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VAPOR-LIQUID EQUILIBRIUM

Vapor-Liquid Equilibrium at 75°C for Binary and Ternary Systems Containing Benzene, n-Heptane and n-Propyl Alcohol.

by

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ABSTRACT

Binary and ternary vapor-liquid equilibrium data were determined at 75°C for the mixture of benzene, n-heptane and n-propyl alcohol using a modified Gillespie type of still.

The equilibrium data for the three binary and the ternary systems are considered to be thermodynamically consistent as shown from the consistency test.

Correlating the data with the Redlich-Kister equations for the binary and ternary systems shows that these equations would represent the data accurately over the entire range of compositions.

The experimental results indicate that two binary systems, namely, n-heptane-n-propyl alcohol and n-propyl alcohol-benzene form an azeotrope at 75°C. Nevertheless no ternary azeotrope is found from the experiment.

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I. INTRODUCTION

As part of a continuing study of thermodynamic properties of solutions, vapor-liquid equilibrium data, x-y-P-T, for the ternary system benzene-n-heptane-n-propyl alcohol and the three binaries which constitute the ternary system were determined at 75°C by means of a modified Gillespie still.

This system was chosen because of the different types of hydrocarbon compounds involved, benzene being an aromatic, n-heptane being a straight chain saturated paraffin and n-propyl alcohol being a polar compound of straight chain aliphatic alcohol. Mixtures of paraffins, aromatics and saturated alcohols were expected to show nonideal volatility characteristics and the equilibrium data for mixtures of saturated alcohols, paraffins and aromatics are incomplete. This work was then undertaken to fill in some of the missing aromatic-paraffin-aliphatic alcohol data, in order that the nonideal behavior could be better understood and predicted. The data reported in this investigation should be useful in seeking some means of predicting multicomponent equilibrium data from binary equilibrium data and extending the equilibrium data of the multicomponent systems from one basic condition to various desired conditions.

For a systematic exploration of the field of vapor-liquid equilibrium, isothermal measurements are far more valuable than isobaric determination (40). It has been observed that most of the ternary data for the past years were determined as isobars and only few ternary systems (20, 26, 47, 52) as isotherms. The complete three binary isotherms and the ternary isotherm studied here enable interpolation for construction of isothermal ternary data.

Finally, it was intended to correlate three binaries and ternary data with an integrated Gibbs-Duhem equation.

II. HISTORICAL DISCUSSION

Evaluation of Vapor-Liquid Equilibrium Data

The widespread interest which has continued over many years in the study of vapor-liquid equilibria has received its main impetus from the demands of process industry for information vital to its basic operations. There has arisen, in addition, a desire for high-quality equilibrium data to be used in the efforts to provide a comprehensive theory of solutions. The varied goals implict in both of these areas has engendered a correspondingly large number of view points, experimental methods and theoretical approaches.

From the engineer's standpoint an adequate description of a system would yield the compositions of coexisting phases over the pressure and temperature ranges common to industry at the cost of relatively little experimental investigation and computation. In other words, a better description would generate such data from the more common and easily measured properties of the pure components. The desire for limiting experimental work to measurements on the pure component is raised by the growing interest in multicomponent systems.

The thermodynamic model of the ideal solution fulfills these requirements well for a system composed of isomers and members of homologous series at moderate pressures. There is also little doubt for the mixtures which belong to some of the combined groups suggested by Ewell, Harrison and Berg (16). Its mathematical relationships are simple. The only experimental data needed are the vapor pressures of the pure components, one of the first properties determined for new compounds. In fact, the only information necessary may be the normal boiling point if it can be shown that the compound is a member of one of the many Cox Chart families.

In the case of systems which cannot be approximated by the ideal solution, experimental data other than the vapor pressures of the components must be obtained. The nature of the data depends on the method used to produce the equilibrium relationship for the non-ideal system.

Great and continued efforts have been turned toward the direct determination of the pressures, temperature and compositions of the equilibrium phases by methods surveyed in the next section. Once these data have been determined, a correlation of them is desirable for the application.

Attempts have been made in the literature to relate the liquid composition to the liquid activity coefficient.

The activity coefficient is a factor into which all the deviations from the ideal solution behavior can be characterized. It is a function not only of composition, but also of temperature and pressure. Any attempt to use it over any but the smallest variation of these variables demands that this dependence be defined.

Semi-empirical equations satisfying the Gibbs-Duhem equation are used to express the activity coefficients of the components in terms of the composition of the solution. Some of the famous relations include the Margules (7, 34), van Laar (7, 49) and Redlich-Kister (41) equations. These equations will be discussed in detail in the theory section.

Mention must be made of other empirical relationships which link the phase compositions directly without recourse to the activity coefficient such as those proposed by Prahl (38) and Hirata (25).

Another avenue of approach is that of finding the compositions of one of the equilibrium phases from properties of the other by calculation. Ljunglin (32) and several other workers (2, 9, 39, 46) have worked in this area with success. This method makes unnecessary the measurement of vapor-phase composition and gives a quick, simple way of obtaining vapor-liquid equilibrium

data. The only drawback of this method is that it is rather impossible to tell whether results are correct from the calculation. Consequently, the vapor-liquid equilibrium data for the purpose of comparison with that of the calculated value are greatly needed. The data presented in this thesis were determined from direct measurements.

EXPERIMENTAL METHODS OF EQUILIBRIUM DETERMINATION

The methods for the direct determination of equilibrium data can be classified for the most part into the following groups:

1. Distillation method
2. Static method
3. Dew and Bubble point method
4. Flow method
5. Circulation method.

The oldest method for the direct determination of vapor-liquid equilibria data is the distillation method in which a small amount of liquid is distilled off from the boiling flask which contains a large charge. The method is very simple but it has marked disadvantages and generates large errors (8). Today, this method is no longer used.

In the static or bomb method the solution is charged into a closed and evacuated cylinder which is placed in a constant temperature bath. Once equilibrium is achieved and pressure determined, samples of both phases are withdrawn for analysis. At low pressures the amount of vapor required for analysis is of the same order as the total amount of the vapor phase in the equilibrium bomb, so that removal of a sample causes a marked disturbance of the equilibrium. For this reason the static method is not used at low or moderate

pressures. On the other hand, at high pressures, particularly if the temperature is in the vicinity of the critical point of one of the constituents, this method is more practical and gives more precise results than the other more complicated experimental apparatus and is frequently used (50).

A method employing apparatus similar to the static method, but omitting the analyses, is the dew-bubble point method. A solution of known composition is introduced into an evacuated chamber located in a constant temperature bath. The pressure is varied in order to totally vaporize or liquefy the enclosed material. The pressure at which the final drop or bubble remains at the end of these processes is noted and from such data the saturation curves of the two phases at constant temperature can be drawn against composition. The compositions indicated at the same pressure are the equilibrium compositions. This method has been used for a long time for the study of the phase behavior of hydrocarbons, particularly those of lower molecular weight, which are gases or low boiling liquids at normal conditions (44, 45).

The flow method is used for measuring equilibrium data in systems of limited miscibility in the liquid phase. In this method, one feeds to the equilibrium chamber a steady

stream of constant composition which can be either in the liquid or in the vapor phase or a combination of the two (11). After the temperatures and in fact the whole operation of the still become steady, samples of both phases are withdrawn for analysis.

The most widely used method of modern times is that employing the circulatory still. It is convenient to use both in the region of medium and low pressures. In this equipment the phases are recirculated into and out of contact with each other. In the meanwhile they are stored in areas from which samples may be withdrawn for analysis. Both phases or the vapor phase alone may be recirculated.

The number and variety of circulatory stills is very great. Four of the most prominent stills are those of Othmer (37), Gillespie (18), Jones, Schoenborn and Colburn (29) and Ellis (15).

The Othmer still recirculates only the vapor phase which is produced by normal boiling in an insulated still pot. It is removed, condensed and the overflow from the condensate storage chamber is returned to the pot. An immersion heater is used to provide turbulent mixing and boiling without bumping.

The Jones still operates in a similar manner. It only circulates the vapor phase, but the overflow con-

densate is vaporized outside the still pot before it is recontacted with the liquid phase contained therein. The heat inputs must be carefully adjusted in this apparatus to prevent the accumulation of one phase and depletion of the other.

The family of Gillespie stills uses the action of a Cottrell pump to recirculate both of the phases. Equilibrium is assumed to have been achieved as the contacted phases separate after leaving the upper end of the Cottrell pump which may be altered to facilitate phase contact. Temperature and pressure are measured at this point. The overflow condensate may or may not be vaporized before being returned to the base of the Cottrell pump and contacted with the liquid.

The Ellis still uses a glass spiral of several turns which functions as the Cottrell pump to recirculate both of the phases. The mixture distilled off from the special boiling flask flows through the glass spiral and spurts on the thermometer well. Equilibrium is assumed to have been obtained as the contacted phases separate after leaving the glass spiral. The overflow condensate may or may not be vaporized before being returned to the flask and contacted with the liquid.

There has long been dispute over the relative

merits of the various types of stills. It arises both from theoretical considerations and the inconsistencies of the reported data. Summaries and discussion of them are given by Hala et al. (21), Fowler (17) and Gillespie (18).

III. THEORY

Evaluation of Liquid Phase Activity Coefficient

Vapor liquid equilibrium data may be critically evaluated and readily extended by the use of activity coefficients. Since the activity coefficient is related to composition and is a precisely defined thermodynamic function, its calculation and correlation is desirable.

