Vapor-Liquid Equilibria at a Subatmospheric Pressure

Ternary System Ethyl Alcohol–Benzene–n-Heptane

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VAPOR-LIQUID equilibrium data at a pressure of 180 mm. of mercury for the ternary system ethyl alcohol-benzene-*n*-heptane have been determined. Nielsen and Weber (*11*) and Katz and Newman (*7*) have determined similar data for the three binary systems which can be made with these three substances. Binary and ternary systems which contained either two or three of the components used in this investigation have been studied at 760 (*2, 4, 7, 10, 12*) and 400 (*7, 11*) mm. of mercury.

The ternary system showed large deviations from ideal liquid phase behavior and a ternary azeotrope was located.

PURITY OF COMPOUNDS

The benzene and *n*-heptane, pure grade materials of 99 mole % minimum purity (Phillips Petroleum Co.), and ethyl alcohol (U. S. Industrial Chemical Co.) were not further purified. Physical constants appear in Table I.

EXPERIMENTAL

Vapor-liquid equilibrium data were obtained using a Braun still as described by Hipkin and Myers (*5*) and the experimental technique outlined by these authors and by Nielsen and Weber (*11*) was followed.

A Perkin-Elmer Fractometer, Model 154-B, was used to analyze the samples obtained from the equilibrium still. A 1-meter column packed with Perkin-Elmer's Type F (a Celite-base material with tetraethylene glycol dimethyl ether as the liquid phase) column material was used to separate the components. The Fractometer was operated at 50° C. and a detector voltage of 5.5 volts. The inlet pressure on the carrier gas, helium, was 8 p.s.i.g. Under these conditions a sample could be analyzed in 15 minutes.

Good sparation of the compounds was obtained with only a slight overlap between the benzene and ethyl alcohol peaks. The degree of overlap was much less than that which occurs for the *n*-heptane and benzene peaks when Perkin-Elmer's Type A or B packing material is used. The compositions reported in this work are believed accurate within ±0.5 mole %. Extensive calibration data were obtained and studied before reaching that conclusion.

VAPOR-LIQUID EQUILIBRIUM DATA

Liquid phase activity coefficients were calculated from

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

Table I. Properties of Pure Compounds

	Density, 25° C., G./Ml.	Refractive Index, 25° C.,	Boiling Point, ° C. 760 mm. Hg.	Boiling Point, ° C. 180 mm. Hg.
Ethyl alcohol				
Exptl.	0.7843	1.3592	78.3	45.8
Lit. (*3*)	0.78404	1.35914	78.33	45.81
Benzene				
Exptl.	0.8732	1.4977	80.0	39.6
Lit. (*1*)	0.87368	1.49790	80.103	39.62
n-Heptane				
Exptl.	0.6786	1.3851	98.4	56.0
Lit. (*1*)	0.67947	1.38517	98.428	55.98

In the derivation of Equation 1 the assumptions are made that the vapor phase forms an ideal solution and the ratio of f_v^0 to f_l^0 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 (*1, 3*) were used in the calculations.

The experimental data and the calculated activity coefficients are in Table II and Figures 1 to 5. Figure 1 is a bubble point diagram; Figures 2 to 4 show the relationship between the liquid phase composition and the activity coefficients for ethyl alcohol, benzene, and *n*-heptane, respectively; Figure 5 shows vapor-liquid equilibrium tie lines.

A minimum boiling ternary azeotrope was found at the following composition $x_{C_2H_5OH} = 0.331$, $x_{C_6H_6} = 0.646$, and $x_{nC_7H_{16}} = 0.023$. The azeotrope was located by first charging the still with the azeotropic mixture of ethyl alcohol and benzene, then adding a small amount of *n*-heptane. The temperature dropped less than 0.1° C. Samples of liquid and

