

# Ternary Vapor-Liquid Equilibria for the System Benzene-*n*-Heptane-1-Propanol at 75° C.

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Vapor-liquid equilibrium data were determined at 75° C. for the ternary system benzene-*n*-heptane-1-propanol, using a modified Gillespie still. Liquid activity coefficient values were evaluated for the three components and the thermodynamic consistency of the data was tested.

VAPOR-LIQUID equilibrium compositions for the binary mixtures of benzene, *n*-heptane, and 1-propanol at 75° C. have been reported (6). In this investigation, vapor-liquid equilibrium data for the ternary system benzene-*n*-heptane-1-propanol were measured at the same temperature, using a modified Gillespie still.

## EXPERIMENTAL

The physical properties of the chemicals used in this investigation are listed in Table I. The spectrograde benzene

Table I. Physical Properties of the Materials

	Normal Boiling Point, ° C.		Refractive Index, 25° C.	
	Exptl.	Lit.	Exptl.	Lit.
Benzene	80.1	80.103(5)	1.4979	1.4979(5)
<i>n</i> -Heptane	98.4	98.43 (5)	1.3852	1.3852(5)
1-Propanol	97.2	97.29 (5)	1.3834	1.3833(3)

Table II. Experimental Vapor-Liquid Equilibrium Data for

No.	Temp., ° C.	Total Pressure, Mm. Hg	Liquid Mole Fraction		Vapor Mole Fraction		Liquid Activity Coefficients		
			$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1$	$\gamma_2$	$\gamma_3$
1	75.00	649.4	0.627	0.319	0.677	0.223	1.08	1.23	3.92
2	75.03	607.0	0.430	0.509	0.521	0.342	1.14	1.11	4.43
3	75.00	683.1	0.732	0.197	0.728	0.153	1.05	1.43	3.72
4	75.00	569.8	0.260	0.663	0.313	0.498	1.06	1.16	4.63
5	75.00	546.8	0.173	0.738	0.276	0.500	1.35	1.01	4.54
6	75.00	681.3	0.625	0.284	0.644	0.200	1.07	1.29	3.80
7	74.95	590.6	0.257	0.647	0.344	0.432	1.22	1.07	4.48
8	74.98	646.5	0.444	0.448	0.492	0.290	1.10	1.13	4.26
9	74.91	702.5	0.761	0.114	0.756	0.832	1.07	1.38	2.94
10	74.92	697.6	0.705	0.169	0.666	0.144	1.01	1.60	3.44
11	75.00	627.4	0.354	0.515	0.405	0.344	1.11	1.13	3.92
12	75.03	704.1	0.813	0.055	0.748	0.049	1.00	1.67	3.52
13	74.98	579.2	0.185	0.668	0.223	0.484	1.08	1.14	3.78
14	75.12	601.0	0.230	0.615	0.320	0.398	1.30	1.05	3.58
15	75.00	701.5	0.660	0.181	0.662	0.142	1.08	1.48	2.81
16	75.00	564.2	0.142	0.692	0.193	0.625	1.19	1.39	2.02
17	75.00	653.4	0.408	0.425	0.464	0.301	1.14	1.25	2.99
18	75.00	646.7	0.382	0.449	0.447	0.313	1.17	1.22	3.00
19	74.95	693.4	0.606	0.225	0.570	0.160	1.00	1.32	3.60
20	74.90	577.5	0.185	0.639	0.238	0.448	1.15	1.10	3.38
21	75.00	676.9	0.492	0.330	0.542	0.239	1.15	1.32	2.72
22	74.97	635.0	0.306	0.503	0.378	0.353	1.21	1.19	2.93
23	75.08	713.2	0.664	0.129	0.664	0.109	1.10	1.62	2.54
24	75.05	677.2	0.473	0.318	0.535	0.238	1.18	1.37	2.38
25	74.98	606.5	0.231	0.556	0.282	0.433	1.14	1.30	2.66
26	75.09	587.5	0.159	0.628	0.223	0.462	1.28	1.18	2.83
27	74.98	554.6	0.071	0.710	0.080	0.596	0.98	1.27	2.67
28	75.00	691.1	0.534	0.246	0.577	0.191	1.15	1.44	2.36
29	74.90	676.4	0.469	0.305	0.519	0.228	1.15	1.37	2.46
30	75.00	689.4	0.520	0.254	0.556	0.200	1.14	1.47	2.41
31	74.97	703.9	0.585	0.156	0.607	0.134	1.12	1.63	2.29
32	74.93	709.4	0.581	0.157	0.622	0.134	1.17	1.63	2.15
33	74.99	587.5	0.134	0.603	0.196	0.481	1.33	1.27	2.37
34	74.93	659.4	0.366	0.359	0.443	0.275	1.23	1.36	2.20
35	75.00	705.6	0.594	0.120	0.647	0.110	1.18	1.74	1.95
36	74.93	582.6	0.112	0.600	0.170	0.483	1.36	1.28	2.30
37	75.01	677.0	0.420	0.290	0.500	0.235	1.24	1.48	2.01
38	75.04	561.0	0.066	0.644	0.097	0.551	1.28	1.31	2.23
39	75.00	640.0	0.308	0.393	0.354	0.326	1.13	1.44	2.24

