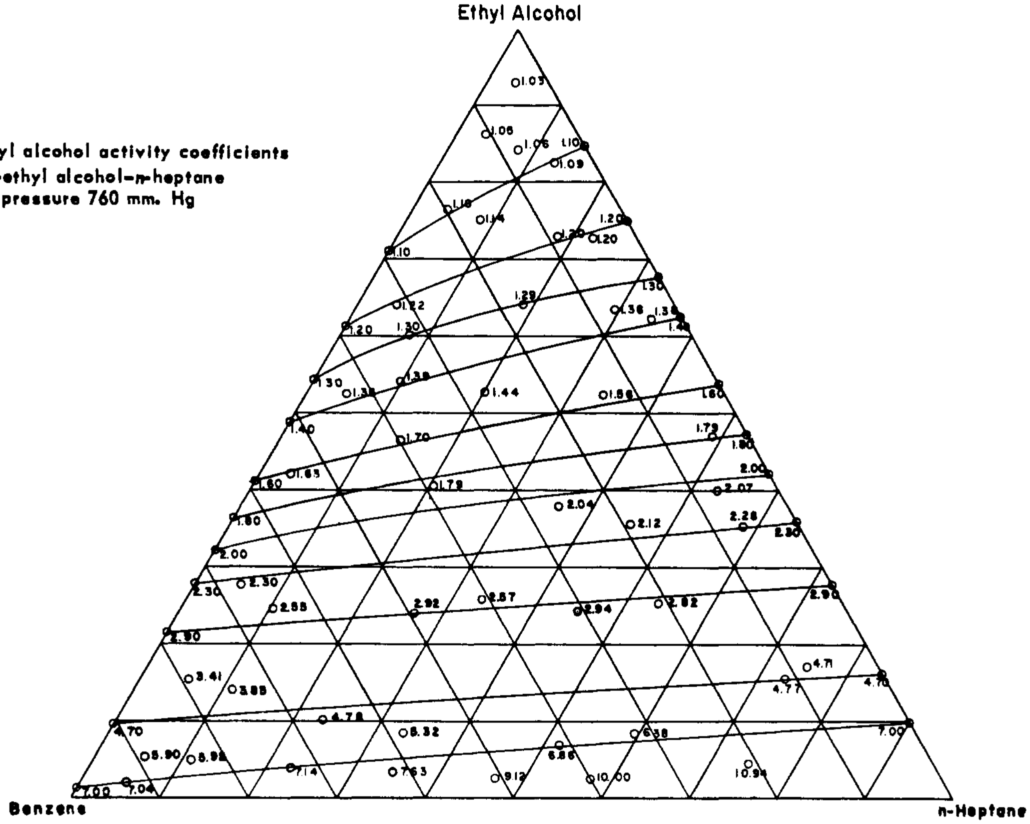

Figure 2. Ethyl alcohol activity coefficients
Benzene–ethyl alcohol–*n*-heptane
Absolute pressure 760 mm. Hg

$$\gamma = yP/xP^0 \tag{1}$$

In Equation 1 the assumptions are made that the standard state vapor fugacity, f_v°, of the pure component at the temperature and pressure of the system is equal to the total pressure, the standard state liquid fugacity, f_L°, of the pure component at the temperature and pressure of the system is equal to the vapor pressure, and the vapor phase activity coefficient, φ, is equal to unity.

The vapor pressure data used in the calculations were those reported in API Research Project 44 (*1*) and (*3*).

