

Figure 3. Compressibility factor for the dew-point gas

ACKNOWLEDGMENT

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NOMENCLATURE

d = differential operator
 H = enthalpy, B.t.u./lb.
 l = latent heat of vaporization, B.t.u./lb.
 $l \ddot{}$ = residual latent heat of vaporization, B.t.u./lb.

m = weight of material, lb.
 P'' = vapor pressure, p.s.i.a.
 $[Q]$ = heat added per unit weight of material withdrawn under idealized conditions, B.t.u./lb.
 Q_{12}^* = net energy added to calorimeter under ideal conditions, B.t.u.
 T = thermodynamic temperature, °R.
 t = temperature, °F.
 V = specific volume, cu. ft./lb.

Subscripts

g = gas phase
 l = liquid phase
 P = pressure
 T = temperature
 1 = initial state
 2 = final state

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Vapor Liquid Equilibrium at Atmospheric Pressure: The Ternary System Benzene-Ethanol-*n*-Hexane

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IN THIS STUDY vapor-liquid equilibrium data at atmospheric pressure for the ternary system benzene-ethanol-*n*-hexane were determined. This is the fourth ternary system investigated involving the compounds benzene, ethanol, *n*-hexane, and methylcyclohexane. The other three ternary systems were studied by Sinor and Weber (14), Belknap and Weber (1), and Kaes and Weber (7). Quaternary data have also been obtained in the previous investigations. The six binary systems which can be made with these four compounds have been investigated (5, 10, 11, 12, 14, 15).

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The ternary system in the present study showed large deviations from ideal liquid phase behavior, although no ternary azeotrope was found. Also, as a part of this investigation, an attempt was made to predict the ternary equilibrium data from binary vapor-liquid equilibrium data by the method proposed by Black (2, 3).

EXPERIMENTAL

Purity of Compounds. The benzene and *n*-hexane used were pure grade materials of a minimum of 99 mole % purity (Phillips Petroleum Co.). The ethyl alcohol (U. S. Industrial Chemical Co.) and the hydrocarbons were not

Vapor-liquid equilibrium data at atmospheric pressure have been determined for the system benzene-ethanol-*n*-hexane. The experimental results have been compared with results obtained by Black's method for the prediction of multicomponent data from binary vapor-liquid equilibrium data. The comparisons are satisfactory.

Table I. Properties of Pure Compounds

	Refractive Index		Boiling Point 760 Mm. of Hg	
	Exptl.	Lit.	Exptl.	Lit.
<i>n</i> -Hexane	1.3723	1.37226(13)	68.7	68.74(13)
Ethanol	1.3591	1.35914(4)	78.3	78.33(4)
Benzene	1.4979	1.49790(13)	80.1	80.10(4)

purified further. Physical constants for the materials are shown in Table I.

Procedure. Vapor-liquid equilibrium data were obtained using a Braun still as described by Hipkin and Myers (6) and the experimental technique outlined by these authors was followed. Nitrogen was used to maintain the operating pressure in the still at 760 ± 0.5 mm. of Hg. The pressure was controlled by a manostat and measured on an absolute mercury manometer.

Temperatures were measured by a copper-constantan thermocouple used with a Leeds and Northrup Type K potentiometer. The reported temperatures are accurate within $\pm 0.1^\circ\text{C}$. *n*-Heptane was used as the jacket fluid. The pressure in the jacket was regulated so that the boiling temperature of the *n*-heptane was 0.1°C . or less, greater than the boiling temperature of the test sample.

The ternary samples were analyzed by gas chromatography, using a Perkin-Elmer model 154-C Vapor Fractometer. Helium was the carrier gas. A 2-meter column packed with Perkin-Elmer material "F" was used. The active agent on the column packing material is tetraethyl-glycol dimethyl ether.

Operating conditions were the same as previously reported (7). Approximately 30 minutes were required for the analysis of a sample, and the peaks were completely separated on the chromatograms.

As previously reported (1, 7, 14) calibration of the Vapor Fractometer was necessary, because the peak areas and mole fractions of the components are not directly proportional. Again, a number of samples of known compositions were run through the Fractometer and calibration constants

determined. The constants were then used to back the calculated compositions. The average deviation was ± 0.003 mole fraction, or less, for each component. Consequently, the error in the reported composition can be estimated, conservatively, to be something less than ± 0.005 mole fraction.

