Vapor-Liquid Equilibrium in the Toluene–*p*-Cresol System

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THE DESIGN OF industrial distillation equipment requires the availability of accurate vapor-liquid equilibrium data for the particular liquid system under study. The failure of most known liquid systems to conform to Raoult's and Dalton's laws usually requires the experimental determination of the needed vapor-liquid equilibrium. These may be determined by one of the conventional methods of equilibrium distillation.

The commercial importance of toluene has led to considerable study of the various methods for its recovery from petroleum by distillation methods (*1, 2, 4, 13*). In the commercial production of toluene from petroleum, the toluene must be separated from paraffinic and naphthenic hydrocarbons having about the same boiling point and volatility (*3*). This fact makes the separation of toluene by ordinary fractional distillation very difficult. However, through the use of a selective solvent, toluene can be separated with ease by an extractive distillation process. Dunn and others (*4*) have given a list of possible solvents which may be used in the extractive distillation of toluene. Included in their listing is *p*-cresol.

From the extractive distillation unit, which removes toluene from its close boiling components, the final commercial grade toluene is separated from the selective solvent in an oridnary fractionating column. The accurate design of the final toluene separating column would then depend upon vapor-liquid equilibrium data for toluene and the selective solvent used.

The absence of available equilibrium data in the literature for the toluene-*p*-cresol system led to the present investigation. The data presented in this study would be of value in the design of a toluene recovery unit employing *p*-cresol as a selective solvent.

EXPERIMENTAL

Apparatus. The Jones, Schoenborn, and Colburn (*11*) still was selected for this work because small samples could be used and a relatively short time was required to establish equilibrium. The particular still and accessory equipment were previously described (*14–16*).

All equilibrium measurements were made with a total still pressure of 760 mm. of mercury. Dry nitrogen, regulated by means of a Cartesian manostat, was used to maintain the desired pressure at the still vent.

Temperature measurements were made by means of a copper-constantan thermocouple connected to a potentiometer (Leeds and Northrup). The reference point, 0° C., for the thermocouple was a melting ice bath. The potentiometer was capable of determining electrical potentials with an accuracy of approximately 0.01 mv. which permitted temperature readings to an accuracy of 0.5° C.

The equilibrium samples were analyzed for composition using the refractive index method and apparatus previously described by Wingard and others (*15*). Temperatures were controlled to within 20 ± 0.1° C.

Materials. Toluene (CP grade) was purified by distillation in a 36-inch Vigreux fractionating column. The toluene was distilled twice with only the heart cut retained from each distillation. Dry nitrogen was introduced under the liquid surface in the distilling flask to provide smoother boiling and an inert atmosphere. The final purified toluene had a refractive index n_D^{20} of 1.4968 ± 0.001 which agrees well with the literature value (*7*).

p-Cresol (Eastman Kodak Co., practical grade) was dried with calcium chloride and then distilled in a 20-inch Vigreux fractionating column in a manner similar to toluene. The purified *p*-cresol had an n_D^{20} of 1.599 ± 0.002 which agrees well with the value reported (*9*) and reasonably well with the value reported in the Handbook of Chemistry and Physics (*7*).

Procedure. The purified chemicals were used in the preparation of the refractive index-composition curve for toluene–*p*-cresol at 20° C. The data are given in Table I.

The nitrogen used to maintain the still pressure was treated to remove any traces of oxygen. This precaution

Table I. Refractive Index–Composition and Equilibrium Composition–Temperature Data for Toluene–*p*-Cresol at 760 mm. Hg