The experimental data and the calculated activity coefficients are reported in Table II. The experimental data are also shown in graphical form in Figures 1 to 4, in-

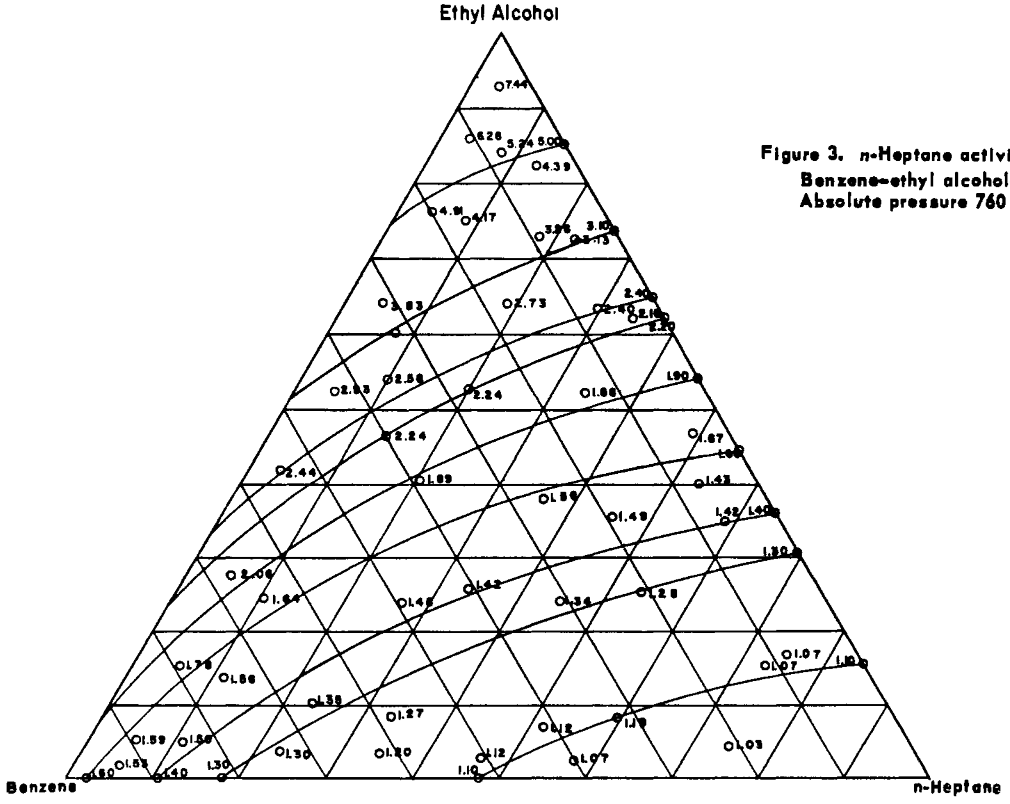

Figure 3. *n*-Heptane activity coefficients
Benzene–ethyl alcohol–*n*-heptane
Absolute pressure 760 mm. Hg

clusive. Figure 1 shows the bubble point temperatures as a function of the liquid phase composition. Figures 2, 3, and 4 show the activity coefficients of ethyl alcohol, *n*-heptane, and benzene, respectively, as functions of composition. The binary data shown on these figures were obtained from (*2, 5, 8*). Before the final figures were made, numerous cross plots were constructed to ensure that the temperature and activity coefficient parameters were properly located.

The smoothed data as shown on Figures 2, 3, and 4 were then tested by the method outlined by Krishnamurty and Rao (*6, 7*). This method, which applies rigorously only to isothermal conditions, may be applied to close boiling mixtures and is consistent with the Gibbs-Duhem equation.

Krishnamurty and Rao defined a Q term as

$$Q = \frac{\Delta G^E}{2.3\,RT} \qquad (2)$$

which is related to the mole fractions and the logarithms of the activity coefficients as follows

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \qquad (3)$$

When the vapor phase is ideal

$$\frac{dQ}{dx} = \log\left(\frac{\gamma_1}{\gamma_2}\right) \qquad (4)$$

Hence,

$$\int_{Q'}^{Q''} dQ = \int_{x_1 \geq 0 = x_1'}^{x_1 \leq (1 - x_3) = x_1''} \log\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 \qquad (5)$$

The right-hand member of the equation may be evaluated by plotting $\log \gamma_1/\gamma_2$ vs. x_1 (at constant x_3) and finding the area between the two limiting values of x_1.

