Vapor-Liquid Equilibria in Binary and Ternary Systems

Cyclohexanol-Phenol, Cyclohexanone-Cyclohexanol, and Cyclohexanol-Phenol-Cyclohexanone

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A FIRM knowledge of the vapor-liquid equilibrium relationships involved is a prerequisite to reliable design of distillation equipment, particularly where difficult separations are involved.

The systems considered here are the cyclohexanol-phenol, cyclohexanol-cyclohexanone, and cyclohexanol-phenol-cyclohexanone systems. The cyclohexanol-phenol system was previously investigated at atmospheric pressure by Agliardi (*1*). Because both cyclohexanol and cyclohexanone form azeotropes with phenol (*3*), it becomes apparent that two of the above systems—cyclohexanol-phenol and cyclohexanol-phenol-cyclohexanone—deviate considerably from ideal behavior. Data for the two binary systems were found thermodynamically consistent and were fitted with 4-suffix Margules equations. Attempts to fit the ternary system with an equation of the same type failed because of incomplete experimental data.

MATERIALS

Cyclohexanol and U.S.P. phenol (Monsanto Chemical Co.) and cyclohexanone (National Aniline Co.) were subjected to fractional distillation. In each case, a 60 to 80% heart cut was taken. The boiling points of the materials as closely as could be ascertained were within 0.5° C. of the values cited in the literature—161.0° C. for cyclohexanol, 155.6° C. for cyclohexanone, and 181.9° C. for phenol (*7*). The refractive indices of cyclohexanol and cyclohexanone were 1.4645 and 1.4484 at 25° C., respectively. Literature values of the refractive indices are 1.46477 n_D^{25} for cyclohexanol and 1.4484 n_D^{25} for cyclohexanone (*8*).

Table I. Refractive Indices of Mixtures of Cyclohexanol Phenol and Cyclohexanone at 25° C.

Wt. % Cyclohexanol	Wt. % Cyclohexanone	Wt. % Phenol	Refractive Index
100	0	0	1.4645
81.8	0	18.2	1.4787
60.6	0	39.4	1.4957
51.2	0	48.8	1.5040
40.0	0	60.0	1.5134
30.7	0	69.3	1.5215
21.8	0	78.2	1.5290
75.6	5.5	18.9	1.4782
37.7	5.0	57.3	1.5104
19.0	5.0	76.0	1.5269
73.6	10.0	16.4	1.4755
27.6	10.0	62.4	1.5140
68.0	15.0	17.0	1.4752
50.6	15.0	34.4	1.4899
33.7	15.0	51.3	1.5043
17.0	15.0	68.0	1.5185
65.4	20.0	14.6	1.4718
48.4	20.0	31.6	1.4868
24.5	20.0	55.5	1.5075

ANALYSIS

The cyclohexanol-phenol system was analyzed by measuring refractive index at 25° C. (Table I). For this purpose a curve of refractive index *vs.* concentration was plotted from measurements with samples of known composition. The estimated error in the analysis was estimated to be ±0.1 mole % (absolute, not relative).

In the ternary system, cyclohexanol-cyclohexanone-phenol, a family of curves of refractive index *vs.* cyclohexanol concentration with cyclohexanone concentration as parameter was plotted from measurements with samples of known composition. Once the cyclohexanone concentration of the sample was determined by chemical means, the phenol and cyclohexanol concentrations could be obtained from the refractive index curves. The estimated maximum error in the cyclohexanone analysis is ±2% of the amount present. The maximum error in the cyclohexanol and phenol analyses was estimated at approximately ±0.3 mole %.

The cyclohexanol-cyclohexanone system was analyzed by vapor phase chromatography with a Perkin-Elmer Model 154-B Vapor Fractometer. The 2-meter column was of firebrick impregnated with 28% Santicizer 409 (Monsanto Chemical Co.). Component concentrations were determined by measuring the areas under the peaks corresponding to these components with a planimeter. The peak areas were first corrected for the relative response of the various components and then were normalized. The correction factors were determined by running with samples of known composition extending over the concentration range to be studied. The maximum analytical error was estimated to be ±3% of the amount present.