By definition,

$$\gamma_i = \frac{f_i}{x_i f_i^o} \tag{1}$$

or $$f_i^l = \gamma_i^l x_i (f_i^o)^l$$

and $$f_i^v = \gamma_i^v y_i (f_i^o)^v$$

where $(^l)$ and $(^v)$ denote the liquid and vapor phases respectively, and

f_i = fugacity of component i in the solution

f_i^o = fugacity of pure component i at the temperature and pressure of the solution

γ_i = activity coefficient.

As a result of the criteria of equilibrium

$$\gamma_i^l x_i (f_i^o)^l = \gamma_i^v y_i (f_i^o)^v \tag{2}$$

or $$\gamma_i^l = \frac{y_i}{x_i} \frac{(f_i^o)^v}{(f_i^o)^l} \gamma_i^v = \frac{y_i}{x_i} \frac{(f_i^o)^v/P}{(f_i^o)^l/P} \gamma_i^v$$

or $$\ln \gamma_i^l = \ln y_i/x_i + \ln \varphi_i^v/\varphi_i^l + \ln \gamma_i^v$$

where φ_i^V = fugacity coefficient of component i in the vapor phase

φ_i^l = fugacity coefficient of component i in the liquid phase

P = pressure of the system.

At moderate pressures, where the virial equation truncated to just two terms is essentially valid (3), fugacity coefficient for the vapor phase is equal to

$$\ln \varphi_i^V = \frac{B_{ii} P}{R T} \qquad (3)$$

where B_{ii} = second virial coefficient of component i

R = gas constant

T = absolute temperature.

The liquid-phase $\ln \varphi_i^l$ must be calculated in two parts. At temperature T and at the vapor pressure of pure component i, the fugacity coefficient for the liquid phase is equal to the fugacity coefficient of the vapor phase and is therefore given by the same equation:

$$\ln \varphi_i^o = \frac{B_{ii} p_i}{R T} \qquad (3a)$$

where p_i is the vapor pressure of pure component i. Now the change in $\ln \varphi_i^l$ in going from the vapor pressure p_i to the total pressure P is given by

$$\ln \varphi_i^l - \ln \varphi_i^o = \int_{p_i}^{P} - \frac{\alpha_i}{R T} dP$$

$$= \frac{1}{R\,T}\int_{p_i}^{P} \left(V_i^{\,l} - \frac{R\,T}{P}\right) dP. \qquad (3b)$$

Since the volumes of liquids are insensitive to small changes in pressure, $V_i^{\,l}$ may be taken as constant in the integral, giving

$$\ln \varphi_i^{\,l} = \frac{B_{ii}\,p_i}{R\,T} + \frac{V_i^{\,l}}{R\,T}(P - p_i) - \ln \frac{P}{p_i}. \qquad (3c)$$

Combining the equations for $\ln \varphi_i^{\,v}$ and $\ln \varphi_i^{\,l}$, we have

$$\ln \frac{\varphi_i^{\,v}}{\varphi_i^{\,l}} = \frac{(B_{ii} - V_i^{\,l})\,(P - p_i)}{R\,T} + \ln \frac{P}{p_i}. \qquad (3d)$$

Substitution of Equation 3d in Equation 2 gives

$$\log \gamma_i^{\,l} = \log \frac{y_i\,P}{x_i\,p_i} + \frac{(p_i - P)\,(V_i^{\,l} - B_{ii})}{2.303\,R\,T} + \log \gamma_i^{\,v} \qquad (4)$$

If the vapor phase is assumed to be an ideal solution, then $\gamma_i^{\,v} = 1$ and the last term of Equation 4 is zero. Thus Equation 4 becomes

$$\gamma_i = \frac{y_i\,P\,Z_i}{x_i\,p_i} \qquad (5)^*$$

where Z_i is defined as

$$Z_i = \exp \frac{(p_i - P)\,(V_i^{\,l} - B_{ii})}{R\,T}. \qquad (5a)$$

The value of the second virial coefficient of the pure component, B_{ii}, can be calculated relatively easily, if the critical pressure and temperature of the component are known. This may be done either from the generalized diagram or from the generalized equations such as given by Keyes et al. (30) and Black (4).

* It is assumed that $\gamma_i^v=1$, therefore, the superscript 1 of γ_i^l will be omitted and γ_i represents the activity coefficient of component i in the liquid phase.

Correlation of Data

A number of integrated forms of the Gibbs-Duhem equation are available for correlating activity coefficients for a binary system. They will be discussed below:

1. van Laar Equations. They were first derived by van Laar (49) and rearranged by Carlson and Colburn (7).

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B}\frac{x_1}{x_2}\right)^2} \qquad (6)$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A}\frac{x_2}{x_1}\right)^2} \qquad (7)$$

where A and B, constants of the van Laar equations, have the property of being equal to the terminal values of log of the two curves.

2. Margules Equations. The Margules equations were originally proposed by Margules (34) and modified by Carlson and Colburn (7).

$$\log \gamma_1 = (2B-A)\, x_2^2 + 2\,(A-B)\, x_2^3 \qquad (8)$$

$$\log \gamma_2 = (2A-B)\, x_1^2 + 2\,(B-A)\, x_1^3 \qquad (9)$$

where A and B are constants of the Margules equations. The Margules equations become identical with those of van Laar when A is equal to B and they are expressed by the following equations:

$$\log \gamma_1 = A\, x_2^2 \qquad (10)$$

$$\log \gamma_2 = A\, x_1^2 \qquad (11)$$

3. Redlich-Kister Equations. The Redlich-Kister equations are the most commonly used equations for relating liquid activity coefficients with the liquid compositions. The authors (41) started from the molar excess free energy; specially from the "Q function", which is related to the molar excess free energy by the following simple relation:

$$Q = \frac{\Delta G^E}{2.303\ RT} \qquad (12)$$

For a binary system Q is equal to

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 \qquad (13)$$

where x_1 and x_2 denote the mole fractions and γ_1 and γ_2 the activity coefficients. The usual convention $\gamma_1=1$ for $x_1=1$ and $\gamma_2=1$ for $x_2=1$ is adopted. The function Q is zero for a perfect solution at any concentration. It is also zero for any solution at the end points $x_1=1$ and $x_2=1$. Redlich and Kister proposed that the Q function be represented by an appropriate power series of the liquid composition, the expansion:

$$Q = x_1 x_2 \left[B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 + \cdots\cdots \right] \qquad (14)$$

(at T,P)

where the constants B_{12}, C_{12}, D_{12} ... depend on the temperature only.

Differentiating Equation 13 with respect to x_1,

$$\text{i.e.} \qquad \frac{dQ}{dx_1} = \log \gamma_1/\gamma_2 \qquad (15)$$

the degree of this function is one unit lower than Q as well as the function. The individual activity coefficients are therefore given conveniently by the thermodynamic relation

$$\log \gamma_1 = Q + x_2 \frac{dQ}{dx_1} \qquad (16)$$

$$\log \gamma_2 = Q - x_1 \frac{dQ}{dx_1} . \qquad (17)$$

so that

$$\log \gamma_1 = x_2^2 \left[B_{12} + C_{12} (3x_1 - x_2) + D_{12} (x_1 - x_2) (5x_1 - x_2) + ... \right] \qquad (18)$$

$$\log \gamma_2 = x_1^2 \left[B_{12} + C_{12} (x_1 - 3x_2) + D_{12} (x_1 - x_2) (x_1 - 5x_2) + ... \right] \qquad (19)$$

In most application, the quantity

$$\log \gamma_1/\gamma_2 = dQ/dx_1 = B_{12} (x_2 - x_1) + C_{12} (6x_1x_2 - 1) + D_{12} (x_2 - x_1) (1 - 8x_1x_2) + ... \qquad (20)$$

is used. It presents the advantage that its order with respect to the mole fraction is lower than that of Q,

$\log \gamma_1$ and $\log \gamma_2$.

The selection of the proper suffix equation depends on the molecular complexity of the system and the precision of the experimental data. It should be mentioned that the Redlich-Kister equations do not have to be limited to the three constants as shown in Equations 18 and 19. In general, this series furnishes for each case the most convenient representation. According to Redlich, Kister and Turnquist (42), only the first term is required for a nearly perfect solution; for solution containing an associated component such as alcohol and acid the third term is necessary; however, only very accurate measurements for an extremely imperfect solution require four terms. This is further supported by Ho, Boshko and Lu (28) that three-constant Redlich-Kister equations such as Equations 18 and 19 are adequate for representing liquid activity coefficients for most systems.

It may be readily shown that the Margules equations (Equations 8 and 9) are one of the typical forms of the Redlich-Kister equations. In comparison with the flexibility of the Redlich-Kister equation, the van Laar equation is much more cumbersome for solutions which can be represented by means of Equations 18 and 19 with one or two terms and it is always entirely insufficient for solutions which require three or four terms.

