Vapor-Liquid Equilibrium of *n*-Hexadecane–Bibenzyl–Phenanthrene System at 100 Mm. of Mercury Absolute

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THIS INVESTIGATION is a part of a research program to study vapor-liquid equilibrium of the higher boiling hydrocarbons normally found in petroleum oils. A number of higher boiling hydrocarbon systems (*6, 9, 10, 12, 13, 15*) have been investigated at atmospheric or subatmospheric pressures.

MATERIALS

Table I lists some properties of the components which comprised the binary and ternary mixtures.

Table I. Properties of Materials

	n-Hexadecane	Bibenzyl	Phenanthrene
Purity (by mass spectrometer), %	99.9	99.5	99.8
B.p., ° C.	286.8(*1*)	284.7(*5*)	339.6(*5*)
Density at 101° C.,	0.7163	0.9262	1.068
exptl.	0.7680(*5*)	0.9275(*5*)	1.063(*5*)
Capacitance, ΔC_S	77.35	112.09	142.21
Vapor pressure Antoine constants			
A	7.09955	1884.584	160.044
B	6.76287	1703.236	156.885
C	7.12376	220.011	180.898

The average per cent deviation between experimental and calculated values of vapor pressure for all three components was 0.3%.

APPARATUS AND PROCEDURE

The equilibria were determined in a modified Colburn still (*8*). Because of the possible crystallization of bibenzyl (m.p. 52° C.) and/or phenanthrene (m.p. 100.5° C.), additional heaters were required on the condensate chamber and on each sample drawoff stopcock. The still condensers were also maintained above the melting point of bibenzyl and/or phenanthrene by passing a regulated mixture of steam and water through them.

Equilibrium temperatures were measured by a copper-constantan thermocouple inserted into the thermal well of the equilibrium chamber. A Leeds and Northrup potentiometer in conjunction with a General Electric galvanometer was used to measure the thermocouple e.m.f.

The pressure in the still was indicated by an absolute mercury-in-glass manometer and the height of the mercury legs was measured by means of a cathetometer. The pressure was controlled at 100 mm. of Hg by a Cartesian manostat placed between the still and a vacuum pump.

Approximately 25- to 30-ml. samples were charged to the still. After recirculation of the condensed vapors was attained, the distillation was continued for 85 to 105 minutes to assure equilibrium.

METHODS OF ANALYSIS

Boiling point and dielectric constant were the two physical properties used for measuring compositions of the binary and ternary mixtures.

Because the dielectric constant is a function of chemical composition, the capacitance of a condenser will also be a function of the chemical composition of the medium between its plates, as shown by Equation 1.

$$C = \frac{\epsilon A}{4\pi d} \tag{1}$$

This property of capacitance afforded a method of measuring compositions using a calibrated condenser.

The heterodyne beat method of measuring the capacity of a condenser was used. The general principle of this method has been described by Chien (*3*) and Smyth (*16*). The oscillator and detection circuitry and the dielectric cell design have been described in detail (*11*). The capacitance, ΔC_S, was determined as the difference between the values measured with the cell containing air at 107° C. and with the cell containing a liquid sample at 107° C.

The ternary compositions were determined by measuring the capacitance at 107° C. and boiling point at 100 mm. of Hg absolute pressure. The boiling point apparatus was of the Cottrell (*4*) type.

EQUILIBRIUM DATA

The activity coefficients were calculated from the experimental data using the relationship,

$$\gamma_i = \frac{y_i P_T}{x_i P_i^*} \tag{2}$$

Equation 2 assumes ideal behavior in the vapor state, which is a valid assumption for the systems at 100 mm. of Hg absolute pressure. Experimental vapor-liquid equilibrium data for the three binaries are given in Table II. Table III

Table II. Binary Correlation Constants

Binary	a_{12}	b_{12}	c_{12}
Hexadecane(1)-bibenzyl(2)	0.01660	0.1789	−0.03819
Bibenzyl(1)-phenanthrene(2)	−0.00114	0.0821	0.01686
Phenanthrene(1)-hexadecane(2)	0.05087	0.2894	−0.00312

Table III. Ternary Correlation Constants

$a_{12} = 0.00415$
$b_{12} = 0.17736$
$c_{12} = -0.03791$
$a_{23} = -0.01825$
$b_{23} = 0.08975$
$c_{23} = 0.01560$
$b_{123} = 0.075$
$a_{31} = 0.01410$
$b_{31} = 0.27694$
$c_{31} = -0.01080$

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gives experimental ternary equilibrium data. Included in these tables are the experimental activity coefficients, calculated vapor compositions, calculated activity coefficients of the components, and equilibrium temperature.