Toluene Liquid, Mole %	n_D^{20}	Toluene Vapor, Mole %	Temperature, ° C.
0.0	1.5400	0.0	202.2
2.5	1.5388	27.3	189.0
5.8	1.5375	46.6	181.0
7.8	1.5367	53.5	175.8
9.7	1.5360	58.8	173.8
10.3	1.5357	60.8	172.9
11.9	1.5352	67.4	167.7
12.5	1.5347	69.4	165.8
15.0	1.5337	75.6	159.8
17.3	1.5327	78.2	157.1
23.4	1.5303	86.0	146.1
25.3	1.5298	87.0	145.2
27.8	1.5285	88.5	142.2
33.0	1.5265	90.9	137.6
49.3	1.5200	95.1	127.8
52.8	1.5184	95.8	125.8
66.5	1.5125	97.2	120.8
76.5	1.5076	98.2	117.0
100.00	1.4669	100.0	110.7

was taken to prevent any possible oxidation of the *p*-cresol in the still. A special nitrogen wash system was used. The nitrogen was bubbled through two wash flasks containing pyrogallic acid, through one flask containing concentrated sulfuric acid, and through one flask containing glass wool. The pyrogallic acid solution removed the oxygen from the nitrogen, the sulfuric acid removed any moisture remaining in the nitrogen and the glass wool prevented any entrained liquid from entering the still. After passing through the wash system, the nitrogen was regulated through a Cartesian manostat and passed into the still vent.

A sample containing a predetermined amount of toluene and *p*-cresol was introduced into the still. The still pressure was then regulated to 760 mm. of mercury. The heat supply to the still was then adjusted by means of variable transformers. When the still began to function properly, the transformers were adjusted to their proper settings. The sample was allowed to remain in the still for 1 hour or until a constant temperature in the still indicated equilibrium.

When equilibrium in the still was assured—i.e., by a constant temperature in the still for some length of time, the transformers were shut off and the three-way stopcock to the still flask boiler was turned off. Samples were then quickly removed from the residue and condensate chambers and cooled in an ice bath. The samples were then analyzed for composition by refractive index measurements.

ANALYSIS OF THE DATA

The experimental equilibrium data were given a preliminary check for consistency by subjecting them to the requirements of the Gibbs-Duhem equation. The data were given a complete check for consistency through the use of the Van Laar equations.

Two statistical tests were applied to the experimental and calculated equilibrium data. A Chi-square test was applied to determine if there was a significant difference between the experimental and calculated data. A correlation coefficient was also run on the experimental and calculated data to estimate how good the correlation was between the two sets of data.

METHOD OF CALCULATION

Experimental activity coefficients were calculated by inserting a deviation factor, γ, into Raoult's law. Raoult's law with this modification becomes, for component 1 (toluene),

$$\gamma_1 = \frac{y_1 \pi}{x_1 P_1^0} \tag{1}$$

where

γ_1 = deviation factor or activity coefficient for toluene
y_1 = vapor phase composition of toluene
x_1 = liquid phase composition of toluene
P_1^0 = vapor pressure of pure toluene at the temperature of the system
π = total pressure, 760 mm. of mercury

The liquid and vapor phase compositions for Equation 1 were obtained from experimental, and vapor pressure data for the two compounds from the literature (*6, 10, 12*).

The Van Laar equations

$$\ln \gamma_1 = \frac{B/T}{\left[1 + \frac{A x_1}{x_2}\right]^2} \tag{2a}$$

$$\ln \gamma_2 = \frac{AB/T}{\left[A + \frac{x_2}{x_1}\right]^2} \tag{2b}$$

were used to calculate the empirical activity coefficients. The constants of Equations 2a and 2b may be evaluated by several methods. The method which gives the best values of the constants, involves plotting the equations as straight lines by rearranging them in the form

$$\frac{1}{(T \ln \gamma_1)^{1/2}} = \frac{1}{B^{1/2}} + \frac{A}{(B)^{1/2}} \frac{x_1}{x_2} \tag{3a}$$

$$\frac{1}{(T \ln \gamma_2)^{1/2}} = \left(\frac{A}{B}\right)^{1/2} + \frac{1}{(AB)^{1/2}} \frac{x_2}{x_1} \tag{3b}$$

In this work the constants were evaluated from Equation 3a. The method of least squares was used to obtain the best straight line.