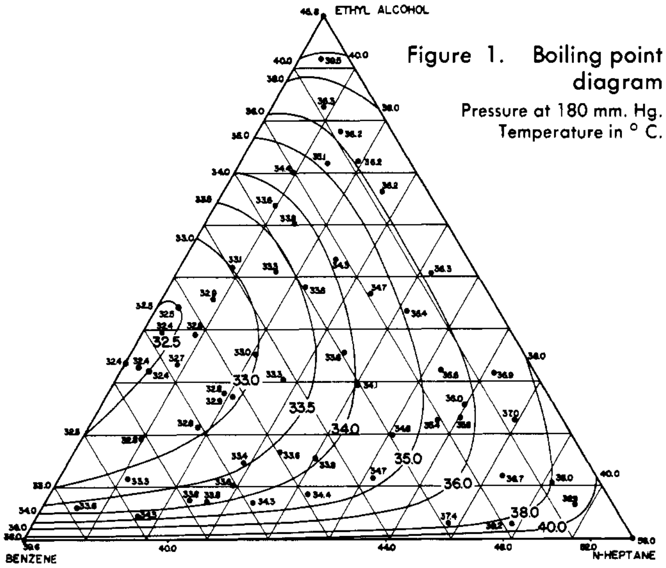

Figure 1. Boiling point diagram
Pressure at 180 mm. Hg.
Temperature in ° C.

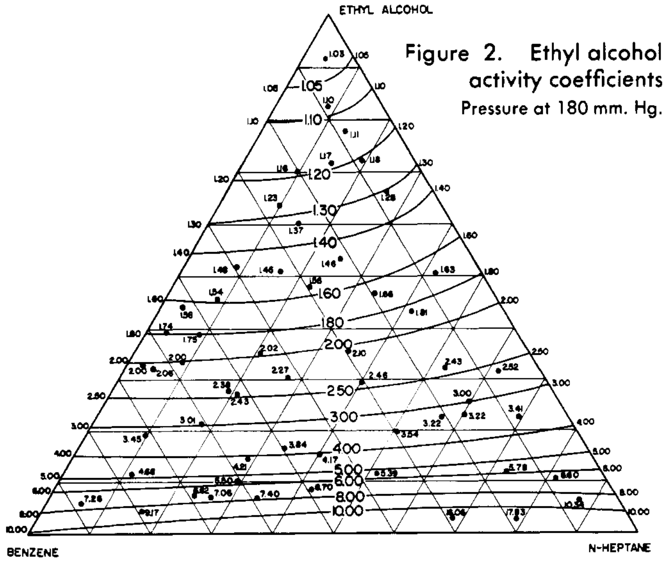

Figure 2. Ethyl alcohol activity coefficients
Pressure at 180 mm. Hg.

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Table II. Vapor-Liquid Equilibrium Data at 180 Mm. Mercury Pressure