VAPOR-LIQUID EQUILIBRIUM DATA

Liquid phase activity coefficients for the components of the ternary system were calculated by two methods. First, from the relationship:

$$\gamma_L = \frac{y_i P}{x_i P^0} \quad (1)$$

was used and second, the more rigorous relationship:

$$\gamma_L = \frac{y_i}{x_i} \frac{\phi_i}{\phi_i \exp[(V/RT)(P - P^0)]} \times \frac{P}{P^0} \quad (2)$$

The liquid phase activity coefficients calculated by Equation 2 reflect only departures from the Lewis and Randall rule, assuming the fugacities of the pure components and partial fugacities can be evaluated correctly. The coefficients calculated by Equation 1 represent a combination of all the deviations from ideal behavior, liquid and gas phase.

The fugacities of pure components and partial fugacities of components in mixtures were calculated from Black's (2) equation of state:

$$V = RT/P + b - a\xi/RT \quad (3)$$

and

$$V_m = RT/P + \sum b_i y_i - \left(\sum (a_i \xi_i^*)^{0.5} y_i \right)^2 / RT - \left(\sum (a_i \bar{\xi}_i)^{0.5} y_i \right)^2 / RT \quad (4)$$

The generalized constants given by Black were used in the calculations. The activity coefficients, calculated from Equations 1 and 2, are reported in Table II. Temperatures and compositions, liquid and vapor phase, are also given. The results show for any given case the two values of the

Table II. Experimental Vapor-Liquid Equilibrium Data
Benzene-Ethanol-*n*-Hexane System at 760 Mm. of Hg

Temp., ° C.	Liquid-Phase Mole Fraction			Vapor-Phase Mole Fraction			Uncorrected Liquid-Phase Activity Coefficients, Equation 1			Corrected Liquid-Phase Activity Coefficients, Equation 2		
	Benzene	Ethanol	<i>n</i> -Hexane	Benzene	Ethanol	<i>n</i> -Hexane	Benzene	Ethanol	<i>n</i> -Hexane	Benzene	Ethanol	<i>n</i> -Hexane
60.9	0.108	0.052	0.840	0.077	0.240	0.683	1.34	9.55	1.05	1.32	9.47	1.04
61.8	0.221	0.046	0.733	0.159	0.230	0.611	1.31	9.92	1.04	1.29	9.85	1.04
59.9	0.218	0.185	0.597	0.154	0.300	0.546	1.38	3.52	1.22	1.35	3.48	1.21
61.7	0.327	0.073	0.600	0.224	0.249	0.527	1.25	6.82	1.10	1.23	6.76	1.09
60.7	0.303	0.307	0.390	0.229	0.333	0.438	1.43	2.27	1.46	1.41	2.24	1.45
64.7	0.625	0.079	0.296	0.421	0.245	0.334	1.11	5.47	1.28	1.09	5.44	1.28
66.2	0.719	0.183	0.098	0.520	0.325	0.155	1.13	2.92	1.72	1.12	2.90	1.73

activity coefficients are practically identical, the differences between the values being less than the experimental error.

Vapor phase activity coefficients,

$$\gamma_{ia} = \frac{F_i}{f_{ia} y_i} \quad (5)$$

were also calculated, but were unity for all practical purposes and are not reported.

The experimental data are shown graphically. Figure 1 is a bubble point diagram and Figures 2-4 show, respectively, γ 's for benzene, ethanol, and *n*-hexane, as functions of composition.

As in previous investigations, the data were checked for internal consistency by the method proposed by Krishnamurthy and Rao (8, 9). The equations employed were:

$$Q = \frac{\Delta G^E}{2.3RT} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \quad (6)$$

If Equation 6 is differentiated, x_3 assuming a constant value, the Gibbs-Duhem equation substituted, and use made of the relationship $dx_1 = -dx_2$, the result is:

$$\frac{dQ}{dx_1} = \log (\gamma_1/\gamma_2) \quad (7)$$

integrating

$$\int_{Q'}^{Q''} dQ = \int_{x_1 \geq 0 = x_1'}^{x_1 \leq (1-x_2) = x_1''} \log (\gamma_1/\gamma_2) dx_1 \quad (8)$$

