Vapor-Liquid Equilibria of the Naphthalene-n-Dodecane and Naphthalene-Dipropylene Glycol Systems at 100Mm. of Mercury

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This investigation of the effect of dipropylene glycol on the vaporization characteristics of naphthalene and *n*-dodecane is part of a program being conducted at the University of Texas. Houser (*5*), Haynes (*3*), Roberts (*10*), and Ward (*12*) have completed similar projects involving vapor-liquid equilibria of hydrocarbons of high molecular weight and other compounds. In this investigation activity coefficients for the naphthalene-*n*-dodecane and naphthalene-dipropylene glycol binaries were calculated from experimental data and checked for thermodynamic consistency. In addition, temperature-miscibility data were determined for the naphthalene-*n*-dodecane-dipropylene glycol system at atmospheric pressure.

APPARATUS

The equipment used in obtaining the vapor-liquid equilibrium samples was a modified Colburn still, similar to that described by Haynes and Van Winkle (*3*).

Pressure was measured to within ±0.5 mm. of mercury, by using a calibrated mercury manometer. An iron-constantan thermocouple and a Leeds & Northrup potentiometer were used to measure temperature to within ± 0.03°C. (± 0.01 mv.).

The temperature-miscibility data for the naphthalene-*n*-dodecane-dipropylene system were determined by using a test tube in which a stirring device and thermometer were placed. The test tube was heated in a mineral oil bath.

PROCEDURE

The procedure for determining vapor-liquid equilibrium data was essentially that described by Haynes and Van Winkle (*3*).

The liquid and vapor samples were analyzed by a Bausch & Lomb precision refractometer and monochromatic sodium *D* light. An electrically heated mineral oil bath maintained the refractometer at a constant temperature.

In determining the temperature-miscibility curves for the naphthalene-*n*-dodecane-dipropylene glycol system at atmospheric pressure a mixture of approximately 10 to 15 grams of the three compounds was weighed into a test tube by using an analytical balance. The test tube containing the mixture of known composition was placed in the mineral oil bath and the Bunsen burner was lighted. The stirring rod and thermometer were placed in the test tube. When the mixture was stirred, it appeared slightly opaque, because of mixing of the two liquid phases. The mixture in the test tube became clear when the two phases were completely miscible; the temperature at this point was recorded and the solution was allowed to cool. At the first appearance of cloudiness, the temperature was recorded and the average of the two temperatures taken as the miscibility temperature for that composition.

DISCUSSION OF RESULTS

Activity coefficients were calculated by the following equation given by Hougen and Watson (*4*).

$$\gamma_1 = \frac{\delta_1 y_1 P_T}{x_1 P_1} \qquad (1)$$

where

γ_1 = activity coefficient of component 1
δ_1 = fugacity coefficient of component 1
y_1 = mole fraction of component 1 in vapor
x_1 = mole fraction of component 1 in liquid
P_T = total pressure
P_1 = vapor pressure of pure component 1 at temperature of liquid

Fugacity coefficients were calculated for each compound by using the reduced charts of Hougen and Watson (*4*). The critical properties of each compound are presented in Table I; for dipropylene glycol the method of Lydersen was used (*8*). All the fugacity coefficients were found to be essentially equal to 1.

The experimental data for the naphthalene-*n*-dodecane system are presented in Table II and those for the naphthalene-dipropylene glycol system in Table III (Figures 1 and 2). Figure 1 indicates that a minimum boiling azeotrope occurs in the system at 66 mole % naphthalene and at 140.2°C. by interpolation of the data. Houser (*5*) found the azeotrope to exist at 67 mole % naphthalene and 140.2°C. These agree within the estimated precision of the data. On Figure 3 are represented the vapor-liquid composition data for both systems, and on Figure 4 the activity coefficient composition data. Activity coefficients calculated from the van Laar equation were used to smooth the experimental activity coefficients in Figure 4. The Redlich-Kister (*9*) thermodynamic consistency test of the smoothed experimental activity coefficients is shown in Figure 5. The positive and negative areas representing smoothed experimental activity coefficients had a deviation of 6% from the average for the naphthalene-*n*-dodecane system.

