Vapor-Liquid Equilibria

Systems *p*-Xylene–Furfural and Ethylbenzene-Furfural

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Vapor-liquid equilibrium data are reported for the binary systems ethylbenzene-furfural and *p*-xylene–furfural at 723 mm of Hg pressure. Both the systems formed minimum boiling azeotropes. The activity coefficients were calculated, taking into consideration the vapor phase nonideality, tested for thermodynamic consistency, and correlated by Wilson's equation.

The present investigation forms part of a continuing experimental program on the separation of close-boiling C_8 aromatic mixtures. Vapor-liquid equilibrium data have been obtained for the systems ethylbenzene-furfural and *p*-xylene–furfural, at 723 mm of Hg pressure.

EXPERIMENTAL

Materials. *p*-Xylene and furfural, C.P. grade, obtained from Riedel-De Haen AG, Seelze-Hannover, Germany and ethylbenzene, L.R. grade, obtained from British Drug Houses, Ltd., Poole, England, were dried over silica gel and further purified by distillation in a 30-mm glass column packed with 3-mm ceramic insulation beads to a height of 1 meter. The column was run at total reflux for 30 minutes and the low boiling impurities were drawn off at a very low rate as rejects. When the desired boiling temperature was reached and remained constant for 15 minutes, the fraction was collected, while the column was operated at nearly total reflux. Table I lists the physical properties of the materials used.

Apparatus and Analytical Procedures. A recirculation type of equilibrium still described by Jones *et al.* (*12*), with the addition of an entrainment trap above the boiler, was used to obtain the equilibrium vapor and liquid samples. The still was operated for 3 hours after recirculation was stabilized. An enclosed-type mercury-in-glass thermometer with an accuracy of ±0.1° C, certified by the National Physical Laboratory, was used for temperature measurements. No pressure control device was used to maintain the system pressure, as the experimental runs were made at atmospheric pressure, which remained constant at 723 mm of Hg with a maximum deviation of 1.5 mm of Hg. The atmospheric pressure was measured by a standard mercury barometer with an accuracy of ±0.1 mm.

The mixtures were analyzed by the density method, using specific gravity bottles calibrated with distilled water. A constant temperature bath with a mercury-to-mercury thermoregulator made by the Precision Scientific Co., Chicago, Ill., was used to maintain the samples at a temperature of 35° ± 0.1° C. The samples were kept in the bath for a minimum of 30 minutes before being filled into the specific gravity bottles. Density was measured with an accuracy of ±0.0002. Freshly distilled furfural was used in all the experimental determinations to avoid oxidation and polymerization. Table II gives the density-composition data for the mixtures. Figures 1 and 2 represent the boiling point–composition diagrams for the two binaries, *p*-xylene–furfural and ethylbenzene-furfural, respectively. Minimum boiling azeotropes formed for both systems. Table III gives the experimental and literature (*11*) azeotropic data.

RESULTS AND DISCUSSION

The liquid phase activity coefficients were calculated from the experimental data, using the equation (*9*)

$$\gamma_i = \frac{\overline{\Lambda} y_i}{P_i^\circ x_i} \exp\left[\frac{(P_i^\circ - \overline{\Lambda})(V_i - \beta_i)}{RT} \right] \tag{1}$$

The Riedel-Plank-Miller equation (*16*) was used to represent the vapor pressure data for the pure compounds. It gave the following maximum errors when compared with the literature data (*1, 15*) over the temperature ranges for the systems:

Compound	Max. % Error, $(P^\circ_{\text{exptl}} - P^\circ_{\text{calcd}})100/P^\circ_{\text{exptl}}$	Source of Data (Ref.)
p-Xylene	−0.115	(*1*)
Ethylbenzene	+0.029	(*1*)
Furfural	+4.506	(*15*)

The gas phase second virial coefficients for ethylbenzene and *p*-xylene were estimated by the Pitzer and Curl correlation (*20*) and for furfural by the O'Connell correlation (*18*), using the parameters reported by Prausnitz *et al.* (*21*). Liquid molal volumes were estimated by the Lydersen-Greenkorn-Hougen correlation, as represented by Wick's equation (*24*).