The liquid activity coefficient for multicomponent system may be expressed by the expansion of Redlich-Kister power series (41) without difficulty. For a ternary system the function Q can be expressed as follows:

$$Q_{123} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \qquad (21)$$

or in the form of

$$\log \gamma_i/\gamma_j = \frac{\partial Q_{123}}{\partial x_i} - \frac{\partial Q_{123}}{\partial x_j} \qquad (22)$$

The following three equations may also be obtained conveniently.

$$\log \gamma_1 = Q_{123} + \frac{\partial Q_{123}}{\partial x_1} - \left(x_1 \frac{\partial Q_{123}}{\partial x_1} + x_2 \frac{\partial Q_{123}}{\partial x_2} + x_3 \frac{\partial Q_{123}}{\partial x_3}\right) \qquad (23)$$

$$\log \gamma_2 = Q_{123} + \frac{\partial Q_{123}}{\partial x_2} - \left(x_1 \frac{\partial Q_{123}}{\partial x_3} + x_2 \frac{\partial Q_{123}}{\partial x_2} + x_3 \frac{\partial Q_{123}}{\partial x_3}\right) \qquad (24)$$

$$\log \gamma_3 = Q_{123} + \frac{\partial Q_{123}}{\partial x_3} - \left(x_1 \frac{\partial Q_{123}}{\partial x_1} + x_2 \frac{\partial Q_{123}}{\partial x_2} + x_3 \frac{\partial Q_{123}}{\partial x_3}\right) \qquad (25)$$

The function, Q_{123}, can be represented as the sum of the Equation 14 for all binary systems involved

plus terms for the interaction of different molecules. These latter terms are to be determined by measurements on the ternary system. The Q function, for the ternary system, is expressed as follows:

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3 \Big[C_{123} + D_3 (x_1-x_2) + D_1 (x_2-x_3) + D_2 (x_3-x_1) + \cdots \Big] \qquad (26)$$

where Q_{12}, Q_{23} and Q_{31} are evaluated from the mole fractions, x_1, x_2 and x_3, of the ternary system.

Formulation of individual activity coefficients of the ternary system is obtained by differentiation of Equation 26.

$$\begin{aligned}\log \gamma_1 = {} & B_{12}x_2 (1-x_1) + C_{12}x_2 (2x_1-x_2-2x_1^2+2x_1x_2) \\ & + D_{12}x_2(3x_1^2-3x_1^3+6x_1^2 x_2-4x_1x_2-3x_1x_2^2 + x_2^2) \\ & - B_{23}x_2x_3 - 2C_{23}x_2x_3(x_2-x_3) - 3D_{23} (x_2-x_3)^2 \\ & + B_{31}x_3(1-x_1) + C_{31}x_3(x_3-2x_1x_3+2x_1^2-2x_1) \\ & + D_{31}x_3(x_3^2+6x_1^2x_3-4x_1x_3-3x_2x_3^2+3x_1^2 -3x_1^3) \\ & + C_{123}x_2x_3(1-2x_1) \\ & + D_1x_2x_3(x_2-x_3-3x_1x_2+3x_1x_3) \\ & + D_2x_2x_3(x_3-2x_1-3x_1x_3+3x_1^2) \\ & + D_3x_2x_3(2x_1-x_2-3x_1^2+3x_1x_2) \qquad (27)\end{aligned}$$

$$\log \gamma_2 = B_{12}x_1(1-x_2) + C_{12}x_1 (x_1-2x_2-2x_1x_2+2x_2^2)$$
$$+ D_{12}x_1 (x_1^2-4x_1x_2+3x_2^2-3x_1^2x_2+6x_1x_2^2 - 3x_2^3)$$
$$+ B_{23}x_3 (1-x_2) + C_{23}x_3 (2x_2-x_3-2x_2^2+2x_2x_3)$$
$$+ D_{23}x_3 (x_3^2+3x_2^2-4x_2x_3-3x_2^3+6x_2^2x_3-3x_2x_3)$$
$$- B_{31}x_1x_3 - 2C_{31}x_1x_3 (x_3-x_1)$$
$$- 3D_{31}x_1x_3 (x_3-x_1)^2 + C_{123}x_1x_3 (1-2x_2)$$
$$+ D_1x_1x_3 (2x_2-x_3-3x_2^2+3x_2x_3)$$
$$+ D_2x_1x_3 (x_3-x_1+3x_1x_2-3x_2x_3)$$
$$+ D_3x_1x_3 (x_1-2x_2-3x_1x_2+3x_2^2) \qquad (28)$$

$$\log \gamma_3 = - B_{12}x_1x_2 - 2C_{12}x_1x_2 (x_1-x_2)$$
$$- 3D_{12}x_1x_2 (x_1-x_2)^2 + B_{23}x_2 (1-x_3)$$
$$+ C_{23}x_2 (x_2-2x_3-2x_2x_3+2x_3^2)$$
$$+ D_{23}x_2 (x_2^2-4x_2x_3+3x_3^2+3x_2^2x_3+6x_2x_3^2 - 3x_3^2)$$
$$+ B_{31}x_1 (1-x_3) + C_{31}x_1 (2x_3-x_1-2x_3^2+2x_1x_3)$$
$$+ D_{31}x_1 (x_1^2+3x_3^2-4x_1x_3-3x_3^3+6x_1x_3^2-3x_1^2x_3)$$
$$+ C_{123}x_1x_2 (1-2x_3)$$
$$+ D_1x_1x_2 (x_2-2x_3-3x_2x_3+3x_3^2)$$
$$+ D_2x_1x_2 (-x_1+2x_3-3x_3^2+3x_1x_3)$$
$$+ D_3x_1x_2 (x_1-x_2-3x_1x_3+3x_2x_3) \qquad (29)$$

THERMODYNAMIC CONSISTENCY TEST OF THE EXPERIMENTAL DATA

1. Consistency of the Binary Isothermal Data

Various thermodynamic relations furnish opportunities to check available experimental data. These tests are particularly valuable because they often reveal systematic errors in sets of data which can be represented by smooth curves. Consistency of binary isothermal data may be tested by the method recommended by Lu, Spinner and Ho (33) and that of Redlich and Kister (41). Lu et al. (33) proposed that consistency of the data can be tested by the visual methods by using the Gibbs-Duhem equation on a $\log \gamma$ vs. x plot at strategic liquid compositions of 0.00, 0.25, 0.50, 0.75 and 1.00 mole fractions. Furthermore, this method has been extended to test the thermodynamic consistency of equilibrium data y-x-P-T directly (33).

Redlich and Kister (41) developed a simple and general test obtained by integration of Equation 15. Since Q is zero for both $x_1=0$ and $x_1=1$, they proposed that the relationship

$$\int_0^1 \log (\gamma_1/\gamma_2)\, dx_1 = 0 \qquad (30)$$

be satisfied for consistent data. In other words, if $\log (\gamma_1/\gamma_2)$ is plotted against x_1 from $x_1=0$ to $x_1=1$, the

net area of the curve is equal to zero. The area condition is strict only at constant temperature. Practically it can be applied also to data obtained in a moderately small boiling interval.

2. Consistency of the Ternary Isothermal Data

Graphical integration methods of testing ternary isothermal vapor-liquid equilibrium data for consistency have been proposed by Herington (23, 24). Before graphical integration can be carried out, experimental data are needed either on lines of constant mole ratio of two or constant mole fraction of one of the components. Such experimental data are not usually available and thus existing results must be interpolated to provide values on the chosen lines. This method requires a large number of experimental results and the necessity for interpolation is a major disadvantage.

Li and Lu (31) proposed a consistency test suitable for ternary isothermal data which involves numerical integration around selected loops of experimental points. This test does not require that the data should lie in any specified part of the composition range or that the whole range should be covered. No data-fitting procedure is involved in this proposed method, therefore, the uncertainty as to whether deviations are due to the experimental errors or to the inadequacy of the employed equation can be avoided.

The authors have suggested the following equation for integration

$$Q_b - Q_a = \int_a^b \log \gamma_1 \, dx_1 + \int_a^b \log \gamma_2 \, dx_2 + \int_a^b \log \gamma_3 \, dx_3 \qquad \text{(at T, P)} \qquad (31)$$

where a and b are any two points on the same curve. A direct method would be integrating each of the integrals graphically. This can be done by plotting $\log \gamma_1$ against x_1, $\log \gamma_2$ against x_2 and $\log \gamma_3$ against x_3. The evaluation of the integrals of Equation 31 may also be carried out by means of a numerical integration. This method has the advantage that it can be applied to almost any set of data without using any graphical procedure provided that the experimental points are reasonably spaced. Loops chosen may be either open or closed, i.e., the first and last points in the loops may or may not coincide. Experimental data over the entire concentration range may be conveniently divided into several small sets and the thermodynamic consistency can be tested on each of them. In doing so the less reliable region may be easily spotted. If one of the experimental points is much in error in a set of data, it may be singled out by successively including points, one by one,

in a set.

Recently McDermott and Ellis (35) have proposed a consistency test that enables the ternary experimental results to be examined in pairs. The authors have suggested the isothermal-isobaric Gibbs-Duhem equation in the form

$$\sum_{i=1}^{N} x_i \, d(\log \gamma_i) = 0 \qquad (32)$$

for integration which is carried out directly round a loop of points a, b, c, ... y, z. The evaluation of the integrals of Equation 32 accomplished by means of trapezoidal rule gives

$$\sum_{i=1}^{N} \left[\frac{x_{ia}+x_{ib}}{2} (\log \gamma_{ib} - \log \gamma_{ia}) + \frac{x_{ib}+x_{ic}}{2} (\log \gamma_{ic} - \log \gamma_{ib}) + \cdots + \frac{x_{iy}+x_{iz}}{2} (\log \gamma_{iz} - \log \gamma_{iy}) \right] = 0 \qquad (33)$$

where N is the number of components in the mixture. The individual terms in Equation 33 give a direct comparison of each point with its neighbour. The form of Equation 33 thus offers a basis for the two-point consistency test. A knowledge of each term in Equation 33 quickly indicates the consistency, of any point in the loop, as each term is the deviation of the pair of points with which it is concerned. Should a particular point be common to several pairs and if

it gives large deviations, then, it may be concluded that this point is inconsistent.