Thermodynamically consistent curves were calculated by using Equation 1 and visually smoothed liquid composition-temperature data and activity coefficients calculated from the van Laar equation. Activity coefficients calculated from the van Laar equation had the following terminal values: $\gamma_N = 1.5$ at $x_N = 0$, and $\gamma_D = 2.5$ at $x_N = 1.00$. Houser (*5*) correlated his data, using terminal activity coefficients of 1.55 and 2.55, respectively.

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Table I. Physical Properties of Naphthalene, *n*-Dodecane, and Dipropylene Glycol

	Naphthalene		*n*-Dodecane		Dipropylene Glycol	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Index of refraction						
$n_D^{99.6}$	1.58659	1.5822 (*6*)	n_D^{25}1.41956	1.41949 (*11*)	n_D^{20}1.44115	1 1.4440 (*1*)
Density, d_{20}^{20}	...	...	0.750	0.751 (*7*)	1.026	1.0252 (*1*)
Melting point, ° C.						
	80.2	80.29 (*11*)	...	...	...	...
		80.21 (*2*)	...	...	...	...
Vapor pressure^a						
A	6.8151	6.84577 (*11*)	6.9928	6.98059 (*11*)	7.144	...
B	1606.39	1606.529 (*11*)	1625.94	1625.928 (*11*)	1641.11	...
C	189.19	187.227 (*11*)	179.46	180.311 (*11*)	150.00	...
Critical properties						
P_c, atm.	...	39.2 (*2*)	...	17.9 (*11*)	...	34.1 (*8*)
T_c, °K.	...	742 (*2*)	...	659 (*11*)	...	648

^{a}Antoine equation used: $\log_{10} P = A - \frac{B}{C + T}$, P in mm. of mercury; T in ° C.,; A, B, and C are constants.

Table II. Experimental Vapor-Liquid Equilibrium Data for Naphthalene–*n*-Dodecane System

			Activity Coefficients	
x_N	y_N	T, °C.	γ_N	γ_D
5.2	8.2	145.17	1.532	1.001
9.9	14.1	144.53	1.413	1.009
21.0	26.8	142.89	1.314	1.040
26.6	32.0	142.45	1.281	1.056
34.3	38.5	141.90	1.218	1.088
50.7	54.7	140.65	1.228	1.118
62.9	63.2	140.25	1.154	1.225
72.1	69.2	140.39	1.097	1.356
80.8	77.7	141.01	1.076	1.395
85.9	79.8	141.41	1.025	1.696
90.0	84.8	142.11	1.015	1.755
96.0	92.9	143.25	1.003	1.966

Table III. Experimental Vapor-Liquid Equilibrium Data for Naphthalene–Dipropylene Glycol System

Naphthalene, Mole %			Activity Coefficients	
x_N	y_N	T, °C.	γ_N	γ_G
5.4	22.3	163.43	2.247	1.009
11.6	41.1	158.11	2.267	1.010
22.1	57.3	152.47	1.982	1.054
28.0	62.9	149.97	1.864	1.110
43.6	69.9	146.97	1.468	1.321
50.6	74.8	145.18	1.435	1.367
68.7	80.2	143.79	1.189	1.807
80.6	84.4	143.31	1.084	2.344
84.8	86.4	143.17	1.059	2.632
93.3	91.6	143.05	1.025	3.709