The activity coefficient data satisfied Herington's consistency criterion (*10*). Black (*2*) and Norrish-Twigg (*17*) tests were applied to the experimental activity coefficient and temperature-composition data. The latent heats of vaporization needed in applying the Norrish-Twigg test were calculated by Watson's correlation (*23*), using latent

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Table I. Physical Properties of Materials

	Furfural	Ethylbenzene	*p*-Xylene
Molecular weight	96.08	106.16	106.16
Normal b.p., ° C	161.7 (*8, 13*)	136.186 (*7*)	138.351 (*7*)
Constants in Riedel-Plank-Miller equation			
G	1.6869[a]	1.6175[a]	1.6355[a]
k	0.5607[a]	0.5447[a]	0.5555[a]
Refractive index at 35° C			
Experimental	1.5185	1.4885	1.4886
Literature	1.5182[b] (*6, 7*)	1.4878[b] (*6, 7*)	1.4878[b] (*6, 7*)
Density at 35° C			
Experimental	1.1561	0.8548	0.8481
Literature	1.1441[c] (*13*)	0.8538[b] (*5*)	0.8480[b] (*5*)
Heat of vaporization at normal boiling point, cal/g	107.51 (*14*)	81.08 (*14*)	81.03 (*14*)

[a] Estimated. [b] Literature values corrected to 35° C. [c] Estimated using Li's equation (*13*).

Table II. Density-Composition Data at 35° C

Ethylbenzene-Furfural System		*p*-Xylene–Furfural System	
Mole % ethylbenzene	Density	Mole % *p*-xylene	Density
0.00	1.1561	0.00	1.1561
3.51	1.1410	3.49	1.1400
7.13	1.1220	6.96	1.1790
10.77	1.1100	10.66	1.1060
14.69	1.0960	14.75	1.0950
18.53	1.0820	18.24	1.0810
22.49	1.0730	22.20	1.0650
22.28	1.0480	26.32	1.0490
31.21	1.0390	30.80	1.0380
35.50	1.0230	35.12	1.0180
40.53	1.0080	40.09	1.0070
43.50	1.0010	45.27	0.9984
50.65	0.9783	49.63	0.9770
55.12	0.9663	55.73	0.9603
59.43	0.9548	60.80	0.9454
68.98	0.9348	66.28	0.9326
72.77	0.9210	72.81	0.9158
77.35	0.9105	79.21	0.8997
87.05	0.8886	86.09	0.8847
92.66	0.8770	92.76	0.8690
100.00	0.8548	100.00	0.8481

heats at normal boiling points taken from the literature (*14*). The data satisfied these tests, with the following deviations from mean values as calculated by the formula

$$\omega = \frac{\Sigma k^2 - (\Sigma k)^2 n^{1\;2}}{n - 1} \tag{2}$$

System	Black's Test	Norrish-Twig Test
p-Xylene(1)-furfural(2)	–0.003	–0.024
Ethylbenzene(1)-furfural(2)	0.006	–0.007

The constants in different correlating equations (*3, 4, 19, 22*) were determined by the least-squares method, using the experimental data. The data fit well in the Wilson equations (*19*):

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{3}$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{4}$$

