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NOMENCLATURE

A = area for heat transfer perpendicular to direction of heat flow, sq. ft.
E = voltage, volts
I = current, amperes
k = thermal conductivity, B.t.u./hr.-ft.-° F.
L = linear dimension, ft.
Q = heat flow rate, B.t.u./hr.
R = electrical resistance, ohms
r = radius, ft.
t = temperature, ° F.
T = absolute temperature, ° R.

Greek Letters

α = thermoelectric power, volts/° R.
Δ = increment or difference
Σ = summation

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Vapor-Liquid Equilibrium in the *n*-Octane–*p*-Cresol System

Z. L. TAYLOR, Jr., and R. E. WINGARD
Department of Chemical Engineering, Auburn University, Auburn, Ala. 36830

Isobaric vapor liquid equilibrium has been measured for the system *n*-octane–*p*-cresol at 760 mm. of Hg pressure. The measurements were made using a Jones type equilibrium still. Liquid phase activity coefficients are calculated, and the data are thermodynamically consistent.

THE possibility of using *p*-cresol as a selective solvent in separation of close boiling hydrocarbons has led to an investigation of vapor-liquid equilibrium of binary systems of *p*-cresol with several hydrocarbons (7). In the present work, isobaric vapor-liquid equilibrium has been measured for the system *n*-octane-*p*-cresol.

APPARATUS

The equilibrium still used to obtain the vapor-liquid equilibrium data was the same as that reported by Jones, Schoenborn, and Colburn (5) except that a small heating coil of three turns of 20-gage nichrome wire was wound around the condensate chamber to provide convective heating currents. This ensured adequate mixing of the condensing vapor and the condensate in the condensate chamber. The temperature was measured with a temperature potentiometer using a copper-constantan thermocouple. This temperature could be read within an accuracy of ±0.2° C. Barometric pressure was recorded for each determination. An absolute pressure of 760 ± 1.0 mm. of Hg was maintained by venting dry nitrogen through a Cartesian manostat and balancing the difference between atmospheric pressure and 760 mm. of Hg on the system.

A Bausch and Lomb Precision Refractometer was used to determine the refractive indices of the still samples. Sodium (589) D illumination was used. A constant temperature bath was used to maintain the refractometer prisms at 20° ± 0.1° C.

MATERIALS

A commercially available 99.9% *n*-octane was used. Chromatographic analysis of the *n*-octane was carried out on a 6-foot column of silicone 550 at 100° C. The analysis indicated three trace impurities of concentrations less than 0.005 mole %. No further purification of the *n*-octane was attempted. The physical properties of the *n*-octane are given in Table I.

The *p*-cresol was commercial practical grade, which was dried over calcium chloride and then distilled three times through a 36-inch Vigreaux fractionating column. After each distillation only the middle cut was retained. To ensure agitation in the boiling flask and prevent oxidation of the *p*-cresol, dry nitrogen was introduced through a capillary tube into the boiling liquid during each distillation. Freezing curves for the *p*-cresol gave a melting point range of 20°

Table I. Physical Properties of Pure Materials

	Refractive Index, n_D^{20}		Boiling Point, ° C.	
Compound	Measured	Literature	Measured	Literature
n-Octane	1.39743	1.39743 (*1*)	125.8	125.7 (*1*)
p-Cresol	1.54046	1.53115@41° C. (*2*) 1.57870@46° C. (*2*) 1.53990 (*6*)	201.9	201.9 (2)

to 30° C. The physical properties of the purified *p*-cresol are given in Table I.

EXPERIMENTAL PROCEDURE

The experimental procedure was the same as reported by Marks and Wingard (*7*) except that the auxiliary heater on the condensate chamber was used. This was connected to a variable transformer and regulated to provide gentle convective heating currents in the condensate. This ensured a homogeneous condensate and considerably reduced the length of time required to attain equilibrium in the still. The heat added in the condensate chamber was compensated for by reducing the heat added in the flash boiler. Evacuated bombs were chilled in ice and used to collect the samples from the still.