CORRELATION OF DATA

The excess free energy per mole of solution in the liquid phase is defined by Equation 3

$$G^E = \sum x_i RT \ln \gamma_i \qquad (3)$$

For ideal solutions where $\gamma_i = 1$, G^E reduces to zero. Differentiating Equation 3 with respect to the mole fraction of any component at constant temperature and pressure yields

$$\left(\frac{\partial G^E}{\partial x_i}\right) P, T, x_{j \neq i, m} = RT\,(\ln \gamma_i - \ln \gamma_m)$$

$$+ RT\left[x_i\left(\frac{\partial\, ln\, \gamma_1}{\partial x_i}\right) + x_2\left(\frac{\partial\, ln\, \gamma_2}{\partial x_i}\right) + \ldots\right]_{P, T, x_{j \neq i, m}} \qquad (4)$$

According to the Gibbs-Duhem equation

$$x_i\left(\frac{\partial\, ln\, \gamma_1}{\partial x_i}\right)_{P, T} + x_2\left(\frac{\partial\, ln\, \gamma_2}{\partial x_i}\right)_{P, T} + \ldots = 0 \qquad (5)$$

Therefore,

$$RT \ln \gamma_i = \Delta G^E + \left(\frac{\partial G^E}{\partial x_i}\right)_{T, P, x_{j \neq i, m}}$$

$$- \sum_{r=1}^{m-1} x_r\left(\frac{\partial G^E}{\partial x_r}\right)_{T, P, x_{j \neq r, m}} \qquad (6)$$

where m = number of components in solution.

Equation 6 makes it possible to relate the dependence of the activity coefficient and solution composition, if the excess free energy can be expressed as a function of the liquid composition.

Redlich and Kister (*14*) related the excess free energy of constant temperature and pressure to liquid composition by a series function

$$\frac{G_{12}^E}{RT} = x_1 x_2[B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \ldots] \qquad (7)$$

for a binary mixture. For the correlation of isobaric equilibrium data Chao and Hougen (*2*) modified the Redlich-Kister correlation by incorporating the Ibl and Dodge (*7*) modification of the Gibbs-Duhem equation. Ibl and Dodge have shown that the correct form of the Gibbs-Duhem relation for a binary solution of isobaric conditions is

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = Z_{12} dx_1 \qquad (8)$$

or

$$(d \ln \gamma_1 / d \ln x_1) = (d \ln \gamma_2 / d \ln x_2) + Z_{12} \qquad (9)$$

The Z term was defined as

$$Z_{12} = \frac{-\Delta H_{12}}{RT^2}\left(\frac{dT}{dx_1}\right)_P \qquad (10)$$

and

$$\Delta H_{12} = H_{12} - x_1 H_1^* - x_2 H_2^* \qquad (11)$$

where H_{12}, H_1^*, and H_2^* are molal enthalpies of the mixture and pure components, respectively.

Differentiating Equation 7 with respect to x_1 gives

$$(dG_{12}^E/RT)/dx_1 = B_{12}(x_2 - x_1) + C_{12}(6x_1x_2 - 1) + \ldots \qquad (12)$$

Since

$$(G_{12}^E/RT) = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (13)$$

$$(dG_{12}^E/RT)/dx_1 = \ln \gamma_1 - \ln \gamma_2 + (d \ln \gamma_1 / d \ln x_1)$$

$$- (d \ln \gamma_2 / d \ln x_2) = \ln(\gamma_1/\gamma_2) + Z_{12} \qquad (14)$$

Equating Equations 12 and 14 and rewriting the result, using the logarithm to the base 10, one obtains

$$\log(\gamma_1/\gamma_2) = a_{12} + b_{12}(x_2 - x_1) + c_{12}(6x_1x_2 - 1) + \ldots \qquad (15)$$

Equation 15 is the Chao-Hougen equation for isobaric equilibrium conditions. When $a_{12} = 0$, the Chao-Hougen equation reduces to the Redlich-Kistler equation.