Temp., °C.	Liquid Mole Fraction			Vapor Mole Fraction			Activity Coefficients		
	n-Heptane	Ethyl alcohol	Benzene	*n*-Heptane	Ethyl alcohol	Benzene	*n*-Heptane	Ethyl alcohol	Benzene
33.3	0.111	0.118	0.771	0.074	0.290	0.636	1.803	4.681	1.072
32.8	0.096	0.194	0.710	0.070	0.342	0.588	2.018	3.449	1.100
32.7	0.086	0.336	0.578	0.075	0.341	0.584	2.434	1.997	1.347
32.8	0.089	0.391	0.520	0.086	0.350	0.563	2.675	1.751	1.438
32.9	0.084	0.459	0.457	0.087	0.363	0.550	2.847	1.539	1.593
36.3	0.086	0.826	0.088	0.212	0.559	0.229	5.688	1.097	2.993
36.2	0.136	0.781	0.083	0.268	0.534	0.198	4.575	1.114	2.753
36.2	0.193	0.724	0.083	0.296	0.523	0.181	3.562	1.176	2.517
36.2	0.262	0.665	0.073	0.329	0.521	0.150	2.917	1.276	2.371
36.3	0.419	0.507	0.074	0.362	0.511	0.127	1.994	1.634	1.974
36.9	0.617	0.316	0.067	0.390	0.508	0.102	1.422	2.516	1.707
37.0	0.694	0.227	0.079	0.390	0.497	0.113	1.256	3.411	1.599
38.0	0.814	0.106	0.080	0.409	0.474	0.117	1.070	6.598	1.567
39.2	0.787	0.028	0.185	0.401	0.358	0.241	1.033	17.83	1.332
37.4	0.682	0.030	0.288	0.338	0.316	0.346	1.088	16.06	1.318
34.7	0.517	0.115	0.368	0.259	0.351	0.390	1.252	5.368	1.302
33.8	0.402	0.155	0.443	0.216	0.348	0.436	1.412	4.166	1.254
33.6	0.340	0.165	0.495	0.184	0.338	0.478	1.432	3.840	1.241
33.4	0.290	0.144	0.566	0.160	0.320	0.520	1.482	4.210	1.190
33.6	0.292	0.103	0.605	0.159	0.302	0.539	1.441	5.498	1.146
34.3	0.340	0.070	0.590	0.176	0.287	0.537	1.322	7.395	1.138
33.8	0.233	0.076	0.691	0.132	0.271	0.597	1.489	6.618	1.101
34.3	0.163	0.046	0.791	0.100	0.234	0.666	1.566	9.174	1.052
33.8	0.264	0.072	0.664	0.147	0.274	0.579	1.463	7.061	1.111
32.9	0.207	0.274	0.519	0.140	0.342	0.518	1.858	2.428	1.321
33.0	0.206	0.354	0.440	0.159	0.370	0.471	2.104	2.022	1.412
33.3	0.162	0.512	0.326	0.162	0.290	0.448	2.707	1.451	1.779
33.8	0.148	0.602	0.250	0.178	0.422	0.400	3.331	1.372	2.125
34.4	0.098	0.701	0.201	0.162	0.453	0.385	4.220	1.161	2.377
33.6	0.099	0.638	0.263	0.143	0.418	0.439	3.822	1.228	2.146
33.3	0.275	0.306	0.419	0.185	0.365	0.450	1.821	2.272	1.391
33.6	0.224	0.482	0.294	0.201	0.400	0.399	2.375	1.556	1.745
34.3	0.249	0.534	0.217	0.239	0.433	0.328	2.451	1.462	1.889
33.1	0.086	0.520	0.394	0.118	0.400	0.482	3.742	1.481	1.607
34.7	0.338	0.469	0.193	0.277	0.443	0.280	2.049	1.663	1.783
35.4	0.415	0.435	0.150	0.314	0.464	0.222	1.828	1.807	1.764
35.6	0.525	0.323	0.152	0.330	0.467	0.203	1.498	2.433	1.582
36.0	0.598	0.256	0.146	0.341	0.465	0.194	1.332	2.999	1.548
33.6	0.056	0.062	0.882	0.043	0.240	0.717	2.032	7.258	1.045
35.8	0.603	0.231	0.166	0.342	0.446	0.212	3.218	2.292	1.498
36.7	0.726	0.119	0.155	0.363	0.434	0.203	1.132	5.784	1.482
35.4	0.567	0.227	0.206	0.316	0.430	0.254	1.346	3.216	1.470
35.1	0.145	0.718	0.137	0.235	0.487	0.278	3.970	1.174	2.451
34.6	0.506	0.199	0.295	0.271	0.397	0.332	1.339	3.538	1.387
34.1	0.404	0.293	0.303	0.245	0.395	0.360	1.559	2.463	1.495
33.6	0.350	0.357	0.293	0.241	0.401	0.358	1.822	2.105	1.571
38.9	0.872	0.062	0.066	0.450	0.454	0.096	1.055	10.34	1.500
39.5	0.037	0.918	0.045	0.158	0.690	0.152	8.492	1.030	3.397
32.8	0.191	0.280	0.529	0.134	0.341	0.525	1.943	2.383	1.318
32.8	0.179	0.214	0.607	0.118	0.329	0.553	1.826	3.008	1.210
32.4	0.032	0.396	0.572	0.035	0.344	0.621	3.112	1.737	1.470
34.4	0.424	0.085	0.491	0.207	0.317	0.476	1.246	6.699	1.203
32.4	0.023	0.331	0.646	0.023	0.332	0.645	2.933	2.005	1.349
32.5	0.036	0.443	0.521	0.042	0.353	0.605	3.278	1.583	1.564
32.4	0.045	0.324	0.631	0.043	0.334	0.623	2.705	2.059	1.336