If the percentage deviation, D , from the equality of Equation 8 is defined as:

$$D = \frac{(Q'' - Q') - \int_{x_1'}^{x_1''} \log (\gamma_1/\gamma_2) dx_1}{\sum'} \times 100 \quad (9)$$

then the consistency checks gave the results presented in Table III. With the exception of those checks involving a constant liquid phase composition of ethanol, the results are good. As expected, those checks in which the quantity dT/dx changed sign over the range of composition involved produced the smaller deviations and those in which dT/dx did not change in sign tended to have larger deviations. In the case of ethanol, the parameters of constant values of the activity coefficients are roughly parallel with the composition parameters. This tends to reduce the value of $Q'' - Q'$ as well as the net area under the $\log (\gamma_1/\gamma_2)$ vs. x curve; consequently, the degree of accuracy is reduced.

A problem of interest in the area of vapor-liquid equilibrium work is the prediction of multicomponent data from binary data. Black (2) has proposed the most recent method to accomplish this. In view of the interest in the

Table III. Result of Internal Consistency Checks

Mole Fraction (x_3 , Equation 8)	"D" (defined by Equation 9)		
	Benzene	<i>n</i> -Hexane	Ethanol
0.1	12.2	0.3	
0.2	2.7	7.2	15.0
0.4	2.1	2.5	15.1
0.5	4.9	5.9	
0.6	6.6	1.9	