The constants of Equation 15 were determined by the least squares fit of the experimental data for each binary. The calculated constants are given in Table II, where the number in parenthesis refers to the subscript for the compound in Equation 15.

The equilibrium vapor compositions for each binary were calculated using the following equations:

$$y_1 = \gamma_1 x_1 P_1^* / E \gamma_2 x_2 P_2^* \qquad (16)$$

$$y_2 = 1/E \qquad (17)$$

$$E = (\gamma_1 x_1 P_1^* / \gamma_2 x_2 P_2^*) + 1 \qquad (18)$$

For the n-hexadecane–bibenzyl and the hexadecane–phenanthrene binaries, the average deviation between the calculated and experimental vapor compositions was 0.3 mole %; for the bibenzyl-phenanthrene binary it was only 0.1 mole %.

Figures 1, 2, and 3 are the equilibrium boiling point diagrams for the respective binaries.

The n-hexadecane–bibenzyl binary exhibited a minimum boiling azeotrope at 79.8 mole % bibenzyl and 200.0° C. at 100 mm. of Hg absolute pressure. The binary correlation

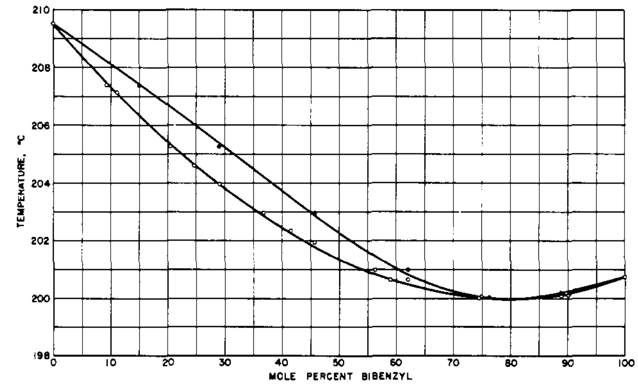

Figure 1. Equilibrium boiling point diagram for n-hexadecane–bibenzyl binary at 100 mm. of Hg absolute

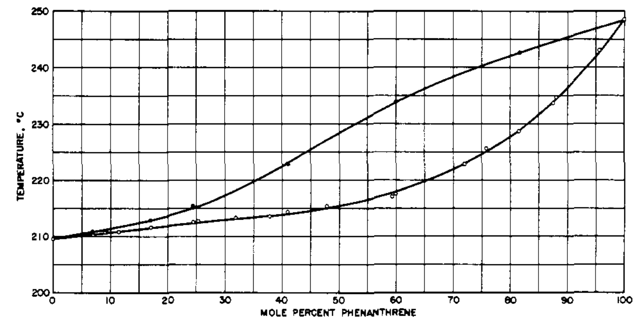

Figure 2. Equilibrium boiling point diagram for n-hexadecane–phenanthrene binary at 100 mm. of Hg absolute

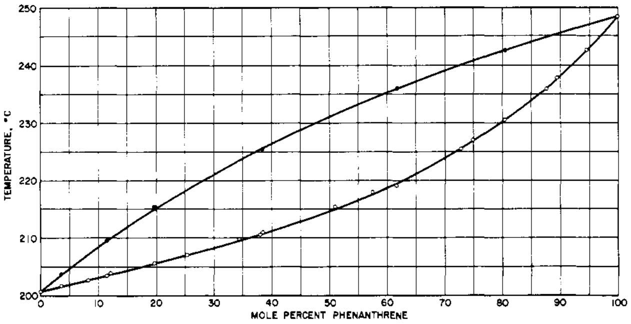

Figure 3. Equilibrium boiling point diagram for bibenzyl-phenanthrene binary at 100 mm. of Hg absolute

predicted the azeotrope at 80.0 mole % bibenzyl, which is in excellent agreement with the measured result.

