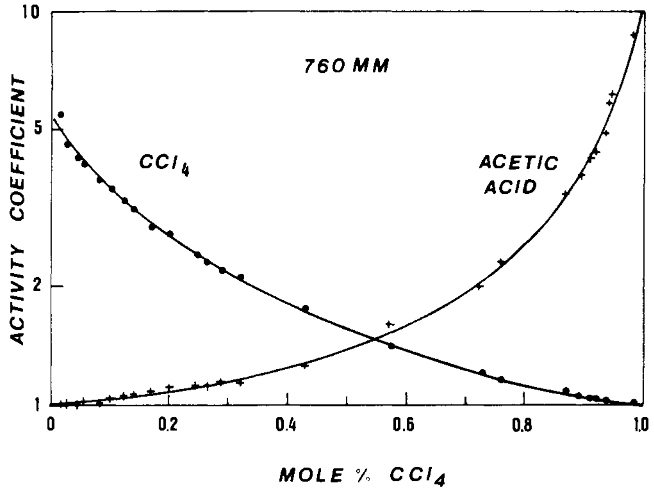

Figure 1. Activity coefficients

Table IV. Parameters of Redlich-Kister and Wilson Equations

		760 mm	417 mm
Redlich-Kister	A	1.53789	1.63322
	B	0.11761	1.28072
	C	0.36467	0.35438
	D	0.22038	−0.15561
	SSQ	0.0957	0.00633
Wilson			
Isothermal	Λ_{12}	0.44353	0.47900
	Λ_{21}	0.19703	0.23875
	SSQ	0.00639	0.00519
Nonisothermal	A_1	50.944	50.873
	A_2	9.0617	11.080
	B_1	45.003	53.733
	B_2	11.872	10.791
	SSQ	0.00470	0.00356

Acknowledgment

Yehudit Reizner helped in the experimental work.

Nomenclature

G^E = excess Gibbs function
K_2 = dimerization constant for acetic acid, mm^{-1} Hg
n = refractive index
p_i° = vapor pressure of pure component i, mm Hg
R = gas constant
t, T = temperature, °C, K
v_i = molar volume of pure component i, cm^3/mol
x_i = mole fraction of component i

Greek Letters

γ_i = activity coefficient of component i
λ_{ij} = energy of interaction
Λ_{ij} = Wilson parameter

Subscripts

1 = carbon tetrachloride
2 = acetic acid

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Vapor-Liquid Equilibrium of Propionic Acid-Toluene System

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Vapor equilibrium data were measured for the system propionic acid–toluene at 500 and 600 mm Hg. These equilibrium data were measured in a vapor recirculating still at temperatures in the range from 95.9° to 127°C, and the analyses were done by refractometry.

Isobaric vapor-liquid equilibrium data were measured for the system propionic acid-toluene. These data were required for the design of a distillation column separating these two components, and no data on this system could be found in the literature. These data were taken at the two pressures of 500 and 600 mm Hg.

Toluene at 99.9% purity (Fisher Scientific Co., Pittsburg) and propionic acid of 99% purity (Anachemia Chemicals Ltd., Montreal) were used with no further purification. The bp of the toluene was 110.6°C, and the bp of the propionic acid was 140.5–141.5°C.

Apparatus and Procedure

The vapor circulating still used was first designed by Othmer (*1*), modified by Othmer (*2*–*4*), and manufactured by Scientific Glass Apparatus Co., Inc., Bloomfield, N.J. (type JD-3630). The still was equipped with an externally heated thermosiphon which ensured active mix-