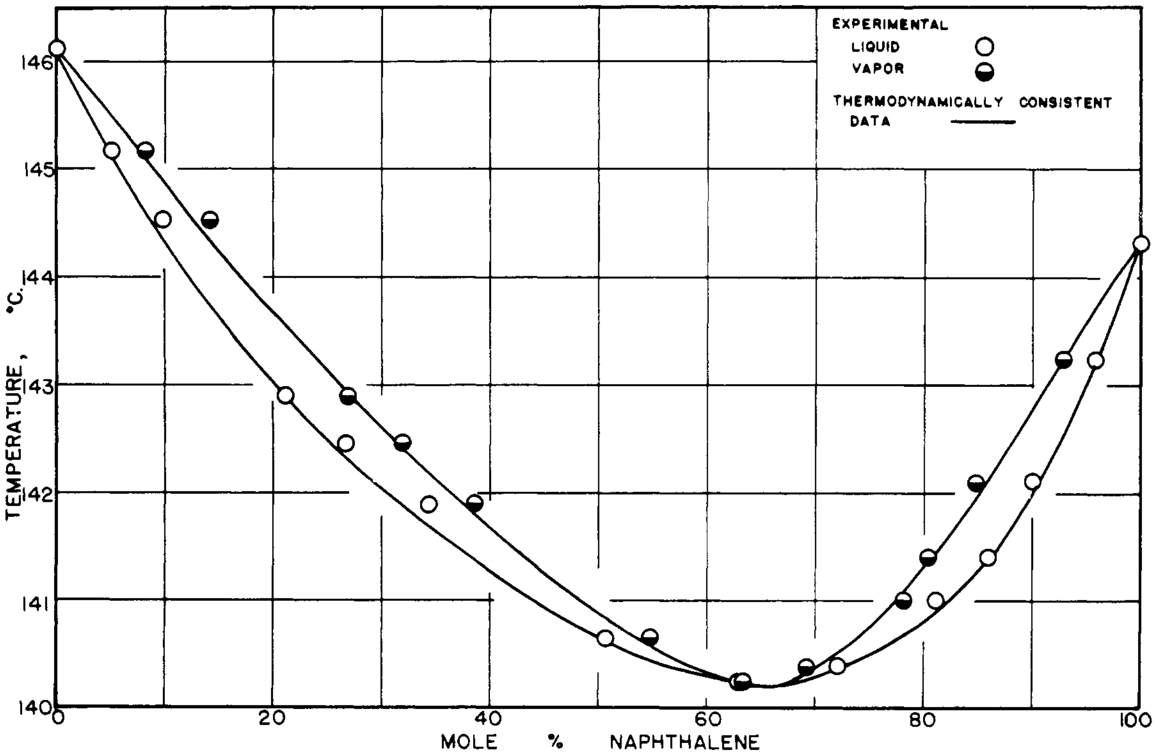

Figure 1. Equilibrium boiling point diagram for naphthalene–*n*-dodecane system

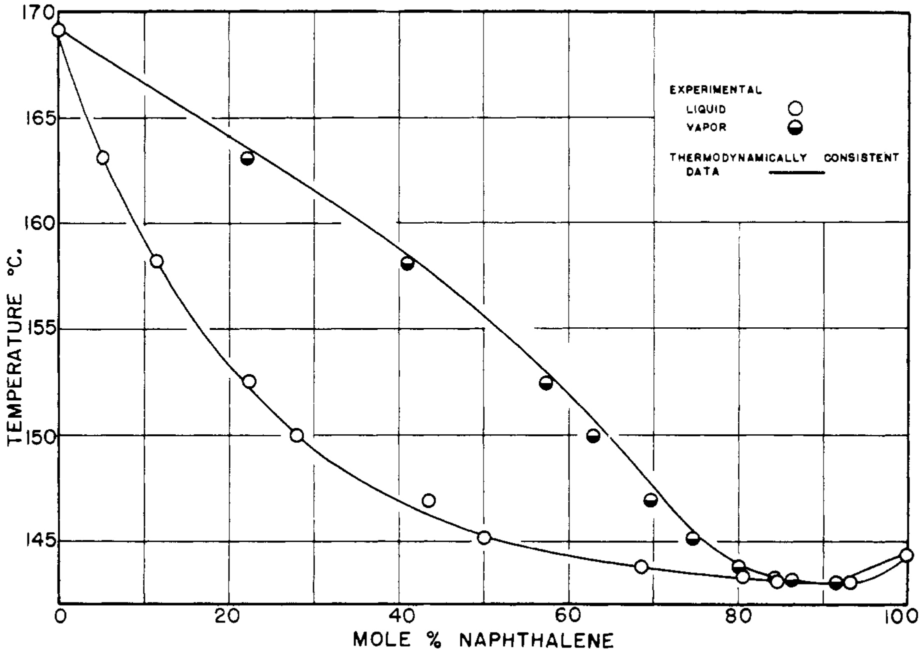

Figure 2. Equilibrium boiling point diagram for naphthalene–dipropylene glycol

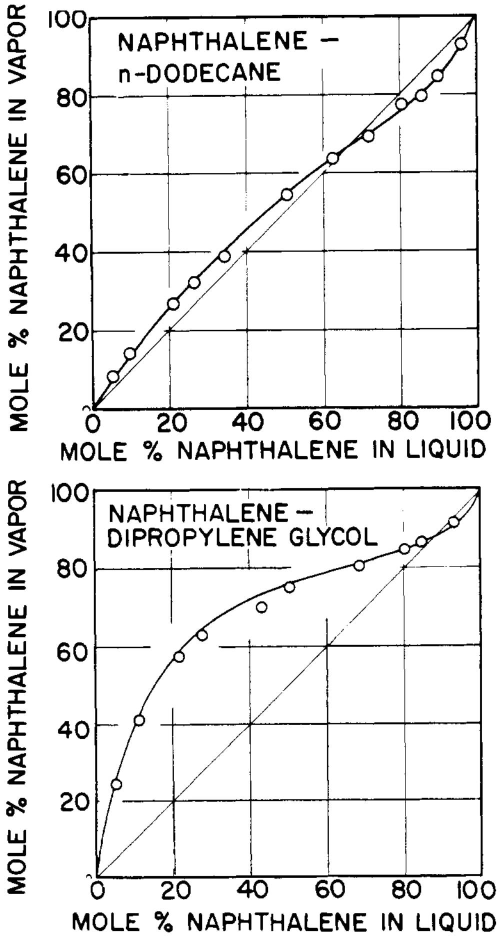

Figure 3. Vapor-liquid equilibrium diagram

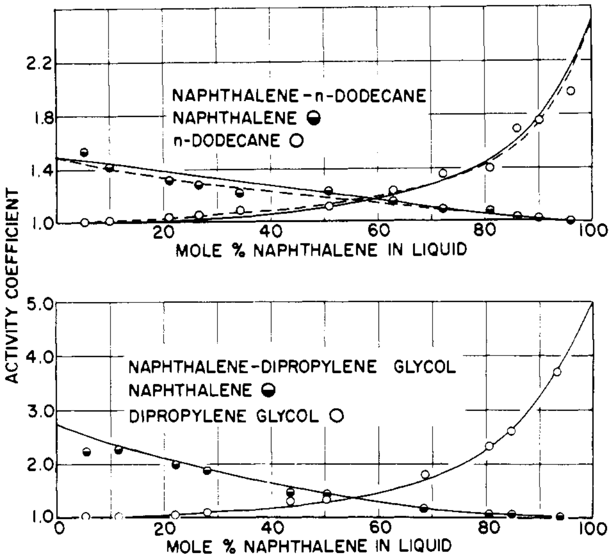

Figure 4. Activity coefficients

Figure 2, the equilibrium-boiling point diagram, indicates that a minimum boiling azeotrope occurs in the naphthalene-dipropylene glycol system at 88 mole % naphthalene and at 142.9° C. by interpolation of data. The liquid composition curve was smoothed visually and vapor composition calculated by using Equation 1 and activity coefficients calculated from the van Laar equation. On Figure 3 is shown the vapor-liquid composition plot for the naphthalene-dipropylene glycol system and on Figure 4 is shown a plot of activity coefficient data and liquid composition data. The experimental activity coefficients were in good agreement with the activity coefficients calculated from the van Laar equation. The van Laar constants, *A* and *B*, were 0.4314 and 0.6990, respectively. On Figure 5 is shown the Redlich-Kister plot for the naphthalene–dipropylene