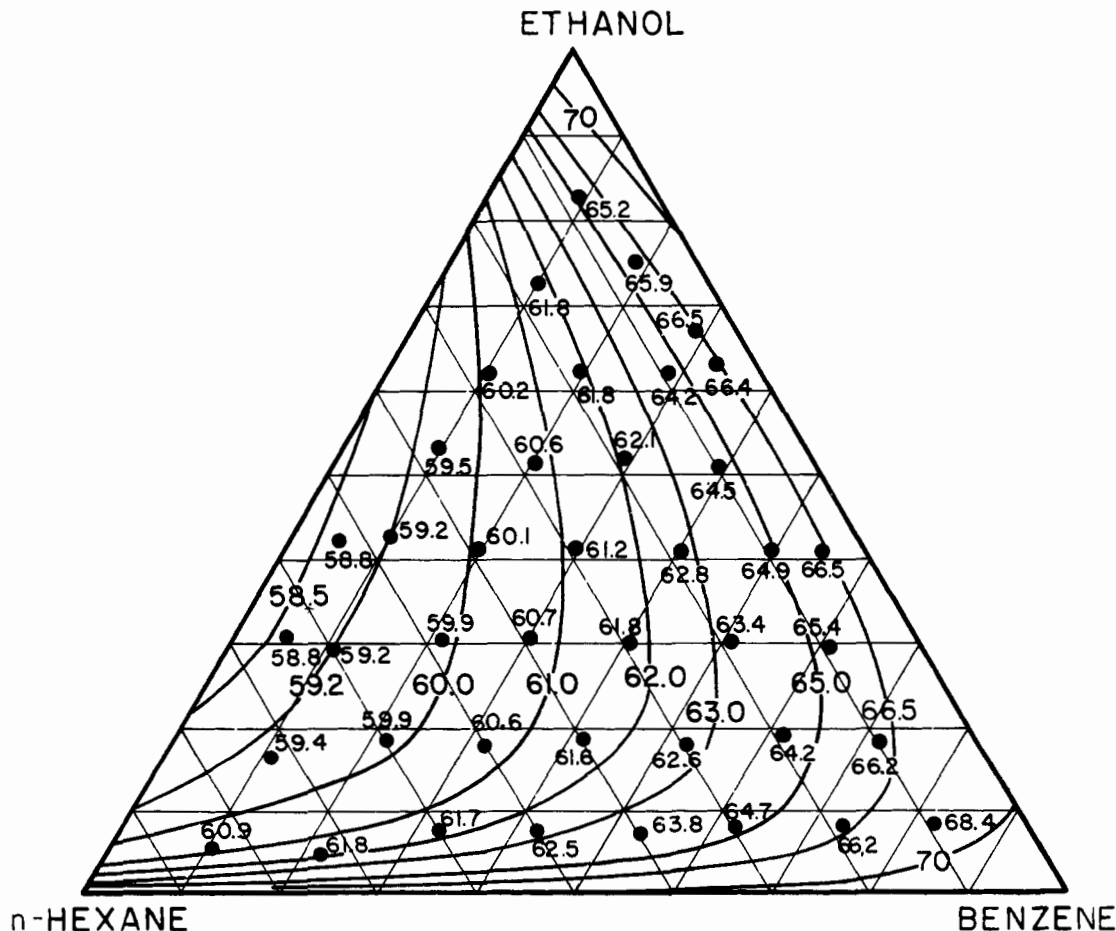


Figure 1. Bubble point diagram of the *n*-hexane-ethanol-benzene system

problem and since vapor-liquid equilibrium data for the binary systems *n*-hexane-benzene (10), ethanol-benzene (15), and *n*-hexane-ethanol (14) are available, an attempt was made, using Black's method, to predict the vapor-liquid equilibrium relationship for the ternary system investigated in this work.

To predict the ternary data, constants, labelled c_{ij} and a_{jk} and a_{ij} by Black, for the three binary systems must be obtained. Due to the scatter of the experimental data, this presented a problem. To obtain the best value of the binary constants the following technique was used:

An initial value of c_{ij} was assumed.

With c_{ij} established, and since a linear relationship is assumed between:

$$[\ln(\gamma_{Li}) - E_i]^{1/2} \text{ and } [\ln(\gamma_{Lj}) - E_j]^{1/2}$$

namely:

$$[\ln(\gamma_{Li}) - E_i]^{1/2} = a_{ij} - (a_{ji}/a_{ij}) [\ln(\gamma_{Lj}) - E_j]^{1/2} \quad (10)$$

the constants a_{ij} and a_{ji} may be calculated using a standard binary linear regression technique.

The above procedure is then followed while varying c_{ij} in such a manner as to converge on the maximum correlation coefficient.

In order to apply the above technique safely, 30 to 40 points are required. This necessitated selecting data from graphical presentations, because insufficient experimental data were presented.

To predict activity coefficients in the ternary system by Black's method, the relationship:

$$a_{jk}^2/a_{ki}^2 = (a_{ij}^2/a_{ji}^2)(a_{jk}^2/a_{ki}^2) \quad (11)$$

must hold. This equality did not exist between the constants

obtained by the method outlined in the previous paragraph. Hence, the benzene-ethanol data were adjusted so that Equation 11 was satisfied. This system was adjusted because it was the one most poorly established. The adjusted constants and the experimental and predicted activity coefficients are reported in Table IV as well as the experimental and predicted vapor phase compositions and bubble point temperatures.

For the ternary system, 41 experimental determinations were made and all of the results were compared with the predictions obtained by the method of Black (3). In eighteen instances the experimental and predicted values of the vapor phase composition agreed with ± 1 mole %, and the maximum difference was 3.6 mole %. Also, 13 of the predicted bubble point temperatures agreed within $\pm 0.04^\circ \text{C.}$ of the experimentally determined temperatures.

In conclusion, vapor-liquid equilibrium data at atmospheric pressure for the system benzene-ethanol-*n*-hexane have been presented. These data appear internally consistent. Further, the method proposed by Black for the prediction of ternary equilibrium data from binary data has been tested on the system with fair to good agreement resulting.

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NOMENCLATURE

- D = deviation in per cent, Equation 9
- E_i = a quantity introduced by Black (3)
- ΔG^E = excess molal free energy of mixing
- P = total pressure