APPARATUS AND PROCEDURE

The experiments were carried out in a Colburn vapor-recirculating still. The design of the still was taken from the article by Jones and others (*5*). The only variation was the use of calibrated standard thermometers rather than thermocouples to determine the equilibrium temperature. Estimated error in the temperature readings was ±0.1° C. Pressure was held constant in the system to within ±0.5 mm. of mercury with an automatic vacuum regulator.

In each run, at least 1 hour of operation at constant conditions was allowed to ensure the attainment of equilibrium.

The vapor pressure data used in the calculations were taken from the article by Stull (*7*).

The estimated maximum error in the activity coefficient is approximately ±5%. This would be the error caused by the most unfavorable combination of errors in analyses and temperature and pressure readings.

RESULTS

Cyclohexanol-Phenol at 90 Mm. of Mercury. In Table II are listed vapor and liquid concentratons, equilibrium tempera-

Table II. Experimental Data for the System Cyclohexanol-Phenol at 90 Mm. of Mercury

Temp., ° C.	Mole Fraction of Cyclohexanol		Activity Coefficients	
	Liquid	Vapor	Cyclohexanol	Phenol
102.4[a]	0.977	0.9963	0.986	0.32
104.3	0.931	0.987	0.927	0.38
106.9	0.801	0.944	0.930	0.45
107.6	0.792	0.934	0.906	0.50
107.8	0.795	0.945	0.891	0.42
111.0	0.705	0.878	0.824	0.565
111.3	0.671	0.855	0.837	0.601
116.0	0.514	0.676	0.713	0.750
118.0	0.430	0.547	0.636	0.831
118.9	0.354	0.417	0.574	0.912
119.2	0.284	0.305	0.520	0.971
111[b]	0.260[b]	0.260[b]	0.530[b]	1.03[b]
119	0.157	0.126	0.52	0.994

[a] Because of low phenol concentrations, analyzed by ultraviolet spectrophotometric method.

[b] This point (azeotropic composition) obtained at 70 mm. of mercury.

tures, and activity coefficients calculated by the following relationship:

$$\gamma_1 = (\pi Y_1)/(P_1 X_1) \tag{1}$$

One experimental point (Table I, 111° C.) was obtained at a pressure of 70 rather than 90 mm. of mercury. The azeotropic composition at 90 mm. was estimated to be a mole fraction of cyclohexanol of 0.29. The estimated equilibrium temperature for the azeotrope at 90 mm. of mercury is 120° C. The method of estimation which was utilized is based on the condition that for any azeotrope the following holds true.

$$P_1/P_2 = \gamma_2/\gamma_1 \tag{2}$$

A comparison of plots of the left side of Equation 2 *vs.* temperature and of the right side of Equation 2 *vs.* liquid phase concentration allows an estimation of azeotropic composition at various pressures. The method is discussed more thoroughly by Carlson and Colburn (2).

The calculated activity coefficients are plotted *vs.* cyclohexanol concentration in Figure 1. The curves in Figure 1 were calculated from the 4-suffix Margules equations.

$$\ln \gamma_1 = X_2^2\,(-0.511 - 3.63X_1 + 3.36X_1^2) \tag{3}$$

$$\ln \gamma_2 = X_1^2\,(-1.205 - 0.852X_2 + 3.36X_2^2) \tag{4}$$

where

1 = cyclohexanol
2 = phenol

The 2-suffix Margules equation gave only qualitative correlation with experiment. The 4-suffix equations above give a good correlation except in the region of high concentration of the component under consideration. Here the equations predict higher activity coefficients than were obtained.

The experimental data were tested for thermodynamic consistency by a modification of the method of Redlich and Kister (6). The Redlich-Kister equation which is given below applies only to isothermal data.