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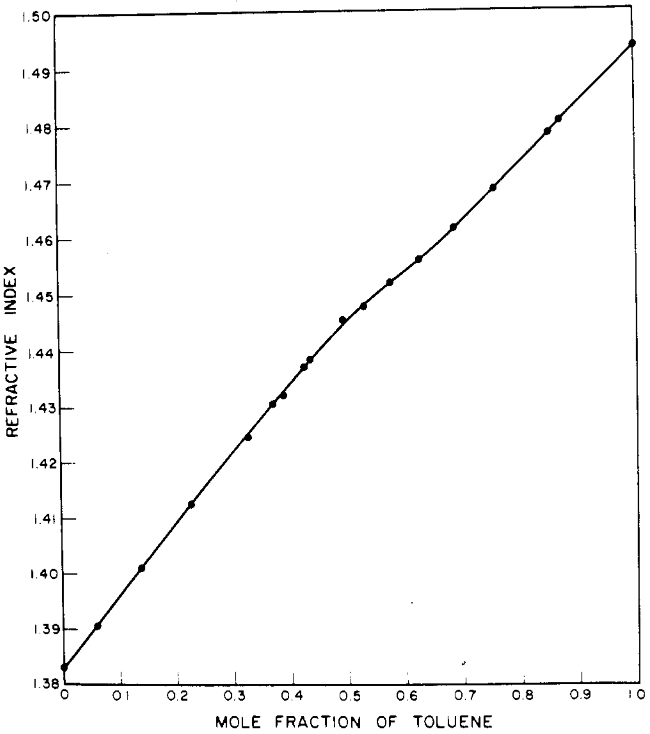

Figure 1. Refractive index-composition data for system propionic acid–toluene at 31°C

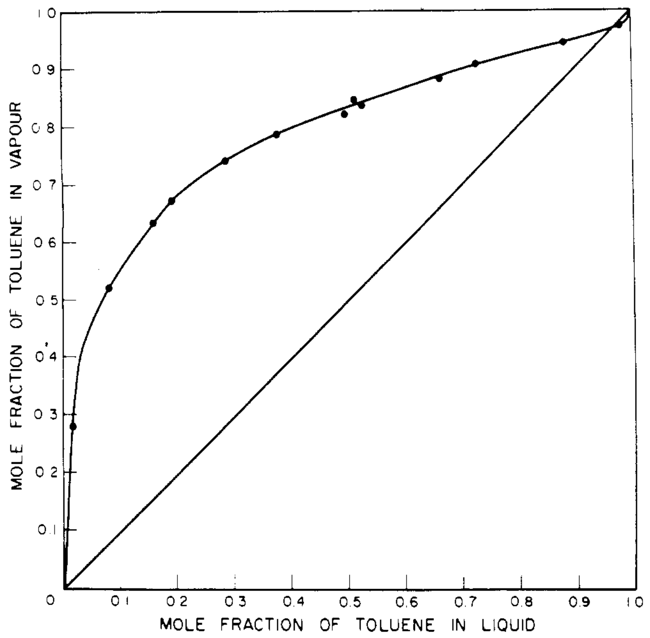

Figure 2. Vapor-liquid equilibrium of propionic acid–toluene mixtures at 500 mm Hg

ing of the circulating condensed vapor and distilling flask contents. The power supplied to the 250-W nicrome wire heater was controlled by a variable autotransformer. Sample ports were located at the base of the condensed vapor collector and distilling flask. For control of pressure a vacuum pump was connected in series with a Cartesian manostat (type 6A, Manostat Corp.) covering a full range of pressures, 0–760 mm Hg. The pressures were

Table I. Refractive Index-Composition Data for System Propionic Acid–Toluene at 31°C

Mole fraction toluene	Refractive index
0.0000	1.3834
0.0609	1.3909
0.1385	1.4013
0.2280	1.4127
0.3277	1.4249
0.3712	1.4305
0.3920	1.4322
0.4286	1.4372
0.4383	1.4378
0.4971	1.4455
0.5310	1.4479
0.5780	1.4520
0.6270	1.4561
0.6850	1.4616
0.7565	1.4689
0.8533	1.4784
0.8727	1.4805
1.0000	1.4934

Table II. Temperature-Composition Data for Propionic Acid–Toluene Mixtures at 500 mm Hg

Mole fraction toluene in liquid	Mole fraction toluene in vapor	Temp, °C
0.017	0.278	116.6
0.082	0.521	110.3
0.159	0.635	105.5
0.193	0.672	104.1
0.287	0.771	102.2
0.376	0.786	101.3
0.496	0.820	100.5
0.512	0.845	99.3
0.527	0.838	99.0
0.662	0.880	98.0
0.726	0.907	97.5
0.880	0.943	96.3
0.977	0.973	95.9