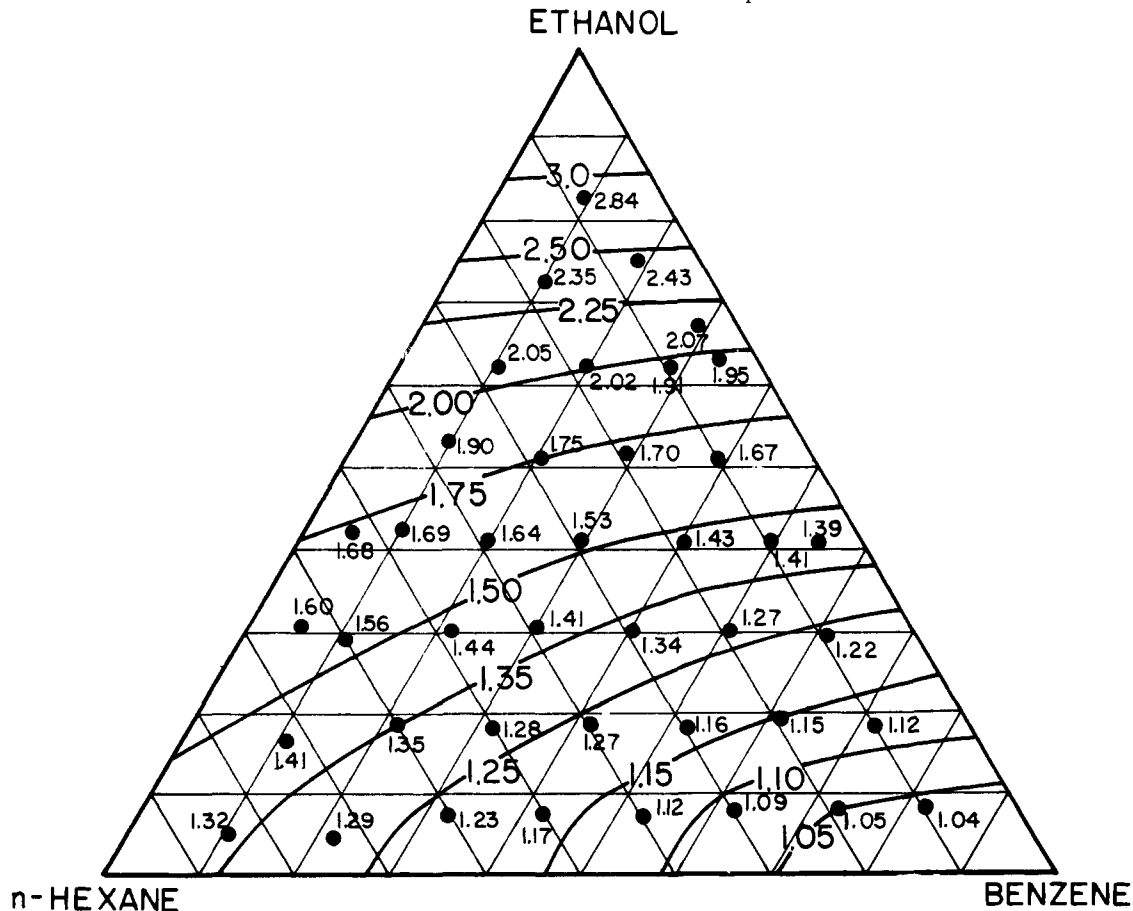


Figure 2. Benzene activity coefficients vs. liquid phase composition of the *n*-hexane-ethanol-benzene system

Table IV. Experimental and Predicted Vapor-Liquid Equilibrium Data

Benzene-Ethanol-*n*-Hexane System at 760 Mm. of Hg

Component	Liquid Phase Mole Fraction	Corrected Vapor-Phase Mole Fraction		Liquid-Phase Activity Coefficients		Bubble-Point Temp., °C.	
		Observed	Predicted	Observed	Predicted	Observed	Predicted
		Ethanol	0.052	0.240	0.242	9.47	9.37
Benzene	0.108	0.077	0.175	1.32	1.27	60.9	61.3
<i>n</i> -Hexane	0.840	0.683	0.683	1.04	1.02		
Ethanol	0.046	0.230	0.209	9.85	8.58		
Benzene	0.221	0.159	0.159	1.29	1.24	61.8	62.6
<i>n</i> -Hexane	0.733	0.611	0.632	1.04	1.04		
Ethanol	0.185	0.300	0.316	3.48	3.63		
Benzene	0.218	0.154	0.143	1.35	1.25	59.9	60.0
<i>n</i> -Hexane	0.597	0.546	0.541	1.21	1.19		
Ethanol	0.073	0.249	0.243	6.76	6.39		
Benzene	0.327	0.224	0.223	1.23	1.19	61.7	62.5
<i>n</i> -Hexane	0.600	0.527	0.543	1.09	1.08		
Ethanol	0.307	0.333	0.334	2.24	2.23		
Benzene	0.303	0.229	0.221	1.41	1.34	60.7	61.0
<i>n</i> -Hexane	0.390	0.438	0.445	1.45	1.46		
Ethane	0.079	0.245	0.251	5.44	5.47		
Benzene	0.625	0.421	0.422	1.09	1.08	64.7	65.2
<i>n</i> -Hexane	0.296	0.334	0.327	1.28	1.23		
Ethane	0.183	0.325	0.345	2.90	3.31		
Benzene	0.719	0.520	0.520	1.12	1.13	66.2	65.8
<i>n</i> -Hexane	0.098	0.155	0.135	1.73	1.15		