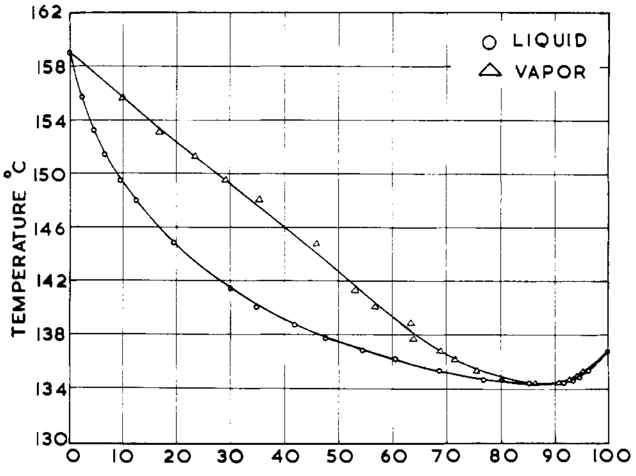

Figure 1. Boiling point–composition diagram for *p*-xylene–furfural system

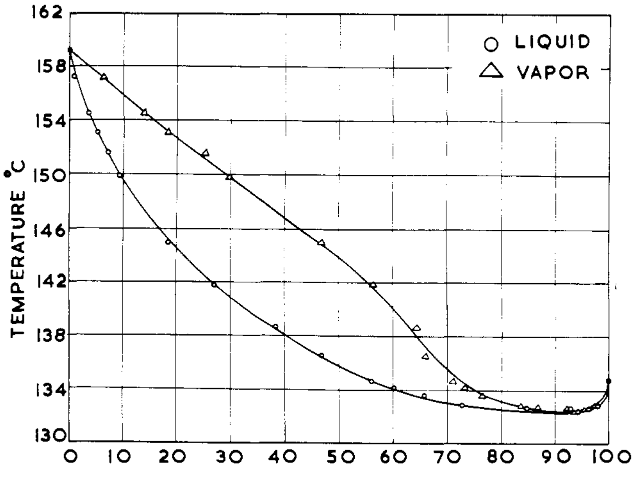

Figure 2. Boiling point–composition diagram for ethylbenzene-furfural system

Table III. Azeotropic Data

System	Experimental (at 723 Mm of Hg)		Literature (*11*)(at 760 Mm of Hg)	
	x_{1az}	t_{az}	x_{1az}	t_{az}
p-Xylene(1)–furfural(2)	0.898	134.20	0.945	138.0
Ethylbenzene(1)–furfural(2)	0.942	132.30	Nonazeotropic	

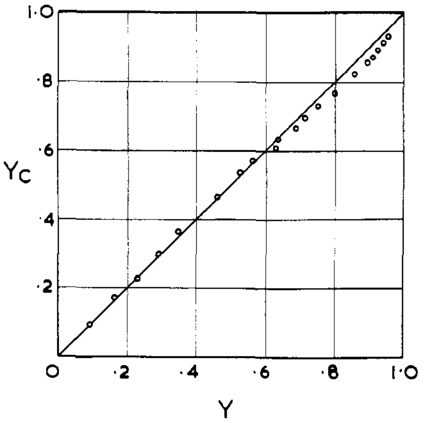

Figure 3. Experimental and calculated vapor compositions for *p*-xylene–furfural system

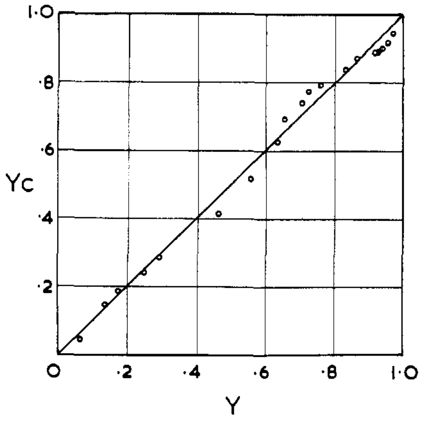

Figure 4. Experimental and calculated vapor compositions for ethylbenzene-furfural system

The values of the constants in the Equations 3 and 4 are

	Λ_{12}	Λ_{21}
p-Xylene(1)-furfural(2)	0.5024	0.6446
Ethylbenzene(1)-furfural(2)	0.4795	0.6629

The deviations between the experimental and calculated activity coefficients, evaluated according to Equation 2, are

	ω_1	ω_2
p-Xylene(1)-furfural(2)	−0.0825	−0.0123
Ethylbenzene(1)-furfural(2)	0.0045	−0.0460

Table IV. Vapor-Liquid Equilibrium Data at 723 mm of Hg

T	x	y	γ_1	γ_2
System *p*-Xylene(1)–Furfural(2)				
135.20	0.962	0.954	1.026	2.426
134.80	0.946	0.942	1.041	2.200
134.60	0.933	0.925	1.042	2.286
134.40	0.917	0.911	1.049	2.204
134.20	0.899	0.897	1.060	2.099
134.40	0.850	0.859	1.067	1.932
134.60	0.765	0.800	1.099	1.738
135.30	0.686	0.752	1.131	1.578
136.20	0.604	0.714	1.191	1.404
136.80	0.542	0.684	1.254	1.313
137.60	0.473	0.634	1.304	1.291
138.80	0.416	0.632	1.435	1.128
140.00	0.345	0.562	1.493	1.154
141.30	0.295	0.526	1.583	1.115
144.80	0.195	0.460	1.922	1.002
148.00	0.125	0.352	2.125	1.006
149.50	0.093	0.289	2.264	1.019
151.50	0.064	0.232	2.520	1.007
153.20	0.044	0.164	2.499	1.022
155.80	0.022	0.096	2.749	1.005
System Ethylbenzene(1)–Furfural(2)				
132.70	0.979	0.974	1.040	2.687
132.50	0.960	0.955	1.045	2.458
132.30	0.942	0.942	1.056	2.198
132.45	0.930	0.931	1.053	2.157
132.50	0.923	0.926	1.054	2.099
132.60	0.847	0.867	1.073	1.893
132.70	0.775	0.835	1.126	1.592
133.50	0.654	0.762	1.192	1.455
134.00	0.600	0.732	1.232	1.395
134.50	0.558	0.709	1.267	1.349
136.40	0.467	0.657	1.335	1.242
138.50	0.381	0.642	1.515	1.046
144.90	0.181	0.468	1.981	0.967
149.80	0.092	0.297	2.197	0.998
152.50	0.050	0.177	2.260	1.034
154.50	0.035	0.138	2.403	1.007