and *n*-heptane (Matheson, Coleman and Bell Co.) were used without further purification. The 1-propanol, from the same company with a boiling range of 96–8°C., was fractionated in an adiabatically operated packed column at a reflux ratio of 50 to 1. Only the middle portion of the distillate was used in this investigation. Refractive index of the pure components was measured with a Bausch and Lomb Abbé-3L precision refractometer at 25°C.

The description of the modified Gillespie still and the experimental technique used in this study have been reported previously (11). The temperature was controlled at 75 ± 0.1°C. by adjusting the total pressure of the still and measured by means of a calibrated copper-constantan thermocouple in connection with a Leeds and Northrup K-3 potentiometer. The temperature measurements are believed to be accurate within ±0.05°C. A vacuum system connected to the vapor condenser line was used to regulate the total pressure, which was measured by a mercury manometer.

Equilibrium liquid and condensed vapor samples were analyzed chromatographically by means of a Perkin-Elmer Model 154 C Vapor Fractometer. Calibrations and determinations of unknowns were carried out using two 2-meter "W" columns with helium as the carrier gas. The Vapor Fractometer was operated at 104°C., 27 p.s.i.g. column pressure, and a bridge voltage of 8 volts. Under these conditions and at a helium flow rate of 73 ml. per minute, an analysis of a ternary sample could be completed in 23 minutes. The peaks were well spaced and completely

separated. The calibration curves used in this investigation are shown in Figure 1. The reproducibility obtained in the calibration was better than ±0.005 mole fraction, and the error in the reported equilibrium compositions is of the same magnitude.

## RESULTS

The experimental total pressure-composition data are listed in Table II. The total pressure-liquid composition diagram is shown in Figure 2. The contours indicate no maximum total pressure value within the triangular diagram, and no ternary azeotrope was detected experimentally in this study.

The liquid activity coefficient values were evaluated from a well-known equation (4)

$$\log \gamma_i = \log \frac{y_i P}{x_i p_i} + \frac{(P - p_i)(\beta_i - v_i)}{2.303 RT} \quad (1)$$

in which the vapor phase is assumed to be an ideal solution but not an ideal gas. The departure of the vapor phase from the ideal gas behavior is represented by the second term on the right hand side of Equation 1. In all cases, the departure was about 2.5% or less. In the calculation, vapor pressures of the pure components were taken from the literature (1, 5). The second virial coefficient,  $\beta_i$ , of 1-propanol was calculated according to the equation given by Keyes, Smith, and Gerry (7). Values of  $\beta_i$  for benzene

Benzene (1)-*n*-Heptane (2)-1-Propanol (3) System at 75°C.