Constants: $a_{13} = 1.550$ $a_{31} = 1.372$ $c_{13} = c_{31} = +0.530$
 $a_{12} = 1.513$ $a_{21} = 1.117$ $c_{12} = c_{21} = +0.178$
 $a_{23} = 0.6023$ $a_{32} = 0.7225$ $c_{23} = c_{32} = -0.034$

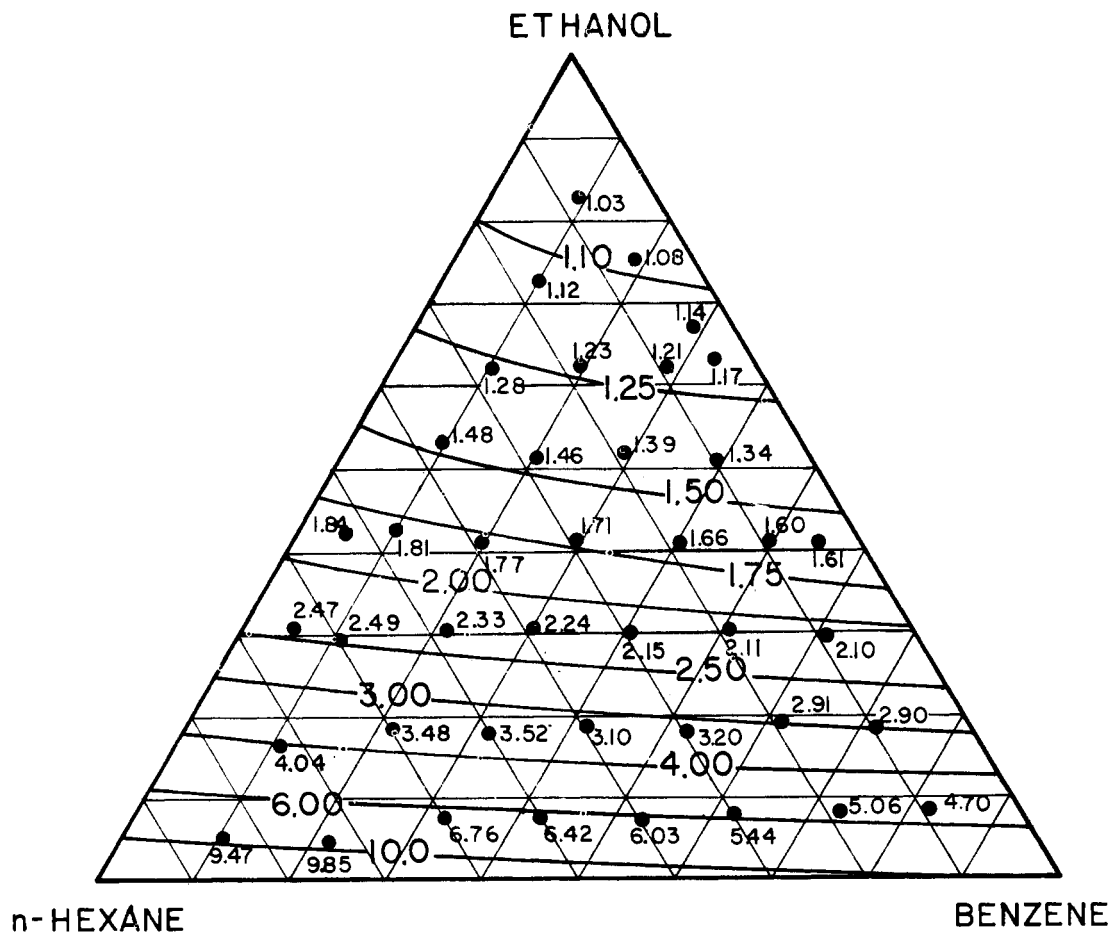


Figure 3. Ethanol activity coefficients vs. liquid phase composition of the *n*-hexane-ethanol-benzene system