Table IV gives the results obtained in this investigation. Experimental and calculated vapor compositions are compared in Figures 3 and 4.

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NOMENCLATURE

k = deviation of experimental from calculated values
n = number of experimental observations
P° = vapor pressure of pure components, mm of Hg
R = gas constant
T = absolute temperature, ° K
t = system temperature, ° C
V = liquid molal volume of pure component, ml/g mole
x = mole fraction in liquid phase
y = mole fraction in vapor phase
β = gas phase second virial coefficient of pure component
γ = activity coefficient
Λ_{12}, Λ_{21} = constants in Wilson equations
$\bar{\Lambda}$ = system pressure, mm of Hg
ω = defined deviation of k from mean value of k

Subscripts

az = azeotropic point
c = calculated values
i = component i
1 = more volatile component
2 = less volatile component

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Volumetric Behavior, Vapor Pressures, and Critical Properties of Cyclopropane

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Pressure-volume-temperature relations of cyclopropane (trimethylene) over the temperature range of 20° to 200° C. and up to a pressure of 310 atm. were measured using the Beattie method. Vapor pressures were determined from 20° C. to the critical temperature at 5° increments. These data were used to derive the critical constants, the orthobaric densities, the heats and entropies of vaporization, the fugacity coefficients, the volume residuals, and the compressibility factors.

The equipment used in this investigation follows, in general, the basic design of that described by Keyes (*10*) and Beattie (*1*). The method involves the direct measurement of pressure as a function of volume, which is continuously variable, for a known mass of material maintained at a controlled temperature. An Amagat dead-weight gage was used for the pressure measurements. Samples were confined over mercury in the *P-V-T* cell. The sample volumes were calculated from the difference between the amount of mercury originally in the system and the amount withdrawn into the thermostated volumetric pump. Four different samples (0.5, 1.5, 3.5, and 8.5 grams) were used for the present work. Sample masses were determined by direct weighing of the samples, contained in specially designed, light-weight weighing bombs, on an analytical balance. A platinum resistance thermometer associated with a Mueller bridge was used for the temperature measurements. Detailed descriptions of the apparatus, the calibrations, and the experimental procedures have been given by Couch (*4*), Hellwig (*8*), Hsu (*9*), and Lin (*11*).

MATERIAL

The purity of the original cyclopropane sample was 99.91% as stated by the Phillips Petroleum Co. The sample was further purified by passage through a molecular sieve column, followed by vacuum distillation with condensation by means of liquid nitrogen. The sample used in the measurements was approximately the 35% center cut, which had a minimum purity of 99.95% as shown by chromatographic analysis. The final impurity consisted chiefly of equal portions of propane and propylene.

PHYSICAL CONSTANTS

The fundamental constants and conversion factors used throughout this work were given by Abramowitz and Stegun (*7*) and Weast (*6*). The molecular weight of cyclopropane, 42.0813, is based on the newest atomic weight scale (*3*). The international temperature scale of 1948 (ITS-48) was used because the platinum resistance thermometer was calibrated by the National Bureau of Standards in 1951.

EXPERIMENTAL RESULTS

Vapor Phase. In the vapor phase, the pressure-volume-temperature behavior of cyclopropane was measured from 20° to 200° C. The major isotherms were spaced at 20° C. intervals, and the pressures were measured from 6 atm. up to the vapor pressure for each isotherm below the critical temperature and up to the maximum pressure allowed by the equipment, 310 atm., for each isotherm at and above the critical temperature. For the isotherms at 130°, 135°, 145°. and 150° C., the pressures were measured from 37 to 127 atm. The results are shown as compressibility factors, $Z = PV/RT$, in Figure 1. For the saturated states, the specific volumes were obtained along isotherms spaced at 5° C. intervals from 20° C. to the critical temperature, and the data are presented in Table I (Tables I to IV deposited with ASIS).

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