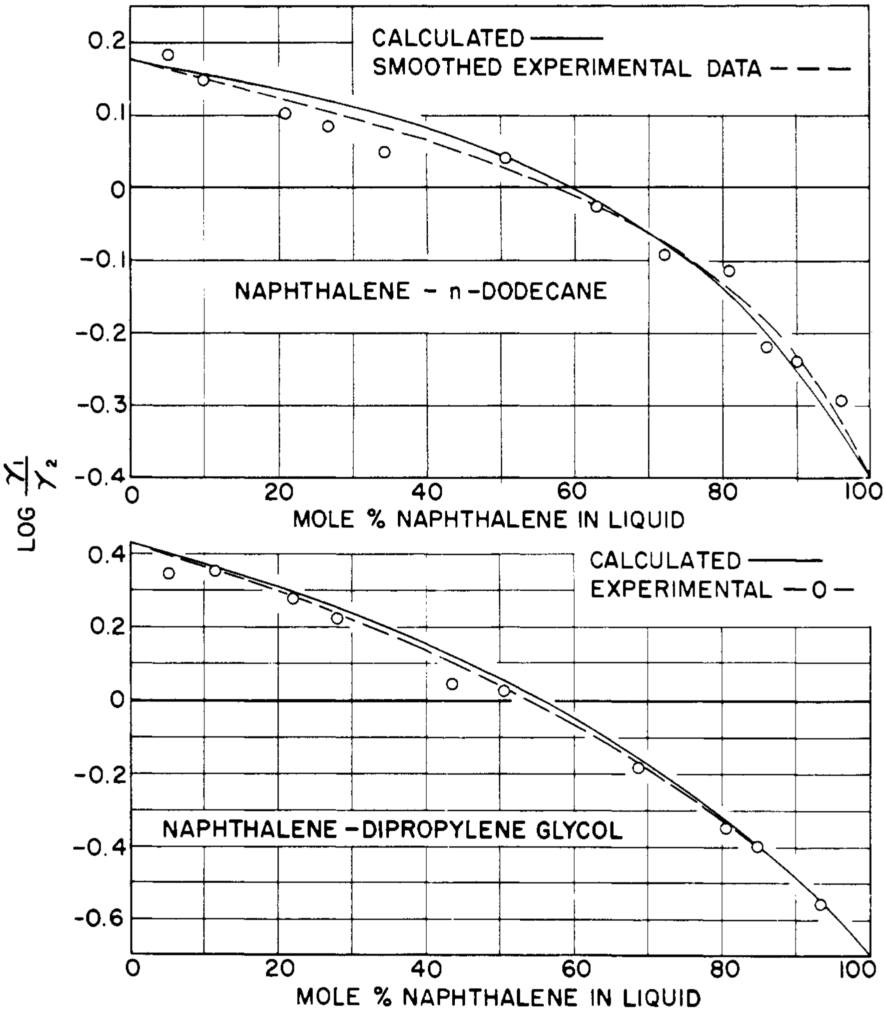

Figure 5. Redlich-Kister plot

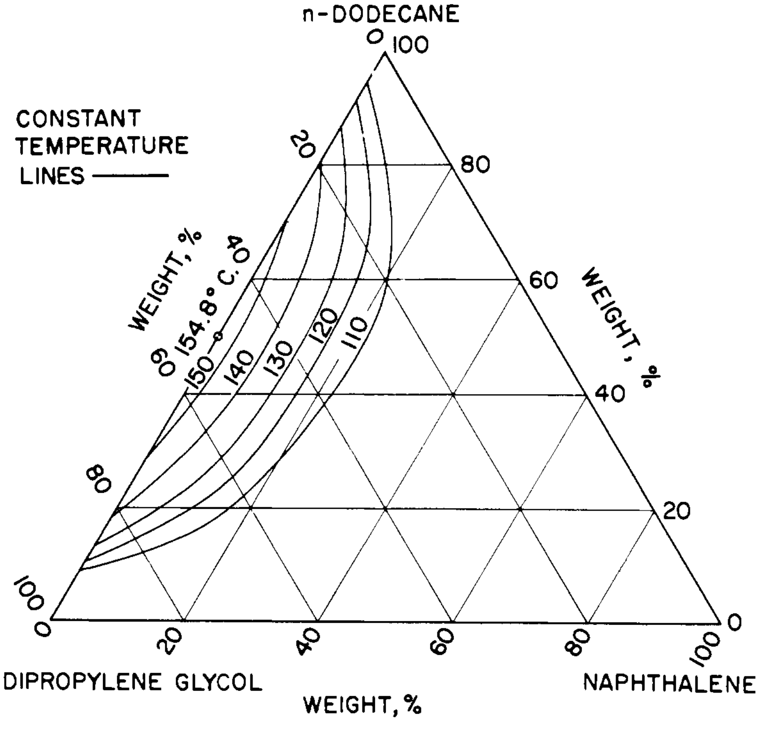

Figure 6. Phase diagram for naphthalene–*n*-dodecane–dipropylene glycol system

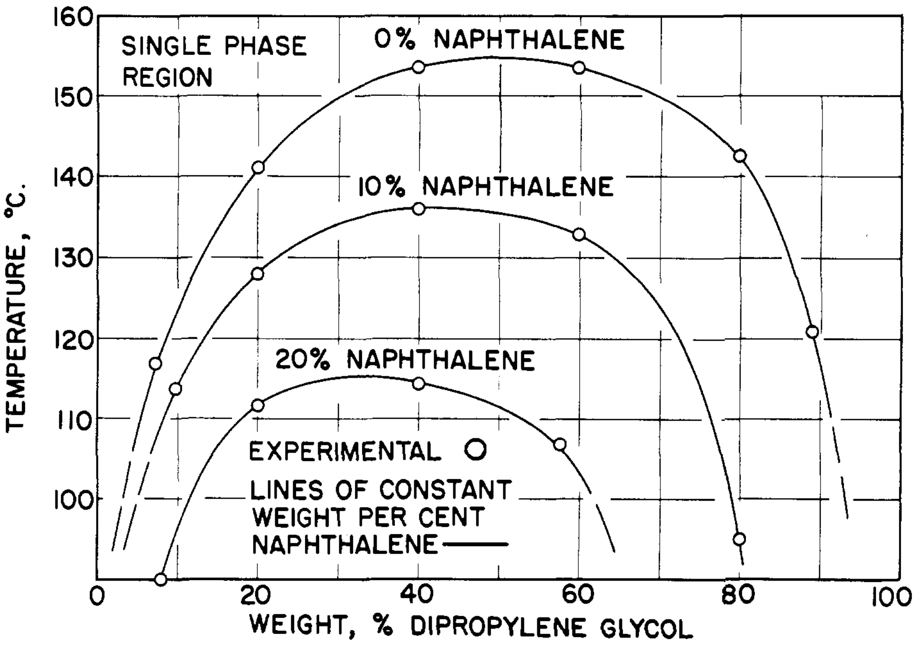

Figure 7. Temperature-composition diagram for naphthalene–n-dodecane–dipropylene glycol system

Table IV. Two-Phase Boundary Data for Naphthalene–n-Dodecane–Dipropylene Glycol System at Atmospheric Pressure

(Composition, weight per cent)

110°C.			120°C.			130°C.		
X_N	X_D	X_G	X_N	X_D	X_G	X_N	X_D	X_G
0.0	94.5	5.5	0.0	91.4	8.6	0.0	86.9	13.1
10.0	81.6	8.4	4.4	85.6	10.0	8.5	71.5	20.0
12.7	77.3	10.0	10.0	76.8	13.2	10.0	67.6	22.4
20.0	62.2	17.8	15.0	65.0	20.0	12.4	57.6	30.0
20.9	59.1	20.0	17.5	52.5	30.0	12.9	47.1	40.0
22.6	47.4	30.0	17.5	42.5	40.0	12.5	37.5	50.0
21.9	38.1	40.0	16.6	33.4	50.0	11.2	28.8	60.0
20.5	29.5	50.0	14.7	25.3	60.0	10.0	25.4	64.6
17.9	22.1	60.0	11.4	18.6	70.0	8.0	22.0	70.0
14.2	15.8	70.0	10.0	17.4	72.6	3.1	16.9	80.0
10.0	13.4	76.6	5.3	14.7	80.0	0.0	13.8	86.2
7.4	12.6	80.0	0.0	10.9	89.1			
0.0	8.7	91.3						

140°C.			150°C.			154.8°C.		
X_N	X_D	X_G	X_N	X_D	X_G	X_N	X_D	X_G
0.0	80.7	19.3	0.0	69.7	30.3	0.0	50.0	50.0