IV. EXPERIMENTAL DETAILS

Materials and Properties

The benzene and n-heptane used in the experimental work were spectro quality reagents obtained from the Matheson Colemn and Bell Co. and had a purity of 99+mole%. They were used without further purification. The n-propyl alcohol obtained from Matheson Colemn and Bell Co. with a boiling point range of 96-98 degrees was fractionated in an adiabatically operated packed column (25 mm. in diameter and packed to a depth of 90 mm. with 3/16 inch diameter Pyrex brand glass helices) at a refler ratio of 50 to 1. The distillation was carried out in an entirely closed system. Only the middle portion of the constant boiling distillate was collected and used in this study for making up the solutions. A chromatographic analysis was performed using a Perkin-Elmer model 154-D vapor fractometer with a column of Calbotwax 1500 on Teffon. At the highest sensitivity only trace amounts of impurities were observed in these compounds respectively. This indicated the purity of the chemicals.

Normal boiling points of the pure components were measured with a Swietoslawsk two-stage ebulliometer. Densities were determined with a calibrated 10-ml pycnometer. Refractive indices measurements were made on a Bausch and Lomb precision

refractometer. The physical properties of the chemicals are listed in Table 1.

TABLE 1

Physical Properties of the Chemicals

	Density, 25°C		Normal Boiling Point, °C		Refractive Index, 25°C	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Benzene	0.8736	0.8736(14)	78.1	78.108(14)	1.4979	1.4979(14)
n-Heptane	0.6794	0.6795(14)	98.4	98.43 (14)	1.3852	1.3852(14)
n-Propyl Alcohol	0.7998	0.7998(10)	97.2	97.29 (14)	1.3834	1.3833(10)

Apparatus

1. Equilibrium Still The circulation method was used to obtain the equilibrium data. The equilibrium still employed in the equilibrium determination was the modified Gillespie type. In addition to the modifications suggested by Fowler and Norris (17), further modifications were necessary to improve the operation of the still. Figure 1 shows the general schematic diagram for the equilibrium still used for this study. The following improvements were made in the still employed in this investigation.

(a). A vacuum-sealed double jacket glass thermowell was used for the thermocouple junction to obtain better temperature measurement.

(b). A double-jacket tube was used in the receiver instead of simple tubing for better mixing of liquid and vapor condensate.

(c). The internal heater in the boiler was placed at the bottom instead of on the top to avoid formation of air bubbles around the opening and eliminate any possible leakage of liquid.

(d). Teflon plug-valves were used instead of glass stopcocks for permitting the elimination of all stopcock grease and any possible contamination.

The still was made of pyrex glass. The boiler was

heated both externally and internally with electric heating elements controlled by powerstats respectively. The Cottrell pump and the equilibrium chamber were insulated with asbestos and raw silk.

2. Accessory Equipment with Still The accessories were classified into two main parts, namely, temperature and pressure measurements.

The temperature was measured by means of a Leeds and Northrup K-3 potentiometer with a SRI Tinsley galvanometer using a copper constantan thermocouple. For isothermal operations, the desired temperature of 75°C was obtained and regulated by a Cartesian manostat of Type 7A (19) incorporated with a vacuum pump and a surge reservoir. The pressure of the system was read directly from a mercury manometer.

3. Equipment for Quantitative Analysis of Sample The equipment employed in this investigation for quantitative analysis of the samples were a refractometer and a vapor fractometer.

(a). Refractometer A Bausch and Lomb Abbe-3L precision refractometer and a sodium lamp were used to determine the refractive indices of the mixtures when refractive index was used to analyze unknown composition mixtures. Prism temperature was controlled at 25 $\pm$ 0.02°C by circulating water which was regulated by constant temperature device.

(b). Vapor Fractometer The vapor fractometer employed in this work was a Perkin-Elmer model 154-D vapor fractometer. A Hamilton 10-microliter syringe with cemented needle was used for injection of samples. The results of the analysis of the samples were recorded by a Philips type PR2216/21 Automatic Compensator. An automatic integrator was employed to evaluate the peak areas.

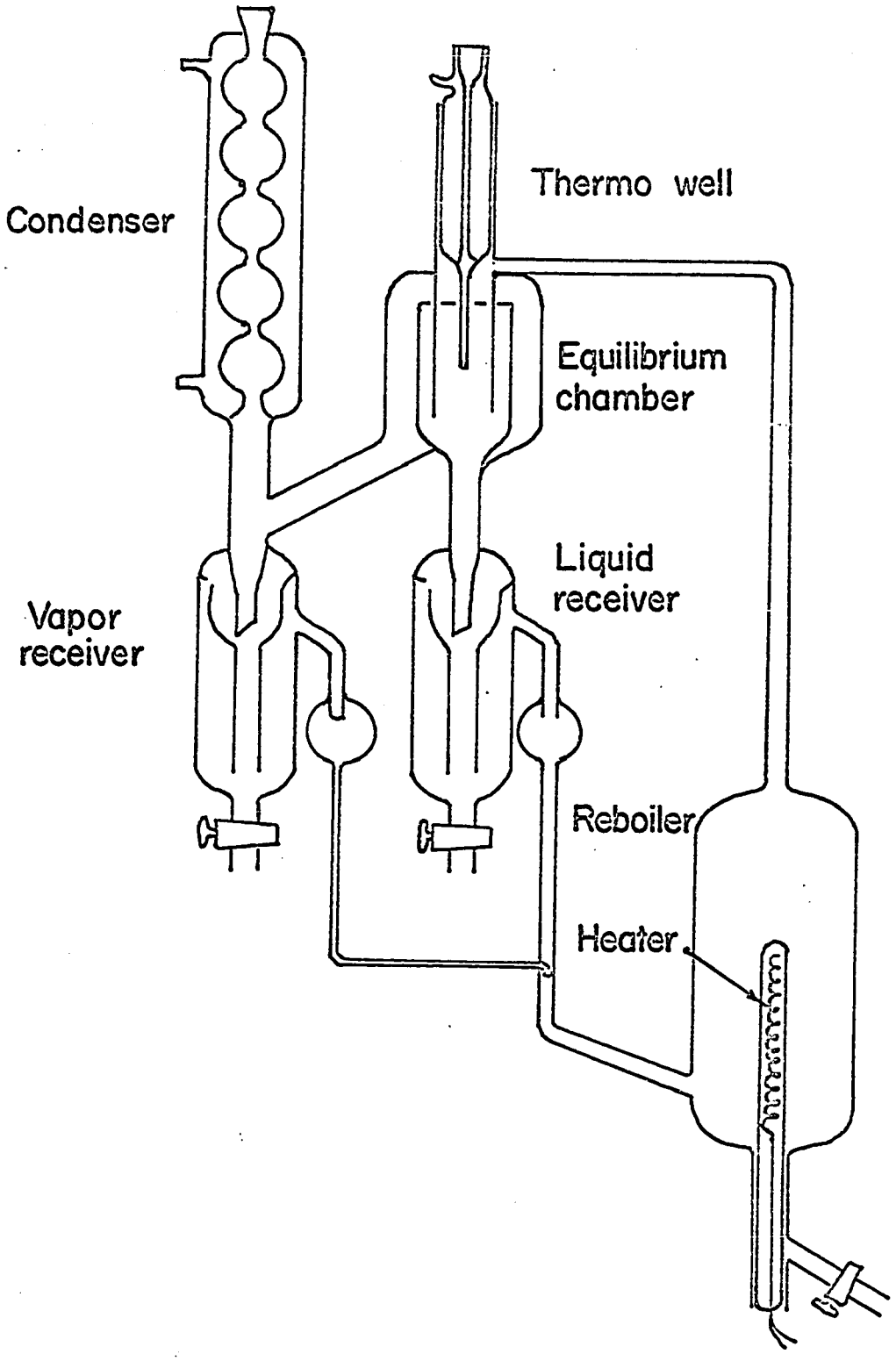
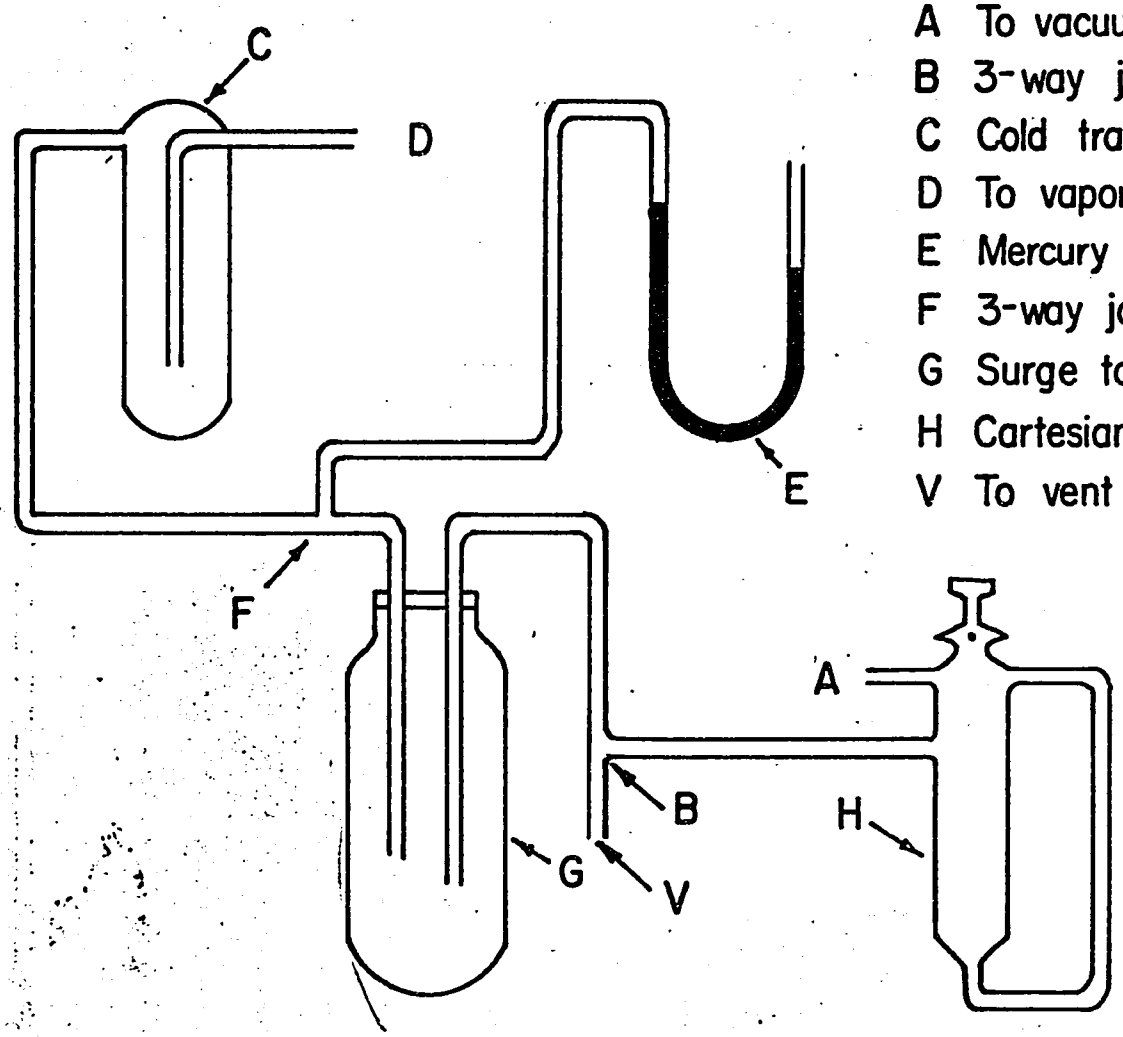