The solid lines showing the activity coefficient-composition relationship (Figures 4, 5, and 6) are the curves calculated using the binary constants listed in Table II. The dotted lines were derived using the ternary constants.

The excess free energy of a ternary mixture may be expressed by the Redlich-Kister (*14*) expansion and Equation 3 as

$$G_{123}^E = G_{12}^E + G_{23}^E + G_{31}^E + RTx_1x_2x_3[B_{123} + C_1(x_2 - x_3) + C_2(x_3 - x_1) + C_3(x_1 - x_2) + \dots] \quad (19)$$

$$\frac{G_{123}^E}{RT} = x_1\ln\gamma_1 + x_2\ln\gamma_2 + x_3\ln\gamma_3 \quad (20)$$

Using Equations 19 and 20 and the Ibl-Dodge form of the Gibbs-Duhem equation, Chao and Hougen derived the activity coefficient ratio equations for a ternary. The following Chao-Hougen equations were used to correlate the ternary data.

$$\log(\gamma_1/\gamma_2) = a_{12} - b_{12}(x_1 - x_2) + c_{12}([2x_1x_2 - (x_1 - x_2)^2] + x_3[b_{31} - b_{23} - c_{23}(2x_2 - x_3) + c_{31}(x_3 - 2x_1) - b_{123}(x_1 - x_2)] \quad (21)$$

$$\log(\gamma_2/\gamma_3) = a_{23} - b_{23}(x_2 - x_3) + c_{23}[2x_2x_3 - (x_2 - x_3)^2] + x_1[b_{12}]b_{31} - c_{31}(2x_3 - x_1) + c_{12}(x_1 - 2x_2) - b_{123}(x_2 - x_3)] \quad (22)$$

$$\log(\gamma_3/\gamma_1) = a_{31} - b_{31}(x_3 - x_1) + c_{31}[2x_3x_1 - (x_3 - x_1)^2] + x_2[b_{23} - b_{12} - c_{12}(2x_1 - x_2) + c_{23}(x_2 - 2x_3) - b_{123}(x_3 - x_1)] \quad (23)$$

where subscripts 1, 2, and 3 refer to *n*-hexadecane, bibenzyl, and phenanthrene, respectively. Only one ternary constant, b_{123}, was required to correlate the ternary equilibrium data for this system.

To calculate the equilibrium vapor composition of the ternary, Equations 16 to 18 are rewritten as

$$y_1 = 1/E \quad (24)$$

$$y_2 = \gamma_2x_2P_2^*/\gamma_1x_1P_1^*E \quad (25)$$

$$y_3 = \gamma_3x_3P_3^*/\gamma_1x_1P_1^*E \quad (26)$$

$$E = 1 + (\gamma_2x_2P_2^*/\gamma_1x_1P_1^*) + (\gamma_3x_3P_3^*/\gamma_1x_1P_1^*) \quad (27)$$

Since only two of the three activity coefficient ratio expressions for the ternary are needed in conjunction with Equations 24 to 27 to calculate the vapor compositions, Equation 23, for example, may be derived from Equations 24 and 22. By adding Equations 21 and 22 to obtain Equation 23 a necessary relationship of the constants a_{12}, and a_{31} is obtained, which is shown by Equation 28,

$$a_{12} + a_{23} + a_{31} = 0 \quad (28)$$

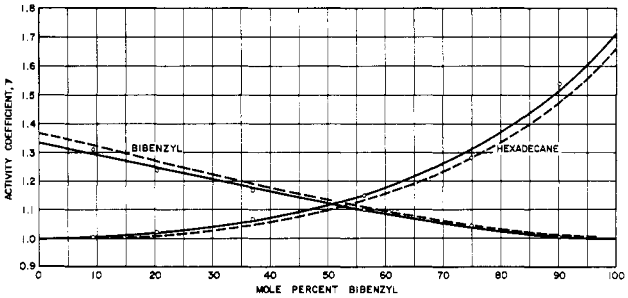

Figure 4. Activity coefficients for *n*-hexadecane–bibenzyl binary at 100 mm. of Hg absolute