No.	Temp., °C.	Total Pressure, Mm. Hg	Liquid Mole Fraction		Vapor Mole Fraction		Liquid Activity Coefficients		
			$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1$	$\gamma_2$	$\gamma_3$
40	75.00	711.1	0.617	0.074	0.675	0.072	1.20	1.87	1.89
41	75.04	687.6	0.469	0.203	0.533	0.181	1.20	1.66	1.95
42	75.00	646.7	0.310	0.357	0.395	0.304	1.27	1.49	1.90
43	75.01	653.8	0.323	0.337	0.413	0.299	1.29	1.57	1.80
44	75.00	617.8	0.218	0.440	0.300	0.357	1.31	1.36	2.03
45	75.05	696.9	0.499	0.142	0.587	0.138	1.26	1.82	1.74
46	74.89	595.6	0.113	0.510	0.210	0.407	1.71	1.29	1.98
47	74.90	630.1	0.245	0.363	0.339	0.344	1.35	1.62	1.67
48	74.92	603.0	0.147	0.449	0.239	0.417	1.52	1.55	1.68
49	74.87	665.3	0.382	0.197	0.502	0.203	1.35	1.85	1.52
50	75.05	668.8	0.348	0.228	0.461	0.221	1.37	1.75	1.64
51	75.00	676.0	0.393	0.179	0.517	0.184	1.37	1.87	1.54
52	75.30	652.4	0.280	0.272	0.393	0.274	1.41	1.78	1.58
53	75.00	590.1	0.097	0.452	0.168	0.457	1.58	1.62	1.60
54	74.98	684.6	0.420	0.111	0.557	0.131	1.40	2.18	1.48
55	75.00	670.6	0.328	0.196	0.587	0.138	1.85	1.27	1.26
56	74.90	559.9	0.039	0.481	0.090	0.503	1.85	1.59	1.55
57	74.99	648.0	0.295	0.208	0.439	0.232	1.49	1.96	1.40
58	75.00	622.6	0.203	0.296	0.303	0.313	1.43	1.78	1.56
59	75.06	675.7	0.418	0.061	0.623	0.079	1.55	2.36	1.26
60	74.87	588.5	0.133	0.322	0.216	0.383	1.48	1.90	1.42
61	75.03	658.4	0.330	0.120	0.509	0.163	1.57	2.41	1.28
62	75.11	622.0	0.201	0.239	0.331	0.308	1.59	2.17	1.31
63	75.02	593.4	0.139	0.238	0.269	0.330	1.78	2.23	1.25
64	75.03	550.0	0.093	0.271	0.211	0.413	1.97	2.28	1.06
65	75.00	615.6	0.210	0.145	0.395	0.225	1.79	2.60	1.18
66	75.08	622.2	0.229	0.111	0.433	0.187	1.82	2.84	1.17
67	75.07	564.7	0.117	0.213	0.244	0.304	1.82	2.19	1.25
68	75.04	591.4	0.152	0.169	0.313	0.276	1.89	2.62	1.17
69	75.00	557.2	0.055	0.265	0.124	0.430	1.95	2.46	1.20
70	75.01	616.1	0.241	0.060	0.482	0.120	1.90	3.35	1.13
71	74.98	596.6	0.247	0.032	0.525	0.066	1.96	3.34	1.11
72	75.07	581.0	0.159	0.110	0.351	0.211	1.99	3.04	1.14
73	74.97	617.1	0.202	0.052	0.472	0.127	2.23	4.10	1.08
74	75.02	513.0	0.055	0.177	0.161	0.360	2.02	2.49	1.10
75	75.00	507.9	0.074	0.085	0.229	0.239	2.44	3.90	1.06
76	75.00	507.9	0.076	0.083	0.225	0.231	2.34	4.03	1.07
77	75.05	461.5	0.028	0.088	0.099	0.283	2.73	4.06	1.06
78	75.00	450.3	0.061	0.032	0.231	0.127	2.63	4.86	1.05