ANALYSIS

Samples of *n*-octane and *p*-cresol were weighed and mixed in various concentrations. The refractive index of each sample was determined and a concentration–refractive index curve was constructed (Table II). Samples taken from the still were cooled in an ice bath. The refractive index of each sample was determined and the composition of the still samples determined from the concentration–refractive index curve. The experimental results are given in Table III and presented in Figure 1 as an *y-x* diagram and in Figure 2 as a *T-y-x* diagram.

CONSISTENCY OF DATA

The liquid phase activity coefficient was calculated for each of the experimental points. For this calculation the fugacity of each component in the vapor phase was written as;

$$\hat{f}_i^V = y_i P \phi_i \tag{1}$$

as the fugacity in liquid phase;

$$\hat{f}_i^L = \gamma_i x_i f_i^L \tag{2}$$

Equating fugacities of each component in the vapor and liquid phase gives;

$$\gamma_i = \frac{y_i P \hat{\phi}_i}{x_i f_i^L} \tag{3}$$

At low pressures the vapor phase fugacity coefficients can be expressed as;

$$\ln \hat{\phi}_i = \frac{2}{V} \Sigma_j y_i B_{ij} - \ln z \tag{4}$$

The fugacity of the pure component at the temperature and pressure of the solution is given by $f_i = P\phi_i$. The fugacity coefficient ϕ_i is given by the expression (*12*);

$$\ln \phi_i = \frac{B_{ii} P_i^\circ}{RT} - \ln \frac{P}{P_i^\circ} + \frac{V_i^L}{RT}(P - P_i^\circ) \tag{5}$$

Table II. Refractive Index–Composition Data for *n*-Octane–*p*-Cresol at 20° C.

n_D^{20}	*n*-Octane, Mole %
1.54046	0.00
1.53085	4.58
1.51612	12.27
1.50177	19.97
1.49349	24.60
1.48664	28.85
1.47616	34.62
1.47002	38.99
1.46647	41.51
1.45696	47.89
1.44681	55.48
1.44054	60.38
1.42835	69.61
1.41601	80.48
1.40769	89.28
1.40427	93.04
1.40251	94.67
1.39743	100.00

Table III. Equilibrium Composition–Temperature–Activity Coefficient Data for the *n*-Octane–*p*-Cresol System at 760 Mm. of Hg

n-Octane				
Liquid mole %	Vapor mole %	Temp., ° C.	γ_1	γ_2
0.0	0.0	201.9		1.000
1.5	27.1	189.5	4.621	1.015
2.8	43.8	180.4	4.604	1.051
3.8	50.9	176.0	4.421	1.053
4.8	58.1	171.0	4.371	1.067
6.4	64.6	165.0	4.085	1.113
8.5	73.0	158.0	3.984	1.090
13.7	81.5	148.2	3.444	1.111
16.8	84.4	143.6	3.215	1.148
23.8	87.3	139.1	2.616	1.212
33.7	89.3	135.0	2.093	1.331
39.2	90.5	133.8	1.875	1.383
48.8	91.7	131.8	1.602	1.567
54.3	92.3	130.9	1.485	1.697
57.4	92.5	130.4	1.426	1.979
63.0	93.1	129.5	1.341	1.987
67.2	93.3	129.3	1.269	2.177
69.2	93.7	129.0	1.243	2.212
73.1	93.8	128.8	1.184	2.530
78.7	94.4	128.1	1.126	2.976
84.4	95.2	127.1	1.088	3.594
89.0	96.2	126.7	1.064	4.101
91.7	96.9	126.1	1.048	4.507
94.4	97.8	126.0	1.030	4.822
100	100	125.8	1.000	

The term containing the molal volume of the liquid was neglected as it was negligible compared with the other terms in Equation 5.

