Vapor-Liquid Equilibria at Atmospheric Pressure

I. 1-Butanol–Toluene System

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Vapor-liquid equilibrium values have been determined at atmospheric pressure for the 1-butanol–toluene system, using a modified Gillespie still. Experimental data meet the thermodynamic requirements of the Gibbs-Duhem equation. An azeotrope has been found at a 0.678 mole fraction toluene with a minimum boiling point of 105.5° C. The binary constants for van Laar equation have been determined.

PHASE EQUILIBRIUM of normal alcohols with aromatic hydrocarbons is important in studying the possible hydrocarbon-nonhydrocarbon relationships and extractive distillation of hydrocarbons. In the literature (*1, 5, 10*) azeotrope compositions for 1-butanol–toluene system have been reported. Discrepancies in these values exist, and no information is available as to either the method of determination or the purity of the materials used by the original investigators. Vapor-liquid equilibrium data at a pressure of 760 mm. of Hg were determined for the 1-butanol-toulene system. The experimental results are given in Table I, and the temperature composition and x-y curves are shown in Figure 1 and 2 respectively. The activity coefficients (Figure 3) were calculated from the equation $\gamma = (y\pi/xP!)P^\circ$ was calculated for different temperatures from the following equations:

$$\text{Toluene } (11)\text{: } \log_{10}P^\circ \text{ mm.} = 6.95508 - \frac{1345.087}{219.516 + t}$$

$$\text{1-Butanol } (12)\text{: } \log_{10}P^\circ \text{ mm.} = 8.19659 - \frac{1781.719}{217.675 + t}$$

The composition of the minimum boiling type azeotrope as determined from experimental data, using Litvinov's method (*6*), is 0.678 mole fraction toluene at a temperature of 105.5° C. Comparison of this with previous results is shown in Table II.

EXPERIMENTAL

The C.P. grade chemicals used were redistilled over CaO, Mg turnings, and activated alumina in turn and middle cuts used. The distillates used in the equilibrium still had boilings ranges of not more than 0.03° C. The physical constants of the material used are given in Table III.

Analysis of samples. Binary compositions were determined from refractive indices at 25° C., using a Zeiss-Abbe refractometer, reading to four decimal places, and giving an accuracy of analysis of ±0.1 mole %. Alternate chemical methods of analysis were less accurate than the refractive index procedures. Refractive index readings were taken on samples with sufficient time allowed for the sample to come to thermal equilibrium at 25° C. These were also checked before and after the 2 hr. refluxing period to make sure that additional components were not formed.

Table I. Experimental Data for 1-Butanol–toluene at 760 Mm. Hg.

Temp., ° C.	x_1	y_1	$y_{1\text{ calcd.}}$	γ_1	γ_2
117.70	0	0	0	. . .	1.000
116.05	0.028	0.075	0.077	2.333	1.004
112.90	0.096	0.221	0.228	2.159	1.022
110.50	0.165	0.321	0.329	1.952	1.056
109.00	0.227	0.399	0.404	1.841	1.069
107.60	0.318	0.487	0.486	1.670	1.092
106.40	0.415	0.554	0.549	1.508	1.159
106.00	0.487	0.595	0.590	1.396	1.220
105.80	0.532	0.617	0.612	1.333	1.274
105.70	0.558	0.627	0.624	1.295	1.317
105.60	0.614	0.653	0.650	1.230	1.411
105.50	0.668	0.675	0.673	1.172	1.542
105.50	0.675	0.676	0.676	1.161	1.571
105.50	0.701	0.687	0.688	1.136	1.649
105.60	0.766	0.720	0.720	1.087	1.878
106.30	0.859	0.784	0.784	1.034	2.338
106.50	0.871	0.794	0.795	1.027	2.419
108.10	0.948	0.894	0.879	1.010	2.956
110.60	1.000	1.000	1.000	1.000	. . .

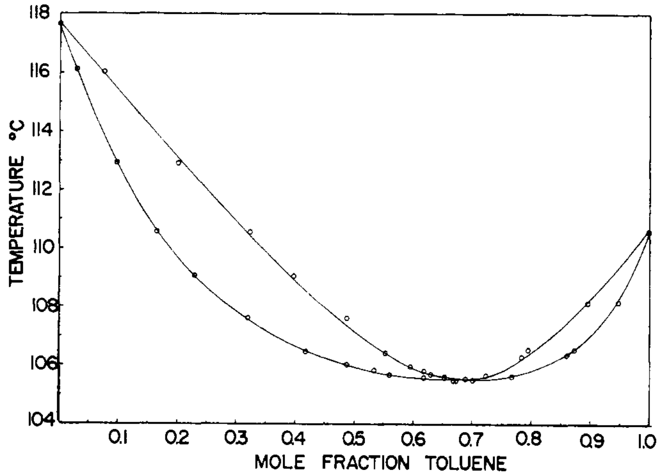

Figure 1. Temperature-composition curves for 1-butanol–toluene system

Equilibrium still and temperature measurements. A Fowler (*3*) modified Gillespie (*4*) still, with very minor changes involving the slight reduction of the volume of the condensate trap, was used for obtaining the liquid and vapor

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Table II. Properties of Pure Compounds

Compound	n_D^{25}		B.P. at 760 Mm. Hg, ° C.		D, Gms./Ml. at 25° C.	
	Exptl.	Lit. (*13*)	Exptl.	Lit. (*13*)	Exptl.	Lit. (*13*)
Toluene	1.4939	1.49405	110.6	110.623	0.8614	0.8662
1-Butanol	1.3974	1.3970	117.7	117.726	0.8056	0.80567

samples. The pressure was controlled on the system manually with a Hg reservoir to within 1 mm. of Hg. All runs were of a minimum duration of 2 hrs., which was the time required to attain equilibrium. Temperatures were measured with a special thermometer covering the required range, which was accurate to within ±0.05° C. and was calibrated against a resistance thermometer with a National Bureau of Standards Certification.