The empirical activity coefficients, calculated from Equations 2a and 2b, were used in Equation 1 to compute the calculated vapor phase composition. A Chi-square test as described by Hoel (*8*) was used to determine whether there was a significant difference at the 1% level between the calculated and experimental vapor phase compositions. The equation used to calculate the Chi-square statistic was:

$$X^2 = \sum_{i=1}^{k} \frac{(y_e - y_c)^2}{y_t} \tag{4}$$

where

k = the number of sample pairs to be compared
y_e = experimental vapor phase composition
y_c = calculated vapor phase composition
X^2 = Chi-square

A correlation coefficient as described by Hoel (*8*) and given by the equation

$$r = \frac{n\Sigma xy - \Sigma x \Sigma y}{[(n\Sigma x^2 - (\Sigma x)^2)\,(n\Sigma y^2 - (\Sigma y)^2)]^{1/2}} \tag{5}$$

where

n = number of sample pairs
x = calculated vapor phase composition
y = experimental vapor phase composition

was calculated from the data. The correlation coefficient value obtained from Equation 5 allowed an estimate of the correlation between the calculated and experimental vapor phase composition values.

DISCUSSION OF RESULTS

The experimental vapor-liquid equilibrium data are presented in Table I and plotted in Figure 1 as the *y-x* diagram and in Figure 2 as the *t-x* diagram. While figures of this type may give little indication of the thermodynamic consistency of equilibrium data, they do serve to indicate any random departure of the experimental data from a smooth curve. The smooth curve drawn through the experimental points in Figure 1 indicates a considerable degree of consistency in the experimental measurements. The smoothness of the curve in Figure 2 would indicate that the experimental temperature measurements are within the limits of experimental error.

Figure 3, in γ *vs.* x curve, yields some information as to the thermodynamic consistency of the data. According to the Gibbs-Duhem equation, if the slope of the curve of

$\ln\gamma$ *vs.* x for one component is zero, corresponding to a maximum, the slope of the curve for the other component must be zero at the same composition. This is obeyed in the low toluene composition range of Figure 3. The Gibbs-Duhem relationship also indicates that plots of $\ln\gamma_1$ and $\ln\gamma_2$ *vs.* x should have slopes of opposite sign at a given composition. The experimental data conforms to this principle, as can be seen in Figure 3.

The scatter of activity coefficient points in Figure 3 is not necessarily due to inconsistencies in the experimental data. The application of Equation 1 to calculated experimental activity coefficients requires the availability of accurate vapor pressure data for each component. As Gilmont (*5*) has pointed out, it is a rare case to have vapor pressure data which are comparable in accuracy to experimental equilibrium data. In the present study there was considerable uncertainty regarding the accuracy of toluene vapor pressure data.

The Van Laar equations allow one to draw more quantitative conclusions concerning the consistency of the experimental data. Calculated values of activity coefficients as well as experimental values are tabulated in Table II. Calculated values are plotted as dotted lines in Figure 3. The agreement between experimental and calculated values of the activity coefficients is good.