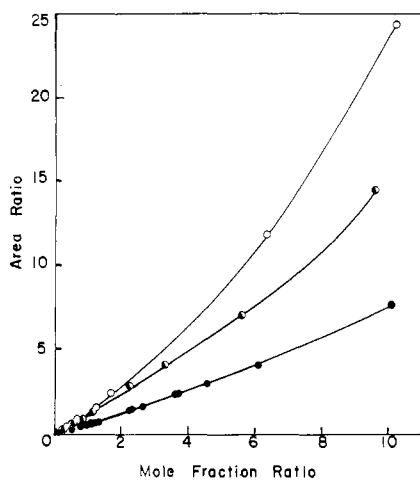


Figure 1. Calibration curves for the ternary system

- n-Heptane-benzene
- Benzene-1-propanol
- 1-Propanol-n-heptane

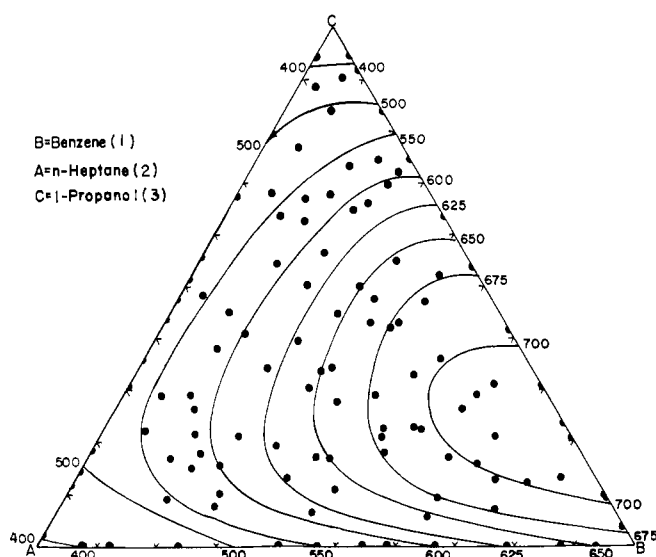


Figure 2. Total pressure-liquid composition diagram for the system benzene (1)-n-heptane (2)-1-propanol (3) at 75°C.—pressure in mm. of Hg

and *n*-heptane were obtained by interpolating the values reported by Brown and Ewald (2). Liquid molal volume values of the pure components,  $v_i$ , were taken from Timmermanns' compilation (10). The calculated  $\gamma_i$  values are also listed in Table II.

The thermodynamic consistency of the data was first tested by the numerical integration method of Li and Lu (8), and when a set of data indicated large deviations, experimental points were then examined by the method of McDermott and Ellis (9). Within the experimental error of the reported equilibrium compositions ( $\pm 0.005$  mole fraction), allowed deviations by the latter method vary considerably with the liquid compositions and are larger in the low 1-propanol concentration regions. For any pair of points, when the calculated deviation was greater than

the allowed deviation and the distance between the two points was less than 0.08 mole fraction for any one of the components, the two points were treated again by new combinations with nearby experimental points. As the allowed deviations depend on the distance apart of the points, the distance of 0.08 mole fraction was arbitrarily chosen. Less consistent points were then singled out. As a result, runs 19, 20, 55, 59, 64, and 74 are considered inconsistent, and the remaining 72 experimental points are considered consistent.

When liquid activity coefficient values obtained in this investigation are examined with the values reported for the three binaries at 75°C. (6), at constant liquid benzene concentrations, the  $\gamma$  value of benzene increases with the increase of the liquid 1-propanol concentration; at constant liquid *n*-heptane concentrations, the  $\gamma$  value of *n*-heptane increases with the increase of the liquid 1-propanol concentration; and at constant liquid concentrations of 1-propanol, the  $\gamma$  value of 1-propanol generally decreases with the increase of the liquid benzene concentration.

## NOMENCLATURE

- $P$  = total pressure
- $p$  = vapor pressure of pure component
- $R$  = gas constant
- $T$  = absolute temperature
- $v$  = liquid molal volume of pure component
- $x$  = liquid mole fraction
- $y$  = vapor mole fraction
- $\beta$  = second virial coefficient of pure component in the vapor phase
- $\gamma$  = liquid activity coefficient

## Subscripts

1, 2, 3,  $i$  = components

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