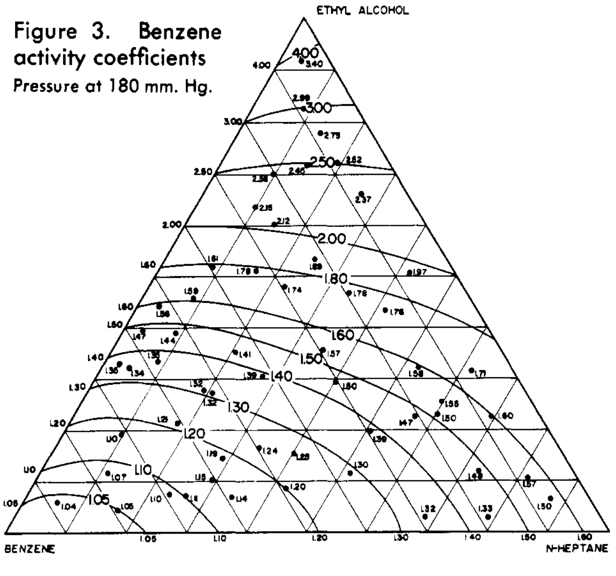


Figure 3. Benzene activity coefficients
Pressure at 180 mm. Hg.

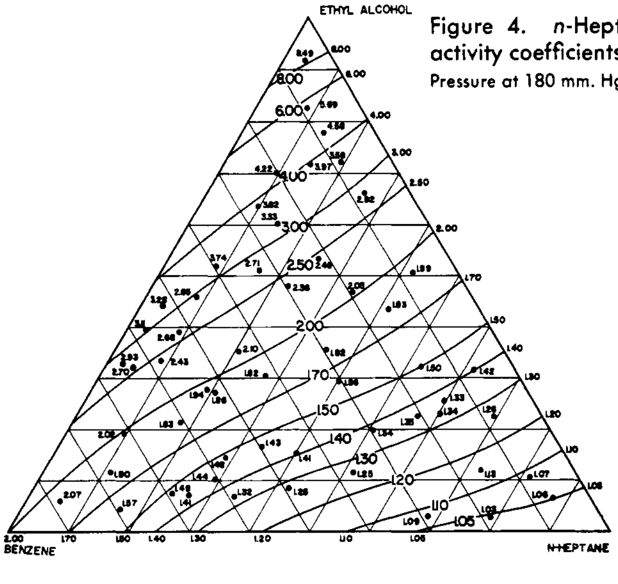
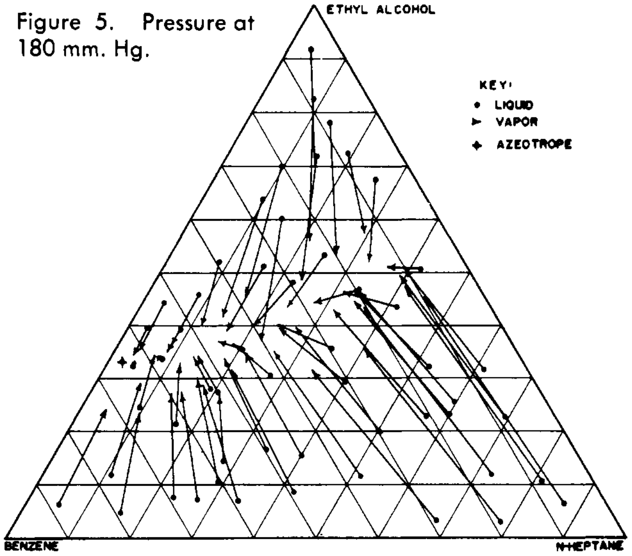


Figure 4. *n*-Heptane activity coefficients
Pressure at 180 mm. Hg.

Figure 5. Pressure at 180 mm. Hg.



vapor, analyzed after equilibration, were identical within the degree of accuracy of the procedure. The estimated temperature of the azeotrope is 32.38° C.