——— Binary constants

-------- Ternary constants

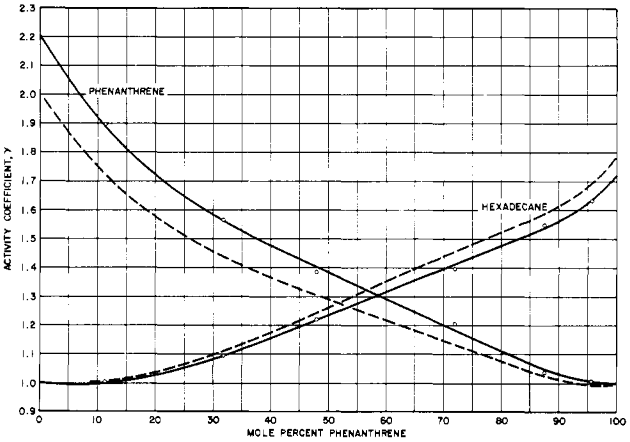

Figure 5. Activity coefficients for *n*-hexadecane–phenanthrene binary at 100 mm. of Hg absolute

——— Binary constants

-------- Ternary constants

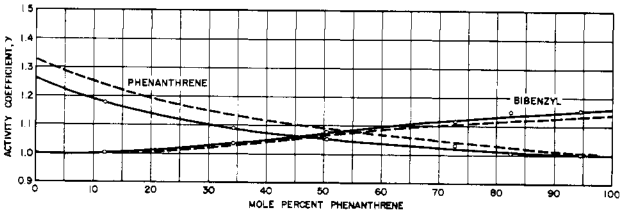

Figure 6. Activity coefficients for bibenzyl-phenanthrene binary at 100 mm. of Hg absolute

——— Binary constants

-------- Ternary constants

The Chao-Hougen correlating constants for Equations 21 to 23 were evaluated using the combined binary and ternary data and the condition given by Equation 28 (Table III).

The composition of the *n*-hexadecane-bibenzyl azeotrope as predicted by the ternary correlation constants was 82.5 mole % bibenzyl.

The calculated activity coefficients for *n*-hexadecane, bibenzyl, and phenanthrene in the ternary mixture as a function of the equilibrium liquid compositions are shown in Figures 7, 8, and 9, respectively.

CONCLUSIONS

The Chao-Hougen method for correlating isobaric vapor-liquid equilibrium data at low pressures resulted in good agreement between the measured and calculated equilibrium vapor compositions. Because this method employs

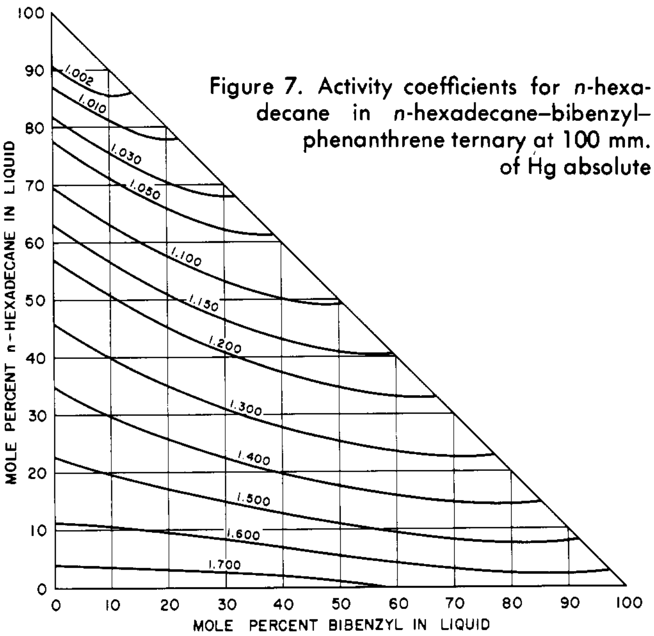

Figure 7. Activity coefficients for *n*-hexadecane in *n*-hexadecane–bibenzyl–phenanthrene ternary at 100 mm. of Hg absolute