Figure 1. Schematic diagram of the modified Gillespie equilibrium still



A To vacuum pump
B 3-way joint
C Cold trap
D To vapor condenser
E Mercury manometer
F 3-way joint
G Surge tank
H Cartesian manostat
V To vent

Figure 2. Sketch of the pressure control system

EXPERIMENTAL PROCEDURE

1. Test of the Equilibrium Still The equilibrium still was used previously to obtain y-x-P-T data on the following three systems: (a). n-hexane-ethanol-benzene at 55°C and 760 mm. Hg., (b). ethanol-cyclohexane at 1 atm. and (c). ethanol-benzene-cyclohexane at 1 atm. (27, 12). Before this study, series of runs were performed with the still on the system of benzene-n-heptane at 80°C and 760 mm. Hg. The results obtained agreed very well with those reported by Brown (5) and Myers (36). This confirmed the consistency of the experimental results over wide ranges of charge volumes and boil-up rates through the use of the equilibrium still.

2. Binary System of Benzene-n-Heptane and Benzene -n-Propyl Alcohol

(a). Preparation of binary liquid mixtures: In order to obtain a reasonable composition range of vapor-liquid equilibrium data with reduced experimental runs for a system, predetermined compositions were desired before starting each run. The procedure was carried out by adding a known amount of one component to another.

(b). Determination of vapor-liquid equilibrium data: The prepared solutions were charged to the still before starting the experiment. The reboiler, liquid sample chamber and vapor condensate chamber were charged with solution

to the appropriate level. The total volume of the solution was about 285 ml. Mention must be made that the heater in the reboiler should always be fully immersed into the liquid before starting heating.

For isothermal operation, the desired temperature was controlled at 75 ± 0.1°C by adjusting the total pressure of the still. A schematic diagram of the pressure control system, which consists of a cold trap, a surge tank and a Cartesian manostat connected in series, is shown in Figure 2. The cold trap was connected to the vapor condenser which, in turn, was connected to the equilibrium still. A temperature-compensated mercury manometer, installed between the cold trap and the surge tank through a three-way joint, was used to measure the pressure in the system. A vacuum pump was attached to the upper arm of the Cartesian manostat for the purpose of manipulating the pressure of the system.

Temperature was measured by means of a copper constantan thermocouple in conjunction with a Leeds and Northrup K-3 potentiometer. The thermocouple was calibrated in a stirred oil bath by comparison with a standard platinum resistance thermometer. The cold junction of the thermocouple was immersed into an ice-water bath in a Dewar flask. The

uncertainty of the calibration was 0.02°C. The calibration curve is shown in Figure 19 and listed in Table 6. When the apparatus was in operation, the thermocouple was inserted into the thermowell of the equilibrium chamber. A few drops of Silicone 704 of Dow Corning Silicones Ltd. was added into the thermowell to provide a good contact for the bead of the thermocouple.

The still was allowed to operate for two and half hours for each run to ensure the attainment of equilibrium. Temperature and pressure were noted before samples were withdrawn for analysis. Prior to sampling, several milliliters of sample were taken to flush the lines. Sample receivers were placed in ice bath to minimize evaporation losses during sampling.

(c). Analysis of mixtures: In a case where a sufficient difference in the refractive index of the two components existed, analysis of the mixtures was made with an Abbe refractometer. The difference in refractive index between benzene and n-heptane at 25°C is 0.1127 and between n-propyl alcohol and benzene is 0.1147, consequently, the composition of the above two binary mixtures can be measured to better than ± 0.1%. However, the refractive index difference at 25°C between n-heptane and n-propyl alcohol is 0.0017,

the sensitivity of determining the composition of this system is much reduced. Therefore, the refractive index method was employed in this study to analyze binary systems of benzene-n-heptane and n-propyl alcohol-benzene. The gas chromatograph method was used to analyze the binary system of n-heptane-n-propyl alcohol and ternary system of benzene-n-heptane-n-propyl alcohol.

Analyzing instruments must be calibrated prior to the determination of the composition of the mixture. Calibration of the Bausch and Lomb Abbe-3L precision refractometer for the refractive index-composition of the systems under studied was carried out by observation of the refractive indices of a mixture of known composition. The known composition of the mixture was determined analytically by weighing components individually with an analytical balance. Table 7 indicates the composition-refractive indices of the calibration and Figure 20 is the calibration plot for the system of benzene-n-heptane. Table 8 shows the composition-refractive indices of the calibration and Figure 21 is the calibration plot for the system of n-propyl alcohol-benzene.

3. Ternary System and the Binary System of n-Heptane-n-Propyl Alcohol

(a). Preparation of binary and ternary liquid mixtures: The planning of the experiment and the method

for preparing solutions for the binary system of n-heptane -n-propyl alcohol were exactly the same as that described previously for the other two binaries. For the ternary system, a procedure similar to that of Severns et al. (47) was followed for the purpose of reducing appreciably the number of experimental determinations. It should be mentioned, however, that the concentration range covered in this investigation was greater than that proposed by Severns et al. In order to precisely obtain the desired concentration, ternary mixtures were prepared by adding known amounts of one component to known mixtures of the other two components.

(b). Analytical method: Samples of the binary system of n-heptane-n-propyl alcohol and the ternary system, obtained by using the same apparatus and experimental technique as described before, were analyzed by means of a gas chromatography.

The instrument used for the technique of gas chromatograph was a Perkin-Elmer vapor fractometer. Calibrations and the determination of unknown compositions of the samples were carried out using two 4-meter, 1/4 inch W columns packed with Calbotwax 1500 on teffon in series and helium as the carrier gas. The vapor fractometer was operated at 104°C, column pressure of 27 psig. and a bridge voltage of 8 volts. Under these conditions and a helium

flow rate of 72.9 c.c. per minute, an analysis of a ternary sample would be completed in approximately 23 minutes. The peaks were well spaced and completely separated. Operating conditions for the gas chromatographic analysis are listed in Table 11. The retention times for the three components in the column were in the following order: n-heptane, benzene and n-propyl alcohol. The peak area of each component was recorded and measured by an automatic integrator.

Numerous known samples of the binary system of n-heptane-n-propyl alcohol and the ternary system were used for calibration purposes. Curves which were similar to that obtained by Despande and Lu (13) were drawn on a (x_i/x_j) mole fraction vs. (x_i/x_j) peak area plot for the components in the binary and ternary mixtures. Table 9 and Figure 22 show the calibration of the binary system of n-heptane-n-propyl alcohol. Table 10 and Figures 23, 24 and 25 show the calibration of the ternary system.

It is found in this investigation that the equation suggested by Wagner and Weber (51) as follows

$$\frac{(x_i/x_j)\ \text{mole fraction}}{(x_i/x_j)\ \text{peak area}} = K_{ij}$$

is only valid over a limited concentration range. This can be shown from Figures 22 to 25.