The experimental data were checked for internal consistency by the method of Krishnamurty and Rao (*8*, *9*), previously discussed (*11*, *12*). The basic equations are

$$\Delta G^{E}/2.3RT = Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \qquad (2)$$

At a constant value of x_3

$$dQ/dx_1 = \log (\gamma_1/\gamma_2) \qquad (3)$$

$$\int_{Q'}^{Q''} dQ = \int_{x_1 \geqq 0 = x_1'}^{x_1 \leqq (1 - x_3) = x_1''} \log \left(\frac{\gamma_1}{\gamma_2} \right) dx_1 \qquad (4)$$

Equations 3 and 4 apply rigorously only at conditions of constant temperature and pressure, since the Gibbs-Duhem relationship was used in their development. By the definition of the terms, similar restrictions apply to Equation 2.

Nine checks for internal consistency were made; constant mole per cents of 10, 30, and 50 for each of three substances were used. In some instances the values of the two members of Equation 4 were small; consequently, the differences between the two members of this equation are reported as percentages which are defined by the following relationship

$$\%\ \text{diff.}\ \frac{\left[Q'' - Q' \right] - \int_{x_1 \geqq 0 = x_1'}^{x_1 \leqq (1 - x_3) = x_1''} \log \left(\frac{\gamma_1}{\gamma_2} \right) dx_1}{\Sigma'} \qquad (5)$$

where Σ' is the total area enclosed by the zero abscissa and a plot of $\log \gamma_1/\gamma_2$ *vs.* x_1. The results of the internal consistency checks are shown in Table III.

Those consistency checks which cover a small temperature range and show a minimum temperature lower than either of the terminal temperatures seem to be good, while the other checks are rather poor. There are three explanations for the apparent poor results. First, the intersections of the activity coefficient and compositions parameters were not distinct, particularly for the checks performed at constant compositions of ethyl alcohol. Second, the magnitude of the terms involved were approximately one half to one quarter those involved in the former. Hence, differences of the same order of magnitude tend to appear much larger in the poor checks.

The percentage differences in the last four checks appear much larger than those in the former five because (*6*) the correct form of the Gibbs-Duhem equation to use for a consistency check of isobaric vapor-liquid equilibrium data is

$$\frac{\partial \ln \gamma_1}{\partial \ln x_1} - \frac{\partial \ln \gamma_2}{d \ln (1 - x_1)} = \frac{\Delta H}{RT^2} \frac{dT}{dx} \qquad (6)$$

Table III. Results of Consistency Check

	n-Heptane	Benzene	Ethyl Alcohol
		10 Mole %	
% diff., Eq. 5	1.4	0.5	21.1
Temp. range, ° C.	34.0-39.0	37.7-39.2	33.0-41.0
Min. temp., ° C.	32.6	35.8	...
		30 Mole %	
% diff., Eq. 5	0.0	4.1	36.9
Temp. range, ° C.	35.0-37.0	34.0-35.6	32.3-38.2
Min. temp., ° C.	33.3	33.5	...
		50 Mole %	
% diff., Eq. 5	5.3	14.2	29.6
Temp., range, ° C.	35.8-37.5	32.6-35.0	32.7-37.5
Min. temp., ° C.	34.5	...	...

Although Equation 6 was developed for a binary system, an analogous relationship would hold for a ternary system. While ΔH may be essentially constant over a short range of temperatures, it is not equal to zero. The quantity dT/dx is not constant (Figure 1). For a true consistency check the right-hand member of Equation 6 should not be neglected.

On the five consistency checks with good results, the minimum temperature was not at either of the terminal conditions, indicating that dT/dx changes sign over the range of compositions. The magnitude of the left member of Equation 6 would tend to be smaller than it would where the minimum temperature existed at one of the terminal conditions. A final conclusion concerning the internal consistency of the data is impossible.

NOMENCLATURE

ΔG^E = excess molal free energy at mixing
ΔH = molal ideal heat of vaporization—i.e., heat required to vaporize 1 mole of solution, when pressure of obtained vapor is sufficiently low for ideal gas laws to be valid
P = total pressure, mm. of mercury
P_v = vapor pressure, mm. of mercury
R = gas law constant, consistent units
T = absolute temperature, ° K.
Q = defined by Equation 2
f^0 = fugacity of a pure component in standard state at temperature and pressure of system
t = temperature, ° C.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = liquid phase activity coefficient

Subscripts

l = liquid phase
v = vapor phase
1, 2, 3 = components in ternary mixture

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