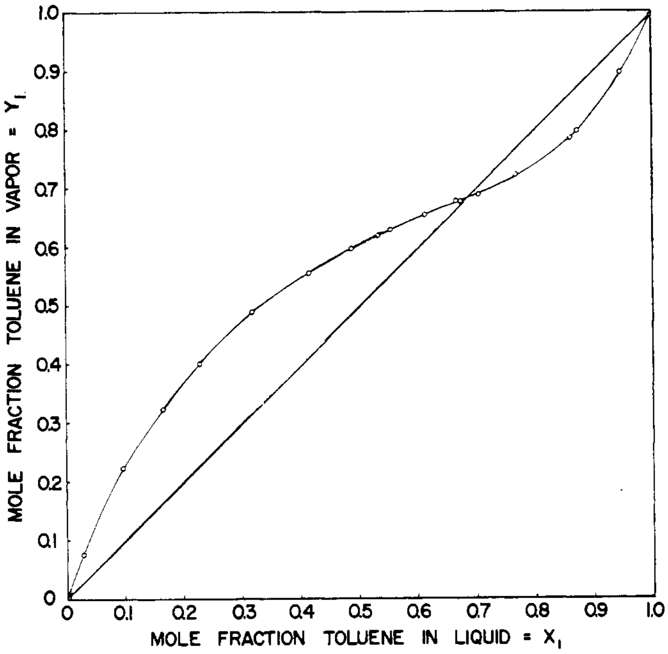

Figure 2. Vapor liquid equilibrium curve for 1-butanol–toluene system

Table III. Azeotrope Compositions

Composition, Mol % Toluene	Boiling Point, 760 Mm. Hg.	Reference
67.5	105.5	(*1, 5*)
67.4	105.5	(*8*)
72.4	105.7	(*7*)
67.8	105.5	Present investigation

THERMODYNAMIC CONSISTENCY

The experimentally determined values of γ and y are in general agreement with the thermodynamically correct values as shown by van Laar equation curve, within the limits of accuracy of the analytical procedure. The values of A and B for van Laar equation curves were obtained as 0.38969 and 0.55954, by determining A and B as terminal values of log γ_1 at $x_1 = 0$, and log γ_2 at $x_2 = 0$, and from azeotrope composition, using the Carlson-Colburn relationships (*2*):

$$\log \gamma_1 = \frac{Ax_1^2}{\left(\frac{A}{B}\, x_1 + x_2\right)^2} \text{ and } \log \gamma_2 = \frac{Bx_1^2}{\left(x_1 + \frac{B}{A}\, x_2\right)^2}$$

Values of y_1 were calculated based on these A and B, and are given in Table I as y_{calcd}. The maximum percentage deviation between $y_{\text{exptl.}}$ and $y_{\text{calcd.}} = (100\ \Delta y / y_{1\,\text{exptl.}})$ is less than 3%. Plots of log (γ_1/γ_2) *vs.* x_1 in accordance with Redlich and Kister equation (*9*) showed variation in net area under the curve of less than 3%, which is probably due to the fact that the temperature correction is not made in the integrated plots.

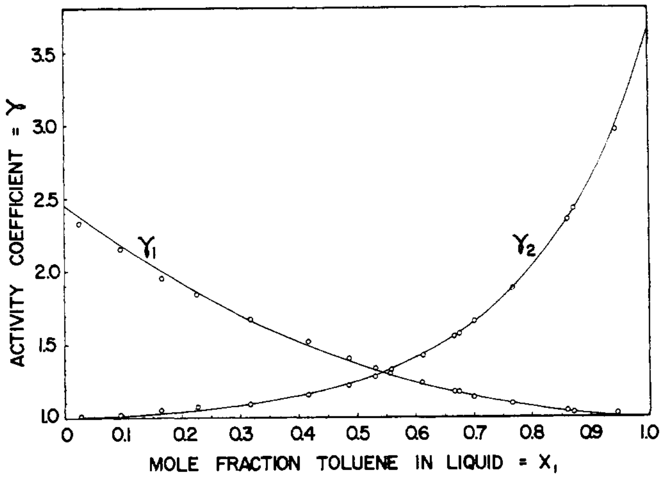

Figure 3. Activity coefficient-composition curve for 1-butanol–toluene system

NOMENCLATURE

A and B = constants in van Laar equation
P° = vapor pressure, mm.
x = mole fraction liquid phase
y = mole fraction in vapor phase
γ = activity coefficient
π = total pressure
t = temperature ° C.

Subscripts

1 = toluene
2 = 1-butanol

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