Table III. Temperature-Composition Data for Propionic Acid–Toluene Mixtures at 600 mm Hg

Mole fraction toluene in liquid	Mole fraction toluene in vapor	Temp, °C
0.037	0.272	127.0
0.043	0.295	125.1
0.065	0.410	122.1
0.070	0.438	121.5
0.136	0.596	116.3
0.158	0.625	114.8
0.204	0.663	113.0
0.296	0.713	110.2
0.313	0.722	109.1
0.429	0.766	107.8
0.533	0.824	106.0
0.585	0.842	105.1
0.597	0.841	105.5
0.808	0.911	103.5
0.845	0.920	102.9
0.965	0.968	102.2
0.977	0.973	102.0

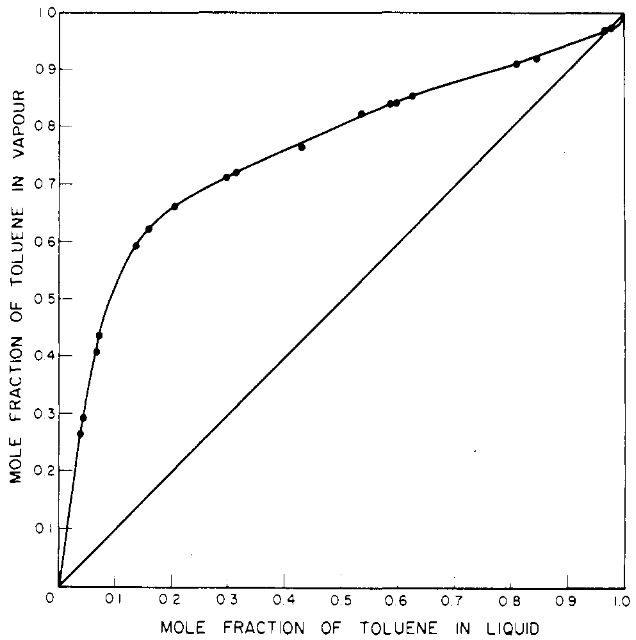

Figure 3. Vapor-liquid equilibrium of propionic acid–toluene mixtures at 600 mm Hg

measured by means of a mercury manometer of 10-mm diam (6-mm i.d.) to an accuracy of 1 mm Hg using a millimeter scale. Temperatures were measured to an accuracy of ±0.1°C by a Sisco partial immersion thermometer with 0.2°C divisions.

A sample of 500 ml of the binary mixture was charged into the flask. The flask·top was covered, and the thermometer was placed in its position. The pressure was set to the desired value, and the liquid was brought to boil. Liquid and vapor samples in equilibrium were collected when the temperature reached a constant value (after approximately 3 hr). The still was open to the atmosphere during the brief sampling period. A second set of samples was taken after ½ hr to check the results.

The mole fraction of toluene in these samples was obtained to an accuracy of ±0.001 by measuring the refractive indices and using a calibration chart shown in Figure 1. This calibration chart was constructed from the data of Table I which gives the measured refractive indices of the toluene–propionic acid system at 31°C, the samples of known composition being prepared by weight. The refractive indices were measured with an Erma Abbe refractometer thermostatically controlled at 31°C.

The maximum errors in temperature, pressure, and composition were estimated to be 0.1°C, 1 mm Hg, and 0.1 mol %, respectively.

Results

The data taken at 500 mm Hg are given in Table II and illustrated in Figure 2. An azeotrope was found with a composition of 97.0 mol % toluene boiling at 95.8°C. The data taken at 600 mm Hg are given in Table III and illustrated in Figure 3. An azeotrope was found with a composition of 97.0 mol % toluene and a boiling point of 101.9°C. The compositions and temperatures of the azeotropes are approximate since they were obtained by interpolation. There is some scatter in the experimental results. However, these data were successfully used to design a distillation column which has been operated successfully. The existence of an azeotrope for this system was verified from the measured distillation column product compositions.

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