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dX_1 = 0 \tag{5}$$

Herington (4) extended the method to include isobaric data. In this case the condition for thermodynamic consistency is

$$D < J \tag{6}$$

D is the percentage deviation from zero of the quantity calculated in Equation 5. *D* is calculated as follows:

$$D = \frac{100\,\left|\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dX_1\right|}{\sum} \tag{7}$$

where $\sum$ is the sum of the absolute values of the areas calculated by Equation 5.

The quantity *J* is a function of the over-all boiling point range of the system and is defined by the following equation.

$$J = \frac{150\,|\,\theta\,|}{T_{\text{min.}}} \tag{8}$$

where θ is the over-all range of boiling points of the system and $T_{\text{min.}}$ is the lowest measured boiling point of the system in degrees Kelvin.

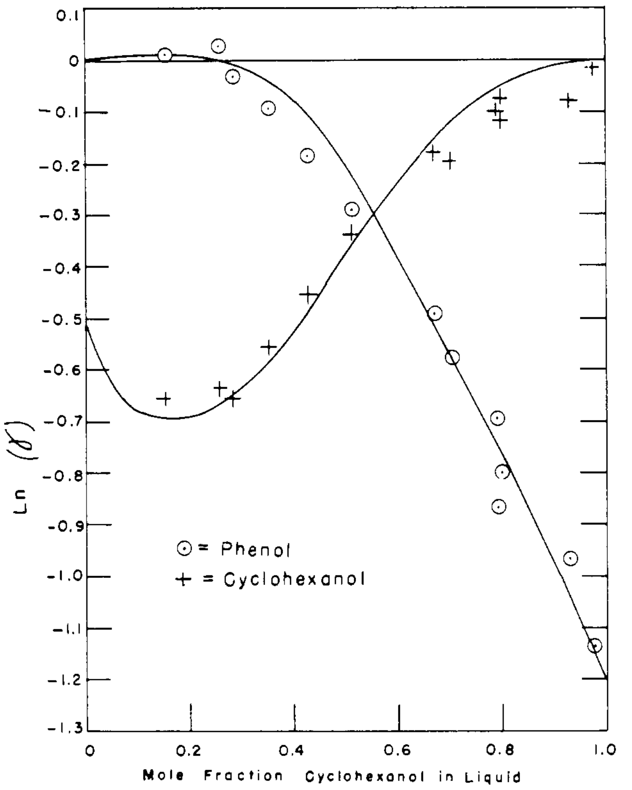

Figure 1. Activity coefficients *vs.* cyclohexanol concentration for the cyclohexanol-phenol system at 90 mm. of mercury

For the cyclohexanol-phenol system, *D* = 1.81 and *J* = 7.16. Hence, the data are thermodynamically consistent.

Cyclohexanol-Cyclohexanone at 100 Mm. of Mercury. Calculated activity coefficients and experimental data for this system are listed in Table III. Activity coefficients are plotted *vs.* cyclohexanone concentration in Figure 2. The curves in this figure were calculated by the following 4-suffix Margules equations.

$$\ln \gamma_3 = X_1^2\,(-0.106 + 1.50X_3 - 1.56X_3^2) \tag{9}$$

$$\ln \gamma_1 = X_3^2\,(+0.122 + 0.58X_1 - 1.56X_1^2) \tag{10}$$

Table III. Experimental Data for the System Cyclohexanol-Cyclohexanone at 100 mm. of Mercury

Temp., ° C.	Mole Fraction of Cyclohexanone		Activity Coefficients	
	Liquid	Vapor	Cyclohexanone	Cyclohexanol
104.6	0.0133	0.0201	0.922	0.984
102.8	0.114	0.180	1.024	0.975
101.6	0.165	0.276	1.130	0.944
99.4	0.285	0.433	1.110	0.955
96.4	0.499	0.625	1.016	1.028
95.2	0.585	0.710	1.030	1.000
92.8	0.801	0.865	1.000	1.093
92.0	0.899	0.932	0.987	1.116
91.2	0.922	0.949	1.000	1.127
91.0	0.945	0.966	1.001	1.068