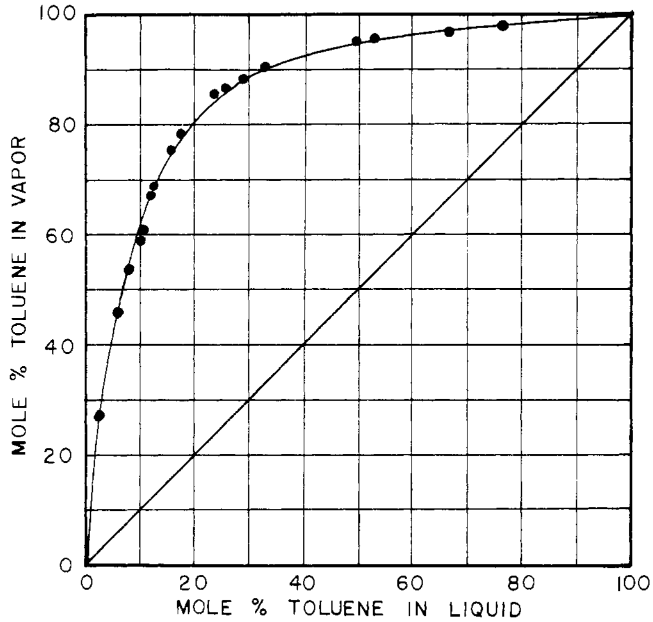

Figure 1. Vapor-liquid equilibrium diagram for toluene–*p*-cresol at 760 mm. Hg

Vapor phase compositions were calculated from empirical activity coefficient values obtained from Equations 2a and 2b and are tabulated with the experimental vapor phase composition values in Table III. The agreement between calculated and experimental vapor phase composition values is good, in most cases. The largest discrepancies between the two sets of data are in the range where the accuracy of the toluene vapor pressure data was uncertain.

While the correlation approach used yields results which agree fairly well with the experimental data, there are certain limitations to the method used which must be realized.

The Van Laar equations, being derived from the Gibbs-Duhem equations, apply strictly to isothermal data. The use of the Van Laar equations on the isobaric toluene–*p*-cresol data where the temperature variation is large is attended by a degree of uncertainty. The temperature effect on activity coefficient is probably not adequately taken care of by the equation. However, the fair agreement between the correlation plots when based on Equations 3a and 3b led the authors to conclude that the temperature effect might be small.

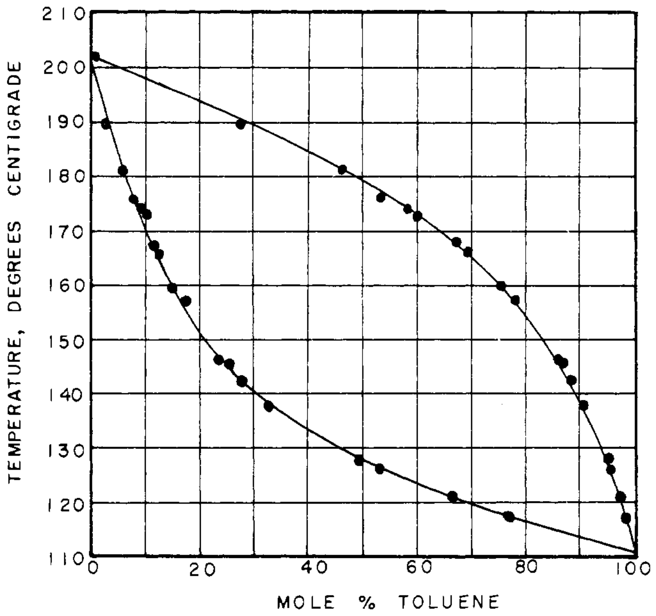

Figure 2. Temperature-composition diagram for toluene–*p*-cresol at 760 mm. Hg

The Van Laar constants were obtained from the experimental data. The values used were $A = 0.395$ and $B = 144.4$.

The disagreement in the calculated vapor phase compositions when based on γ_1 and then γ_2 is thought to be due mainly to poor vapor pressure data for toluene in the higher temperature range of the system. This assumption seems to be justified by the fact that the agreement between the two sets of data is good in the lower temperature range where the toluene vapor pressure data is more accurate.