The data obtained in this investigation were checked for internal consistency at constant compositions of 25, 50, and 75 mole % *n*-heptane. Ethyl alcohol was considered to be component 1 and the lower limit of x_1 was zero in all cases. The upper limits were 75, 50, and 25 mole %, respectively. The maximum difference between the value of the two members of Equation 5 was 3%. Hence, the experimental data were considered to be internally consistent.

No ternary azeotrope was found.

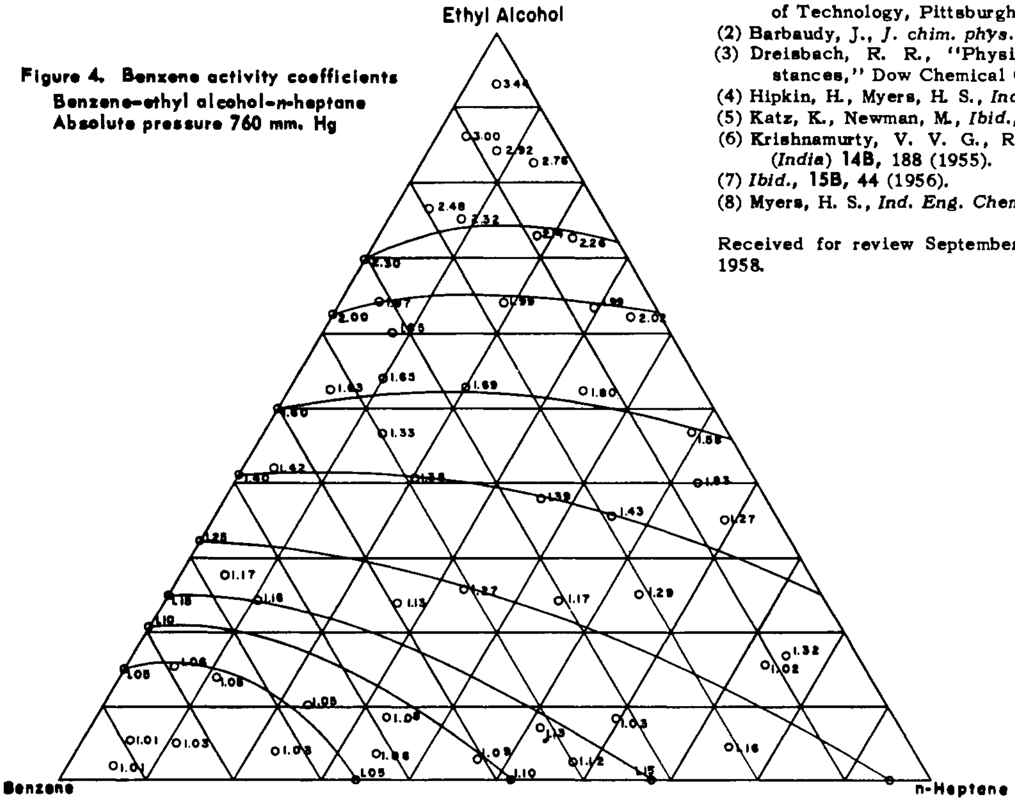

Figure 4. Benzene activity coefficients Benzene-ethyl alcohol-*n*-heptane Absolute pressure 760 mm. Hg

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NOMENCLATURE

ΔG^E = excess molal free energy at mixing
P = total pressure, mm. of mercury
P° = 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
r_a = ratio of mole fractions of two components as they actually exist in a mixture
r_m = ratio of mole fractions of two components as determined by vapor phase chromatographic equipment
t = temperature, °C.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = liquid phase activity coefficient
φ = vapor phase activity coefficient

Subscripts

L = liquid phase
V = vapor phase
1,2,3 = components in ternary mixture

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