1.0	79.0	20.0	2.3	57.7	40.0			
6.6	63.4	30.0	2.8	47.2	50.0			
8.0	52.0	40.0	2.0	38.0	60.0			
8.0	42.0	50.0	0.0	30.0	70.0			
6.9	33.1	60.0						
3.7	26.3	70.0						
0.6	19.4	80.0						
0.0	18.3	81.7						

glycol system. The positive and negative areas representing the experimental data had a deviation of 4% from the average.

The limits of the two-phase (liquid-liquid) region for the naphthalene–*n*-dodecane–dipropylene glycol system were determined at atmospheric pressure. Figure 6 is a plot of temperature *vs.* weight per cent dipropylene glycol with parameters of 0, 10, and 20 weight % naphthalene. A cross plot of temperature *vs.* weight per cent naphthalene was made to aid in interpolation. Lines of constant temperature were then plotted on the ternary diagram (Figure 7). The points obtained by interpolation and used to plot Figure 7 are presented in Table IV.

The experimental vapor-liquid equilibrium data were estimated to be accurate to: temperature ± 0.05°C., pressure ± 0.5 mm. of mercury, and composition ± 1.0 mole %.

The accuracy of the experimental miscibility-temperature data was estimated to be to ± 1.0 weight % and ± 0.1°C.

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