From the experimental measurements, the average deviation obtained in the calibration is ±.0.5 mole% and the error in the reported equilibrium composition is of the same order. At a peak area of one component is in much large than others, an uncertainty of as much as 5 mole% in composition is possible. This shows why the experimental determination of the reliable terminal vapor-liquid equilibrium data is difficult.

V. RESULTS

Summarized data for binary systems of benzene-n-heptane, n-heptane-n-propyl alcohol and n-propyl alcohol-benzene are given in Tables 2, 3 and 4 and Figures 3 to 14. The ternary data are summarized in Table 5 and plotted on triangular diagrams as shown in Figures 15, 16, 17 and 18.

TABLE 2

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Gas Law Deviation Z_1	Gas Law Deviation Z_2
1	75.05	394.1	0.0741	0.1530	1.0128	0.9974
2	74.95	414.9	0.1220	0.230	1.0117	0.9953
3	74.97	465.0	0.2386	0.4002	1.0092	0.9918
4	75.00	528.4	0.4032	0.5652	1.0060	0.9869
5	75.00	544.4	0.4688	0.6109	1.0055	0.9856
6	74.96	569.9	0.5442	0.6772	1.0004	0.9836
7	74.92	574.2	0.5860	0.7060	1.0003	0.9833
8	75.00	599.8	0.6655	0.7645	1.0023	0.9813
9	75.00	624.1	0.7895	0.8410	1.0012	0.9793
10	75.00	638.6	0.8772	0.9015	1.0005	0.9783
11	75.00	643.6	0.9378	0.9456	1.0002	0.9779

.... continued

TABLE 2 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2) System at 75°C

Run	Activity Coefficient		log γ		log γ_1/γ_2
	γ_1	γ_2	log γ_1	log γ_2	
1	1.2721	0.9946	0.1045	-0.0025	0.1070
2	1.2212	0.9951	0.0904	-0.0021	0.0925
3	1.2146	1.0049	0.0843	0.0021	0.0822
4	1.1489	1.0509	0.0606	0.0216	0.0590
5	1.1008	1.0872	0.0416	0.0363	0.0053
6	1.0948	1.0981	0.0393	0.0407	-0.0014
7	1.0680	1.1091	0.0286	0.0450	-0.0164
8	1.0657	1.1462	0.0278	0.0593	-0.0315
9	1.0272	1.2770	0.0116	0.0891	-0.0775
10	1.0133	1.3862	0.0057	0.1319	-0.1262
11	1.0007	1.5226	0.0003	0.1825	-0.1822

TABLE 3

Vapor-Liquid Equilibrium Data for n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction x_2	Vapor Mole Fraction y_2	Gas Law Deviation Z_2	Gas Law Deviation Z_3
1	75.07	371.3	0.0564	0.2311	0.9992	0.9964
2	75.00	490.0	0.2061	0.3980	0.9899	0.9902
3	75.00	519.2	0.3236	0.4950	0.9876	0.9887
4	75.00	530.9	0.4464	0.5370	0.9867	0.9881
5	75.00	535.0	0.4878	0.5395	0.9864	0.9869
6	75.01	534.5	0.5279	0.5452	0.9863	0.9879
7	75.00	534.5	0.5656	0.5630	0.9863	0.9879
8	75.02	534.3	0.6426	0.5847	0.9864	0.9879
9	74.95	531.1	0.6930	0.5970	0.9866	0.9881
10	74.96	505.4	0.8169	0.6472	0.9887	0.9894
11	75.02	479.9	0.8583	0.6896	0.9906	0.9907
12	74.86	476.6	0.8827	0.7052	0.9909	0.9909
13	75.00	422.0	0.9803	0.8478	0.9952	0.9937

.... continued

TABLE 3 (continued)

Vapor-Liquid Equilibrium Data for n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Activity Coefficient		log γ		log γ_2/γ_3
	γ_2	γ_3	log γ_2	log γ_3	
1	4.2052	1.0015	0.6238	0.0006	0.6232
2	2.5911	1.2223	0.4135	0.0872	0.3263
3	2.1697	1.2732	0.3364	0.1049	0.2315
4	1.7431	1.4576	0.2413	0.1636	0.0777
5	1.6145	1.5770	0.2080	0.1978	0.0102
6	1.5060	1.6899	0.1778	0.2278	-0.0500
7	1.4516	1.7647	0.1619	0.2466	-0.0847
8	1.3265	2.0376	0.1227	0.3091	-0.1864
9	1.2486	2.2886	0.0964	0.3596	-0.2632
10	1.0951	3.2009	0.0395	0.5052	-0.4657
11	1.0565	3.4600	0.0239	0.5391	-0.5152
12	1.0423	3.9431	0.0180	0.5958	-0.5778
13	1.0047	10.7634	0.0020	1.0319	-1.0299

TABLE 4

Vapor-Liquid Equilibrium Data for n-Propyl Alcohol(3)-Benzene(1) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction x_3	Vapor Mole Fraction y_3	Gas Law Deviation Z_3	Gas Law Deviation Z_1
1	75.00	678.3	0.0376	0.0768	0.9805	0.9849
2	75.00	702.9	0.0920	0.1435	0.9793	0.9973
3	74.91	706.2	0.0984	0.1490	0.9791	0.9971
4	75.02	714.6	0.2048	0.2085	0.9787	0.9967
5	74.97	710.8	0.2344	0.2145	0.9789	0.9969
6	75.03	708.3	0.3092	0.2420	0.9790	0.9970
7	74.98	697.9	0.4172	0.2797	0.9795	0.9975
8	74.96	664.0	0.5390	0.3185	0.9813	0.9992
9	75.00	634.5	0.6340	0.3494	0.9828	1.0007
10	75.00	580.3	0.7440	0.4225	0.9855	1.0034
11	75.00	506.1	0.8395	0.5265	0.9894	1.0070
12	74.98	41208	0.9190	0.6868	0.9942	1.0120
13	74.99	381.6	0.9495	0.7695	0.9958	1.0134

.... continued

TABLE 4 (continued)

Vapor-Liquid Equilibrium Data for n-Propyl Alcohol(3)-Benzene(1) System at 75°C

Run	Activity Coefficient		log γ		log γ_3/γ_1
	γ_3	γ_1	log γ_3	log γ_1	
1	4.5131	0.9889	0.6545	-0.0049	0.6584
2	3.5670	1.0204	0.5523	0.0088	0.5435
3	3.4783	1.0256	0.5413	0.0110	0.5303
4	2.3654	1.0940	0.3739	0.0390	0.3349
5	2.1153	1.1219	0.3254	0.0500	0.2754
6	1.8030	1.1957	0.2560	0.0776	0.1784
7	1.5225	1.3277	0.1826	0.1231	0.0595
8	1.2791	1.5135	0.1069	0.1800	-0.0731
9	1.1417	1.7417	0.0576	0.2410	-0.1834
10	1.0789	2.0270	0.0330	0.3069	-0.2739
11	1.0433	2.3202	0.0184	0.3652	-0.3468
12	1.0189	2.4927	0.0081	0.3967	-0.3886
13	1.0231	2.7579	0.0099	0.4406	-0.4307

TABLE 5

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptene y_2
1	75.00	649.4	0.6272	0.3186	0.6766	0.2231
2	75.03	607.0	0.4297	0.5091	0.5213	0.3420
3	75.00	683.1	0.7316	0.1974	0.7282	0.1529
4	75.00	569.8	0.2603	0.6634	0.3130	0.4978
5	75.00	546.8	0.1733	0.7381	0.2756	0.5003
6	75.00	681.3	0.6247	0.2843	0.6444	0.1998
7	74.95	590.6	0.2565	0.6465	0.3436	0.4318
8	74.98	646.5	0.4439	0.4484	0.4920	0.2903
9	74.91	702.5	0.7613	0.1141	0.7564	0.0832
10	74.92	697.6	0.7054	0.1693	0.6662	0.1439
11	75.00	627.4	0.3538	0.5149	0.4054	0.3437

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	z_1	z_2	z_3	γ_1	γ_2	γ_3
1	1.0000	0.9774	0.9820	0.1081	1.2295	3.9206
2	1.0020	0.9807	0.9842	1.1386	1.1062	4.4332
3	0.9983	0.9748	0.9803	1.0474	1.4267	3.7256
4	1.0040	0.9836	0.9861	1.0615	1.1634	4.6288
5	1.0050	0.9854	0.9873	1.3486	1.0103	4.5364
6	0.9883	0.9749	0.9804	1.0718	1.2912	3.7992
7	1.0030	0.9820	0.9850	1.2246	1.0715	4.4750
8	1.0000	0.9776	0.9821	1.1057	1.1319	4.2638
9	0.9973	0.9733	0.9733	1.0742	1.3791	2.9422
10	0.9975	0.9737	0.9795	1.0141	1.5971	3.4405
11	1.0010	0.9791	0.9831	1.1105	1.1343	3.9157

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptane y_2
12	75.03	704.1	0.8126	0.0552	0.7483	0.0486
13	74.98	579.2	0.1846	0.6684	0.2227	0.4843
14	75.12	601.0	0.2297	0.6153	0.3201	0.3976
15	75.00	710.5	0.6599	0.1814	0.6616	0.1422
16	75.00	564.2	0.1420	0.6919	0.1932	0.6254
17	75.00	653.4	0.4082	0.4245	0.4638	0.3014
18	75.00	646.7	0.3823	0.4492	0.4472	0.3129
19	74.95	693.4	0.6057	0.2253	0.5704	0.1597
20	74.90	577.5	0.1854	0.6389	0.2383	0.4481
21	75.00	676.9	0.4921	0.3298	0.5421	0.2385
22	74.97	635.0	0.3064	0.5026	0.3775	0.3529