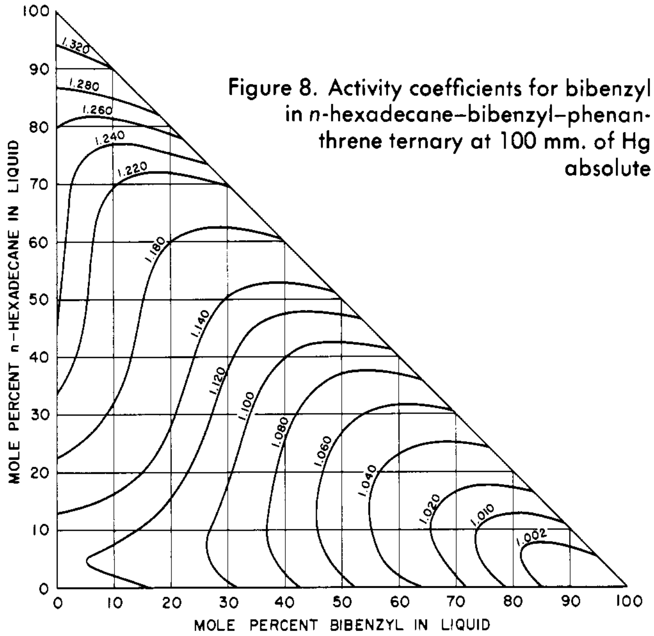

Figure 8. Activity coefficients for bibenzyl in *n*-hexadecane–bibenzyl–phenanthrene ternary at 100 mm. of Hg absolute

the Ibl-Dodge modification of the Gibbs-Duhem equation, the Chao-Hougen expression is applicable not only for systems which obey the Gibbs-Duhem equation but also for systems where

$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 + \ldots = 0$$

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NOMENCLATURE

A, B, C = Antoine equation constants
A = surface area of an electrical conductor
$a_{12}, b_{12}, c_{12}, b_{123}$ = constants in Chao-Hougen (2) equation
$B_{12}, C_{12}, D_{12}, B_{123}, C_1, C_2, C_3$ = constants in Redlich-Kister (*14*) equation
C = capacitance of condenser
ΔC_S = dielectric cell capacitance
d = distance between two electrical conductors
G^E = excess free energy per mole of solution
H = molal enthalpy of mixture
H^* = molal enthalpy of pure compound
ΔH = molal heat of mixing
j = any component
m = number of components insolution
P = total pressure
P^* = vapor pressure
R = gas constant
t = temperature, C.
T = absolute temperature
x = mole fraction in liquid
y = mole fraction in vapor

Greek Letters

γ = activity coefficient
ϵ = dielectric constant

Subscripts

i = ith component
1, 2, 3 = components
12, etc. = binary mixture of components 1 and 2
123 = ternary mixture of components 1, 2, and 3

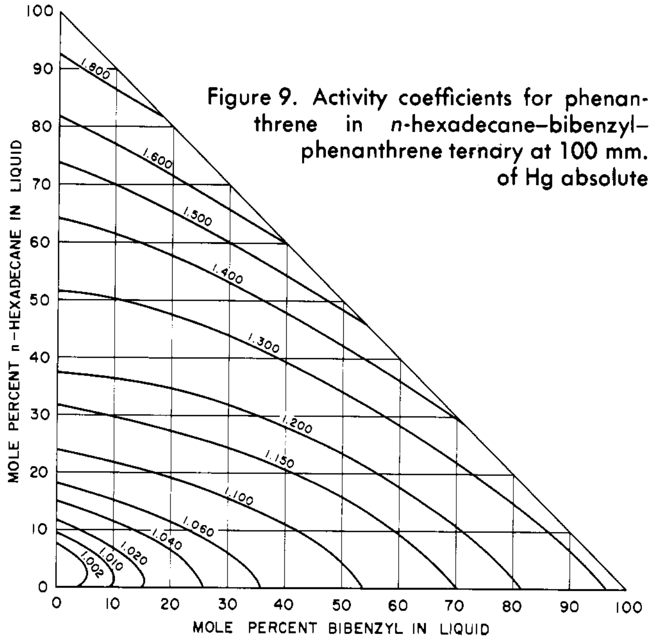

Figure 9. Activity coefficients for phenanthrene in *n*-hexadecane–bibenzyl–phenanthrene ternary at 100 mm. of Hg absolute

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