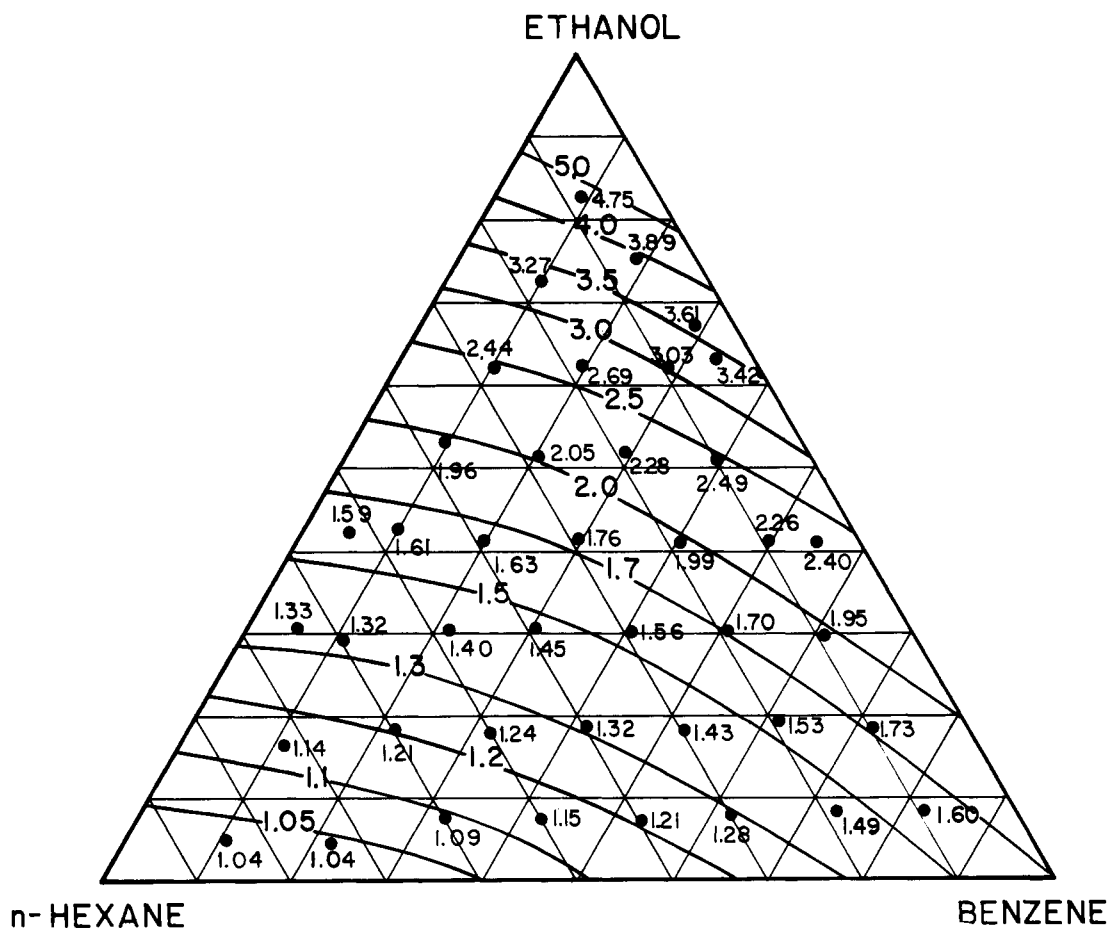


Figure 4. *n*-Hexane activity coefficients vs. liquid phase composition of *n*-hexane-ethanol-benzene system

P° = vapor pressure
 Q = defined by Equation 6
 R = gas law constant
 T = absolute temperature
 a = van der Waals' attraction coefficient
 a_{ij} = a coefficient introduced by Black (3)
 b = van der Waals' covolume
 c_{ij} = an interaction coefficient introduced by Black (3)
 f° = fugacity of a pure component in standard state at temperature and pressure of system
 f = partial fugacity of a component
 x = mole fraction in liquid phase
 y = mole fraction in vapor phase
 \sum' = total area enclosed by abscissa axis and the $\log \gamma_1/\gamma_2$ plot
 ϕ = fugacity coefficient for a pure component
 Φ = fugacity coefficient for a component in a mixture
 γ = activity coefficient
 ξ = Black's attraction coefficient

Subscripts

L = liquid phase
 i, j, k = components "i", "j", "k", respectively, in a mixture
 m = mixture
 v = vapor
 1,2,3 = components in a ternary mixture

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