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol (3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	Z_1	Z_2	Z_3	γ_1	γ_2	γ_3
12	0.9972	0.9732	0.9792	0.9977	1.6688	3.5189
13	1.0033	0.9828	0.9856	1.0819	1.1409	3.7802
14	1.0025	0.9812	0.9845	1.2957	1.0541	3.5802
15	0.9969	0.9727	0.9789	1.0959	1.4986	2.8566
16	1.0041	0.9840	0.9864	1.1894	1.3881	2.0192
17	1.0003	0.9773	0.9818	1.1453	1.2541	2.9929
18	1.0000	0.9776	0.9831	1.1674	1.2182	3.0040
19	0.9977	0.9740	0.9797	1.0053	1.3242	3.6043
20	1.0035	0.9830	0.9857	1.1494	1.1014	3.3755
21	0.9985	0.9753	0.9805	1.1490	1.3206	2.7163
22	1.0006	0.9785	0.9827	1.2081	1.1940	2.9263

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptane y_2
23	75.08	713.2	0.6636	0.1294	0.6643	0.1090
24	75.05	677.2	0.4726	0.3177	0.5353	0.2383
25	74.98	606.5	0.2312	0.5563	0.2819	0.4327
26	75.09	587.5	0.1590	0.6276	0.2232	0.4624
27	74.98	554.6	0.0705	0.7096	0.0804	0.5964
28	75.00	691.1	0.5336	0.2456	0.5774	0.1905
29	74.90	676.4	0.4693	0.3050	0.5192	0.2284
30	75.00	689.4	0.5195	0.2535	0.5560	0.2000
31	74.97	703.9	0.5848	0.1555	0.6072	0.1336
32	74.93	709.4	0.5810	0.1568	0.6216	0.1337
33	74.99	587.5	0.1343	0.6033	0.1964	0.4806

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	z_1	z_2	z_3	γ_1	γ_2	γ_3
23	0.9967	0.9725	0.9787	1.0981	1.6162	2.5397
24	0.9985	0.9753	0.9805	1.1819	1.3704	2.3816
25	1.0020	0.9808	0.9842	1.1399	1.3022	2.6632
26	1.0030	0.9822	0.9852	1.2765	1.1761	2.8330
27	1.0048	0.9848	0.9869	0.9807	1.2698	2.6722
28	0.9979	0.9742	0.9799	1.1516	1.4445	2.3650
29	0.9986	0.9753	0.9806	1.1531	1.3666	2.4643
30	0.9880	0.9743	0.9800	1.1363	1.4659	2.4126
31	0.9972	0.9732	0.9792	1.1247	1.6281	2.2855
32	0.9969	0.9728	0.9789	1.1676	1.6278	2.1531
33	1.0030	0.9822	0.9852	1.3298	1.2716	2.3670

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptane y_2
34	74.93	659.4	0.3655	0.3589	0.4428	0.2745
35	75.00	705.6	0.5939	0.1199	0.6473	0.1099
36	74.93	582.6	0.1123	0.5998	0.1700	0.4831
37	75.01	677.0	0.4202	0.2899	0.5004	0.2352
38	75.04	561.0	0.0657	0.6443	0.0970	0.5510
39	75.00	640.0	0.3083	0.3930	0.3537	0.3264
40	75.00	711.1	0.6171	0.0740	0.6751	0.0722
41	75.04	687.6	0.4692	0.2026	0.5328	0.1811
42	75.00	646.7	0.3099	0.3568	0.3951	0.3040
43	75.01	653.8	0.3231	0.3366	0.4130	0.2994
44	75.00	617.8	0.2184	0.4404	0.3000	0.3571

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene (1)-n-Heptane (2)-n-Propyl Alcohol (3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	z_1	z_2	z_3	γ_1	γ_2	γ_3
34	0.9994	0.9766	0.9815	1.2320	1.3625	2.2056
35	0.9972	0.9731	0.9791	1.1834	1.7409	1.9471
36	1.0030	0.9826	0.9854	1.3651	1.2755	2.2981
37	0.9985	0.9753	0.9805	1.2423	1.4819	2.0113
38	1.0044	0.9843	0.9865	1.2837	1.3063	2.2324
39	1.0004	0.9782	0.9825	1.1330	1.4420	2.2373
40	0.9973	0.9727	0.9788	1.1966	1.8668	1.8916
41	0.9980	0.9745	0.9800	1.2025	1.6568	1.9515
42	1.0000	0.9776	0.9821	1.2723	1.4900	1.9049
43	0.9997	0.9773	0.9818	1.2892	1.5721	1.8038
44	1.0015	0.9799	0.9836	1.3115	1.3579	2.0289

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptane y_2
45	75.05	696.9	0.4991	0.1423	0.5866	0.1378
46	74.89	595.6	0.1131	0.5098	0.2098	0.4073
47	74.90	630.1	0.2450	0.3630	0.3388	0.3438
48	74.92	603.0	0.1470	0.4490	0.2390	0.4171
49	74.87	665.3	0.3818	0.1966	0.5018	0.2027
50	75.05	668.8	0.3476	0.2284	0.4605	0.2211
51	75.00	676.0	0.3934	0.1789	0.5174	0.1835
52	75.30	652.4	0.2801	0.2717	0.3930	0.2739
53	75.00	590.1	0.0970	0.4515	0.1680	0.4571
54	74.98	684.6	0.4198	0.1112	0.5565	0.1314
55	75.00	700.6	0.3277	0.1960	0.5874	0.1380

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	z_1	z_2	z_3	γ_1	γ_2	γ_3
45	0.9976	0.9737	0.9796	1.2610	1.8177	1.7431
46	1.0027	0.9816	0.9848	1.7095	1.2921	1.9786
47	1.0010	0.9789	0.9830	1.3460	1.6160	1.6662
48	1.0020	0.9810	0.9844	1.5159	1.5461	1.6787
49	0.9992	0.9762	0.9812	1.3483	1.8523	1.5200
50	0.9990	0.9759	0.9810	1.3659	1.7477	1.6368
51	0.9986	0.9754	0.9806	1.3701	1.8708	1.5401
52	1.0000	0.9772	0.9819	1.4126	1.7752	1.5817
53	1.0003	0.9820	0.9850	1.5777	1.6228	1.6034
54	0.9982	0.9746	0.9802	1.3980	2.1809	1.4836
55	0.9974	0.9735	0.9794	1.9330	1.3284	1.3143

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptane y_2
56	74.90	559.9	0.0386	0.4807	0.0902	0.5027
57	74.99	648.0	0.2947	0.2075	0.4388	0.2324
58	75.00	622.6	0.2030	0.2957	0.3027	0.3127
59	75.06	675.7	0.4175	0.0607	0.6232	0.0785
60	74.87	588.5	0.1334	0.3221	0.2163	0.3831
61	75.03	658.4	0.3298	0.1204	0.5094	0.1630
62	75.11	622.0	0.2006	0.2393	0.3314	0.3083
63	75.02	593.4	0.1394	0.2381	0.2693	0.3299
64	75.03	550.0	0.0925	0.2709	0.2106	0.4133
65	75.00	615.6	0.2098	0.1448	0.3950	0.2252
66	75.08	622.2	0.2290	0.1110	0.4330	0.1873

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	z_1	z_2	z_3	γ_1	γ_2	γ_3
56	1.0049	0.9844	0.9866	1.8492	1.5944	1.5542
57	1.0000	0.9775	0.9820	1.4890	1.9624	1.3964
58	1.0010	0.9795	0.9833	1.4341	1.7839	1.5604
59	0.9986	0.9757	0.9807	1.5542	2.3582	1.2585
60	1.0030	0.9821	0.9851	1.4770	1.9016	1.4170
61	0.9995	0.9767	0.9815	1.5686	2.4082	1.2792
62	1.0010	0.9796	0.9834	1.5872	2.1715	1.3072
63	1.0037	0.9818	0.9848	1.7756	2.2329	1.2500
64	1.0050	0.9852	0.9871	1.9688	2.2790	1.0613
65	1.0018	0.9800	0.9837	1.7918	2.5954	1.1839
66	1.0010	0.9795	0.9833	1.8173	2.8447	1.1693

.... continued

TABLE 5 (continued)

Vapor-Liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Temp., °C.	Total Pressure mm. Hg.	Liquid Mole Fraction		Vapor Mole Fraction	
			Benzene x_1	n-Heptane x_2	Benzene y_1	n-Heptane y_2
67	75.07	564.7	0.1172	0.2133	0.2441	0.3039
68	75.04	591.4	0.1521	0.1688	0.3134	0.2758
69	75.00	557.2	0.0547	0.2648	0.1237	0.4296
70	75.01	616.1	0.2411	0.0601	0.4816	0.1204
71	74.98	596.6	0.2471	0.0321	0.5249	0.0661
72	75.07	581.0	0.1587	0.1095	0.3513	0.2108
73	74.97	617.1	0.2015	0.0520	0.4715	0.1273
74	75.02	513.0	0.0552	0.1766	0.1613	0.3600
75	75.00	507.9	0.0740	0.0851	0.2288	0.2389
76	75.00	507.9	0.0758	0.0826	0.2254	0.2310
77	75.05	461.5	0.0275	0.0877	0.0990	0.2828
78	75.00	450.3	0.0611	0.0322	0.2312	0.1266