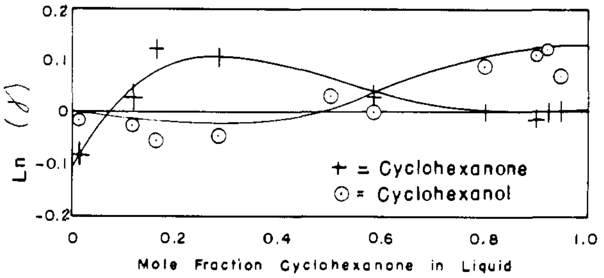

Figure 2. Activity coefficients vs. cyclohexanone concentration for the cyclohexanol-cyclohexanone system at 100 mm. of mercury

Table IV. Experimental Data for the Cyclohexanol-Phenol-Cyclohexanone System at 90 Mm. of Mercur

Temp., ° C.	Vapor Mole Fractions		Liquid Mole Fractions		Activity Coefficients		
	Cyclohexanol	Cyclohexanone	Cyclohexanol	Cyclohexanone	Cyclohexanol	Cyclohexanone	Phenol
103.1	0.801	0.178	0.801	0.099	0.928	1.037	0.41
105.1	0.879	0.060	0.798	0.056	0.944	0.58	0.52
109.1	0.717	0.175	0.582	0.113	0.886	0.725	0.532
110.8	0.800	0.067	0.637	0.042	0.837	0.71	0.574
112.7	0.567	0.229	0.428	0.157	0.828	0.605	0.632
116.0	0.544	0.158	0.389	0.121	0.757	0.486	0.684
118.5	0.383	0.155	0.272	0.132	0.697	0.405	0.793
119.0	0.408	0.045	0.316	0.054	0.628	0.282	0.878
120.8	0.205	0.136	0.159	0.140	0.583	0.313	0.881
121.2	0.184	0.046	0.164	0.062	0.500	0.237	0.923
102.2	0.779	0.189	0.762	0.103	0.979	1.092	0.475
102.4	0.800	0.175	0.763	0.099	0.994	1.040	0.360

where

3 = cyclohexanone, and 1 = cyclohexanol

Equation 9 correlating the cyclohexanone data deviates slightly from the experimental data at both low and high cyclohexanone concentrations.

The experimental data were subjected to the modified Redlich and Kister test and were found to be thermodynamically consistent ($D = 3.2$ and $J = 5.4$).

Cyclohexanol-Phenol-Cyclohexanone at 90 Mm. of Mercury. Equilibrium concentrations and temperatures and calculated activity coefficients for this system are presented in Table IV. These data are incomplete in that only the region of low cyclohexanone concentration has been investigated. Preliminary calculations were made in trying to fit the data with a ternary 4-suffix Margules equation, but the data were too sketchy to allow the quantitative fitting of an equation. Over the range of cyclohexanone concentration covered by the data, the effect of cyclohexanone on the cyclohexanol-phenol system is slight and consists of a small increase in the activity coefficient of cyclohexanol in mixtures rich in phenol.

ACKNOWLEDGMENT

The author acknowledges the invaluable assistance of R.E. Howard and J.F. Quinn in suggestions and advice, of E.M. Emery and A. Bybell in the analytical work, and of L. Copper and D.J. Kaufman in aiding in the attempt to fit an equation to the ternary data.

NOMENCLATURE

D = percentage deviation from zero in the Redlich-Kister test
J = function of boiling point range and boiling temperature, $\frac{150|\theta|}{T_{\text{min.}}}$
P_1 = vapor pressure of pure component 1 at equilibrium temperature, mm. of mercury
$T_{\text{min.}}$ = lowest measured boiling point of the system, ° K.
X_1 = mole fraction of component 1 in the liquid phase
Y_1 = mole fraction of component 1 in the vapor phase
γ_1 = activity coefficient of component 1
θ = over-all range of boiling points of the system, ° C.
π = total pressure on the system, mm. of mercury
$\sum$ = sum of the absolute values of the areas calculated in the Redlich-Kister test

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Received for review June 17, 1959. Accepted December 14, 1959.