The resultant equation for the calculation of the liquid phase activity coefficient is;

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ z} \exp\left[\frac{2}{V} \Sigma_j y_j B_{ij} - \frac{B_{ii} P_i^\circ}{RT}\right] \tag{6}$$

The vapor pressure data for the *n*-octane was taken from the compilation of API Project 44 (*1*) and for *p*-cresol from the compilation of Stull (*11*). Virial coefficients for the pure components were estimated by the correlations of Pitzer and Curl (*9*). The critical constants were taken from the compilation of Kobe and Lynn (*6*), and the acentric factor was determined from the vapor pressure data. The cross virial coefficient was calculated by the method given by Huff and Reed (*4*). Prausnitz (*10*) has proposed a correlation for the polar contribution to the virial

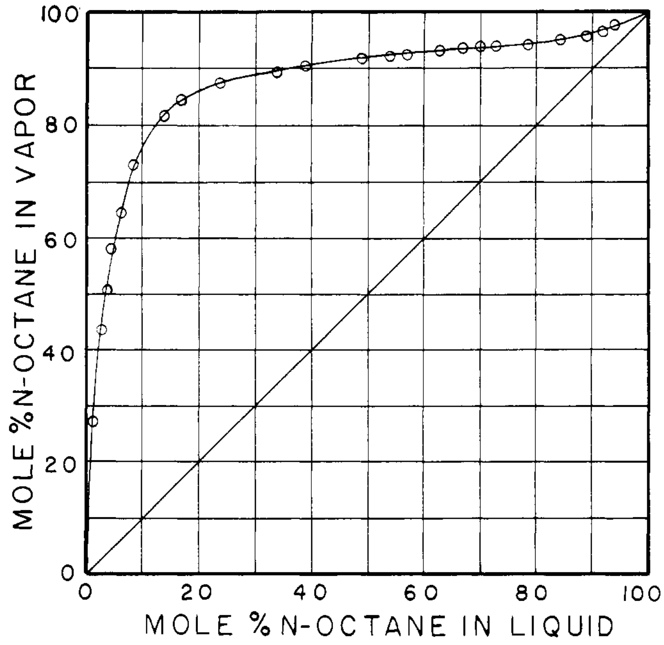

Figure 1. Experimental vapor-liquid composition for the system *n*-octane–*p*-cresol at 760 mm. of Hg pressure

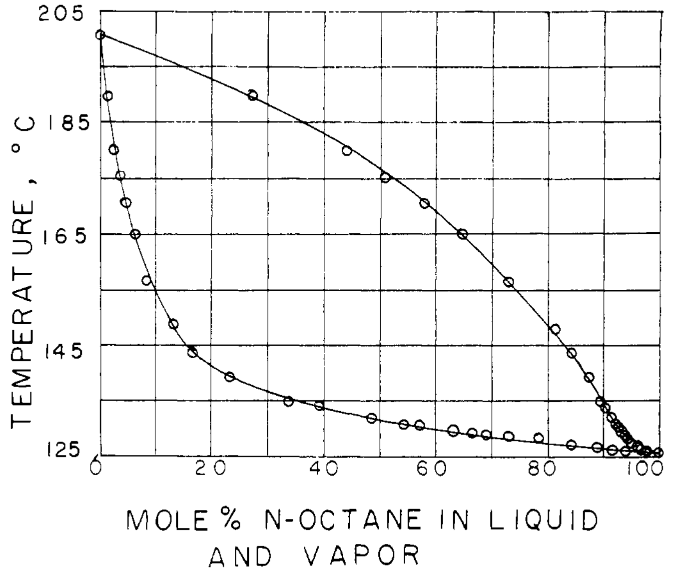

Figure 2. Temperature-composition for the system *n*-octane–*p*-cresol at 760 mm. of Hg pressure

coefficient; however, the large critical volume and small dipole moment of *p*-cresol gives a negligible contribution for his correlation. The molar volume of the vapor phase was calculated from the virial equation for each point. The values of γ_1 and γ_2, as calculated from the experimental data, are given in Table III and shown in Figure 3.