Calculated vapor phase compositions were computed using experimental temperature values. Better agreement between experimental and calculated vapor composition values might have resulted, if temperature values which

Table II. Activity Coefficients Toluene–*p*-Cresol, at 760 mm. Hg

Toluene Liquid, Mole %	Experimental		Calculated	
0.0	. . .	1.000	. . .	1.000
2.5	1.706	1.065	1.358	1.000
5.8	1.434	1.027	1.345	1.000
7.8	1.321	1.069	1.332	1.001
9.7	1.212	1.026	1.346	1.001
10.3	1.204	1.008	1.345	1.002
11.9	1.291	1.001	1.344	1.002
12.5	1.324	1.011	1.343	1.002
15.0	1.377	1.024	1.338	1.004
17.3	1.321	1.038	1.332	1.005
23.4	1.424	1.052	1.316	1.010
25.3	1.359	1.039	1.308	1.012
27.8	1.362	1.062	1.300	1.015
33.0	1.327	1.077	1.280	1.024
49.3	1.205	1.118	1.207	1.073
52.8	1.194	1.114	1.190	1.090
66.5	1.013	1.286	1.122	1.196
76.5	1.079	1.393	1.073	1.345
100.0	1.000	. . .	1.000	. . .

corresponded to a total system pressure of 760 mm. of mercury had been calculated for each composition value. However, this was not attempted because of the poor vapor pressure data available for toluene.

Since the system pressure was 760 mm. of mercury, vapor imperfections if they existed were ignored.

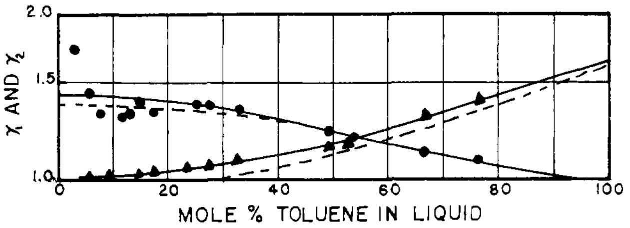

Figure 3. Activity coefficient-composition diagram for toluene–*p*-cresol at 760 mm. Hg

——Experimental ----Calculated

The results of the Chi-square and correlation coefficient calculations are given in Table III. The results of these tests indicate that the probability of a correlation between experimental and calculated vapor-phase data when based on γ_1 or γ_2 values is good. The results of statistical tests of this nature are of little value other than to give the investigator an indication of whether the difference in experimental data may be significant or not.

Table III. Experimental and Calculated Equilibrium Vapor-Phase Compositions Toluene–*p*-Cresol at 760 mm. Hg

Toluene, Mole %			
Liquid	Vapor, exptl.	Vapor, calcd.[a]	Vapor, calcd.[b]
0.0	0.0	0.0	0.0
2.5	27.3	21.7	31.8
5.8	46.6	44.0	48.0
7.8	53.5	54.8	56.5
9.7	58.8	65.3	59.8
10.3	60.8	67.9	61.0
11.9	67.4	70.2	67.4
12.5	69.4	70.4	69.7
15.0	75.6	73.4	76.1
17.3	78.2	78.8	78.9
23.4	86.0	79.5	86.6
25.3	87.0	83.7	87.3
27.8	88.5	84.5	89.0
33.0	90.9	87.7	91.4
49.3	95.1	95.2	95.3
52.8	95.8	95.4	95.9
66.5	97.2	97.7	97.4
76.5	98.2	98.1	98.3
100.0	100.0	100.0	100.0

[a] Calculated from γ_1; $x^2 = 4.214$; $r = 0.981$.
[b] Calculated from γ_2; $x^2 = 0.876$; $r = 1.00$.

The raw data are recommended for equilibrium calculations might be made on the toluene–*p*-cresol system. These data were obtained with care and were readily repdoducible.

CONCLUSIONS

Isobaric vapor-liquid equilibrium data for the system toluene–*p*-cresol have been obtained experimentally and are presented in the form of equilibrium liquid and vapor-phase compositions along with the equilibrium temperature. The data obtained are of sufficient accuracy for distillation calculations on this system. As far as known to the authors, these are the only such data available on this particular system.

Thermodynamic consistency of the data have been demonstrated through the use of the Van Laar equations. The agreement between experimental and calculated equilibrium data has been good.

The application of the Chi-square and correlation coefficient statistical tests to the experimental and calculated equilibrium data has shown that the data correlate well and the experimental data are sound.

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