A rigorous test for thermodynamic consistency is obtained by writing the Gibbs-Duhem equation at constant pressure and integrating over composition. The resulting equation is;

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = \int_0^1 \frac{\Delta H}{RT^2}\left(\frac{dT}{dx_1}\right) dx_1 \qquad (7)$$

To apply Equation 7 to vapor-liquid equilibrium, it is necessary to have data on heat of mixing as a function of composition over the temperature range of the boiling mixtures. No heat of mixing data were available in the literature for the system studied here. An examination of the *T*-*X* curve indicated that the right hand side of Equation 7 would be dominated by the temperature derivative, since it is very small in the concentration range where the heat of mixing would be expected to be a maximum, and where the temperature derivative is large, the heat of mixing must go to zero. To test the effect of the temperature derivative, the heat of mixing was assumed to be three times the excess Gibbs free energy (*3*). The right hand integral of Equation 7 was evaluated numerically and was +0.087. The left hand side of Equation 7 was evaluated from Figure 4 and was −0.024. The absolute value of the area in Figure 4 is 0.769, so even if the heat of mixing were considerable for this system, the temperature derivative is so small that the right hand side of Equation 7 would be negligible. Therefore, the small

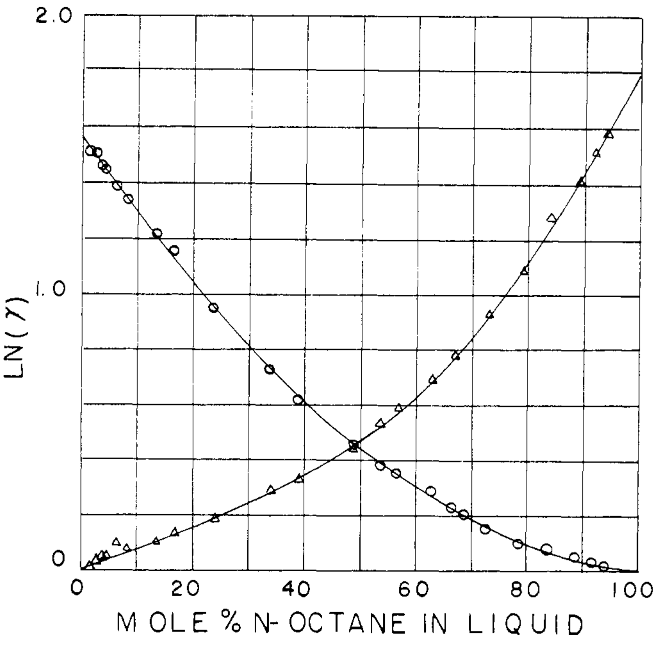

Figure 3. Liquid phase activity coefficients for the system *n*-octane–*p*-cresol at 760 mm. of Hg pressure

○ *n*-Octane

△ *p*-Cresol

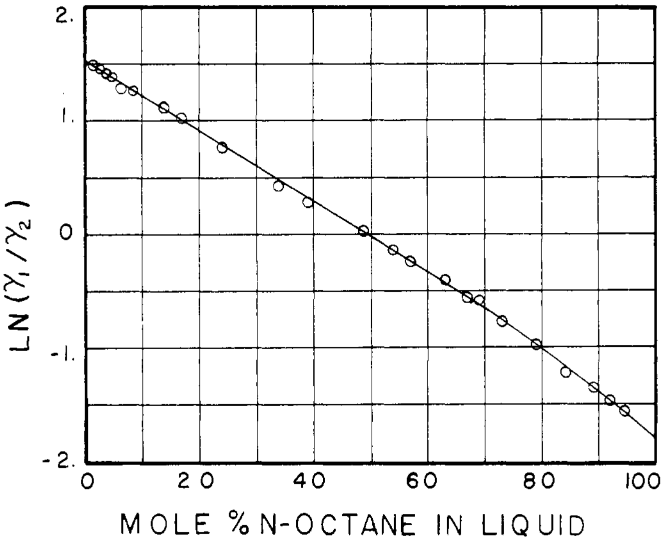

Figure 4. ln γ_1/γ_2 vs. liquid composition for the system *n*-octane–*p*-cresol at 760 mm. of Hg pressure

value obtained for the left hand side of Equation 7 indicates that the data are consistent.

Constants were determined for several correlation equations including the Wilson equation (*13*). However, it was not possible to obtain a satisfactory correlation of the experimental activity coefficients. In particular, the behavior of the *p*-cresol activity coefficient at high cresol concentrations could not be reproduced by any of the equations.

This behavior has been observed in other systems where association is known to occur, and Meehan and Murphy (*8*) have proposed correlating equations for systems involving an associating component. Future work will be concerned with the application of these equations and the measuring of vapor densities and heats of mixing for *p*-cresol with selected hydrocarbons. These measurements will make possible a more rigorous thermodynamic analysis of this system.

NOMENCLATURE

f_i = fugacity of pure component i at the temperature and pressure of the solution
$\hat{f}_i$ = fugacity of component i in mixture
x_i = mole fraction of component i in liquid
y_i = mole fraction of component i in vapor
z = compressibility factor
B_{ii} = second virial coefficient of component i, cc./g.-mole
P = total pressure, atm.
P_i^s = vapor pressure of pure component i, atm.
R = gas constant, 82.06 cc.-atm./g.-mole ° K.
T = temperature, ° K.
V = molar volume of vapor phase
V_i^L = molar volume of pure component i in liquid phase
γ_i = liquid phase activity coefficient of component i
ϕ_i = fugacity coefficient for pure component i
$\hat{\phi}_i$ = fugacity coefficient of component i in solution
ΔH = molar enthalpy change upon mixing

Subscripts

1 = component 1, *n*-octane
2 = component 2, *p*-cresol

Superscripts

v = vapor phase
L = liquid phase

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Critical Temperatures and Pressures of the Ethane–*n*-Butane–*n*-Heptane System

OKAN EKINER and GEORGE THODOS
Northwestern University, Evanston, Ill. 60201

Experimental critical temperatures and pressures have been established for three different mixtures of the ethane–*n*-butane–*n*-heptane system. These critical values, in conjunction with the critical behavior of the corresponding binaries of this ternary system, have been utilized to generate critical temperature and critical pressure relationships which cover the entire composition range of this ternary system. These relationships are presented graphically on triangular plots from which the critical temperature and critical pressure can be readily obtained for any composition of this ternary system.

CONTINUED interest in the experimental determination of the critical properties of hydrocarbon systems having more than two components, has brought to focus the need of investigating a ternary hydrocarbon system. Therefore, this study was limited to the experimental investigation of the critical temperatures and critical pressures of three different mixtures of the ethane–*n*-butane–*n*-heptane system.

The details of the experimental equipment and procedure are described at length eleswhere (*1*). In this study, a visual *PVT* cell using mercury as the pressurizing medium was used to obtain, at isothermal conditions, the relative amounts of the coexisting vapor and liquid phases in equilibrium with each other. The hydrocarbons used were obtained from the Phillips Petroleum Co., were research grade, and were claimed by the manufacturer to have the following purities: ethane, 99.96; *n*-butane, 99.94; and *n*-heptane, 99.78 mole %.

The experimental determination of the critical temperature and critical pressure of a ternary mixture involved the establishment of several pressure-liquid volume per cent isotherms in the vicinity of the critical point. In the course of investigating a mixture, small samples were removed for analysis after increasing the temperature and pressure of the system sufficiently to ensure the existence of a single homogeneous phase. The composition of these samples was determined with a mass spectrometer. Duplicate samples were always taken, and the composition of each mixture was not considered final unless each component agreed within 1 mole %.