.... continued

TABLE 5 (continued)

Vapor-liquid Equilibrium Data for Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3) System at 75°C

Run	Gas Law Deviation			Activity Coefficient		
	Z_1	Z_2	Z_3	γ_1	γ_2	γ_3
67	1.0041	0.9840	0.9864	1.8225	2.1900	1.2492
68	1.0029	0.9819	0.9850	1.8860	2.6245	1.1707
69	1.0045	0.9846	0.9867	1.9532	2.4621	1.1989
70	1.0020	0.9800	0.9837	1.9029	3.3460	1.1281
71	1.0025	0.9815	0.9847	1.9606	3.3355	1.1074
72	1.0032	0.9827	0.9854	1.9911	3.0405	1.1382
73	1.0015	0.9799	0.9836	2.2317	4.0950	1.0794
74	1.0070	0.9881	0.9890	2.0218	2.4903	1.0997
75	1.0070	0.9885	0.9893	2.4403	3.8988	1.0567
76	1.0070	0.9885	0.9893	2.3439	4.0303	1.0745
77	1.0095	0.9921	0.9917	2.7293	4.0610	1.0558
78	1.0100	0.9930	0.9922	2.6342	4.8631	1.0519

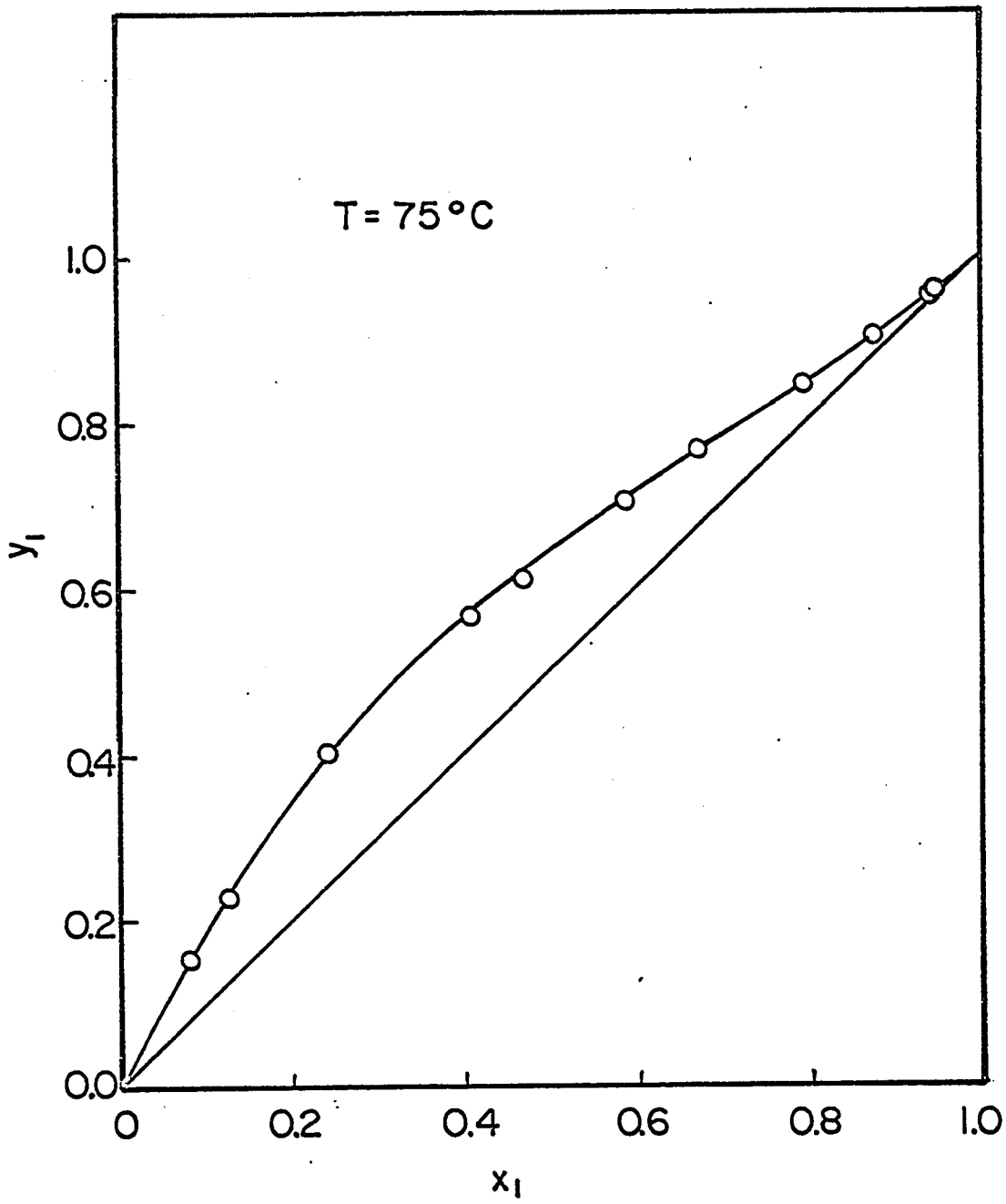


Figure 3. Binary x-y curve for the benzene(1)-n-heptane(2) system at 75°C

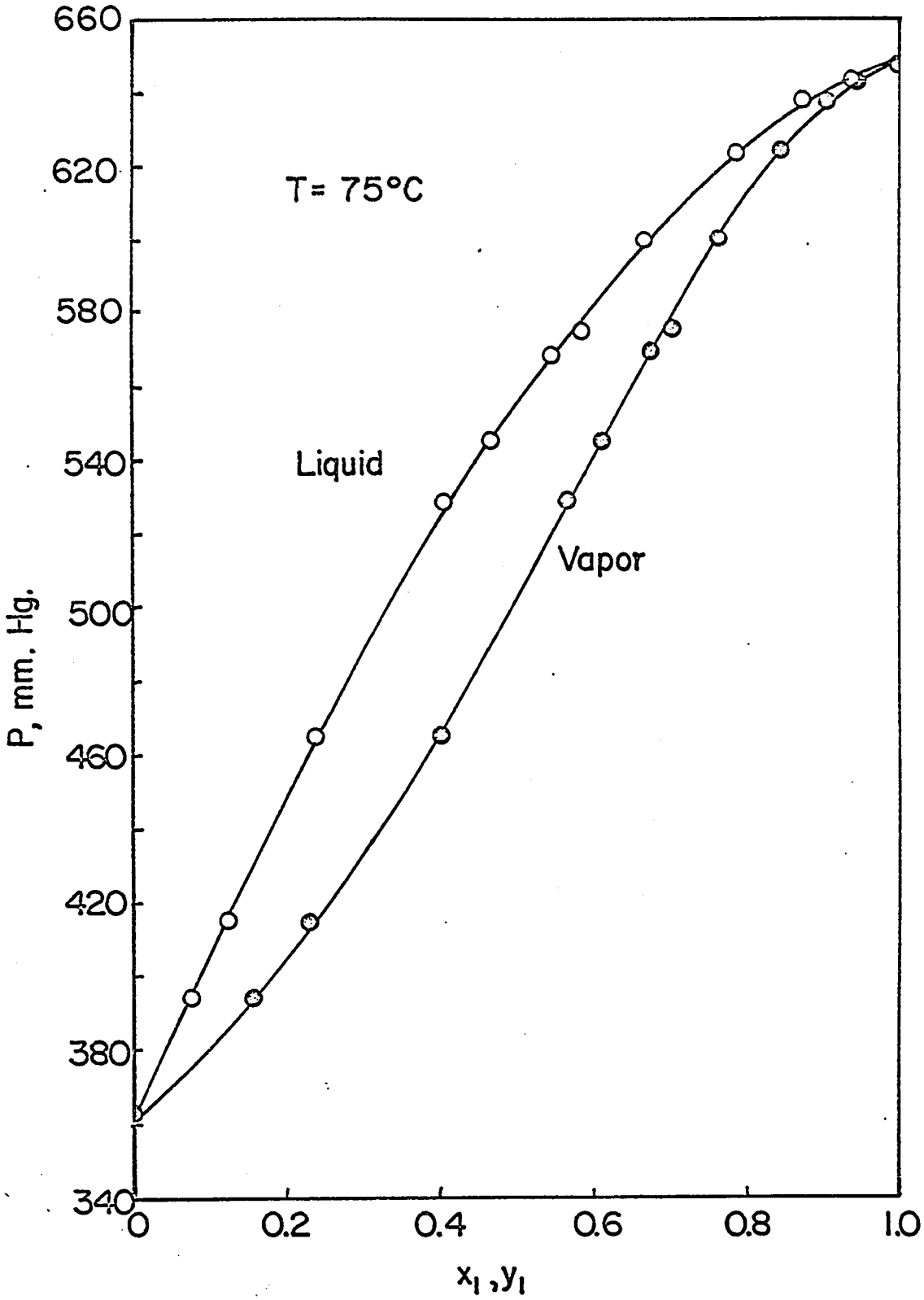


Figure 4. Total pressure vs. composition diagram for the benzene(1)-n-heptane(2) system at 75°C

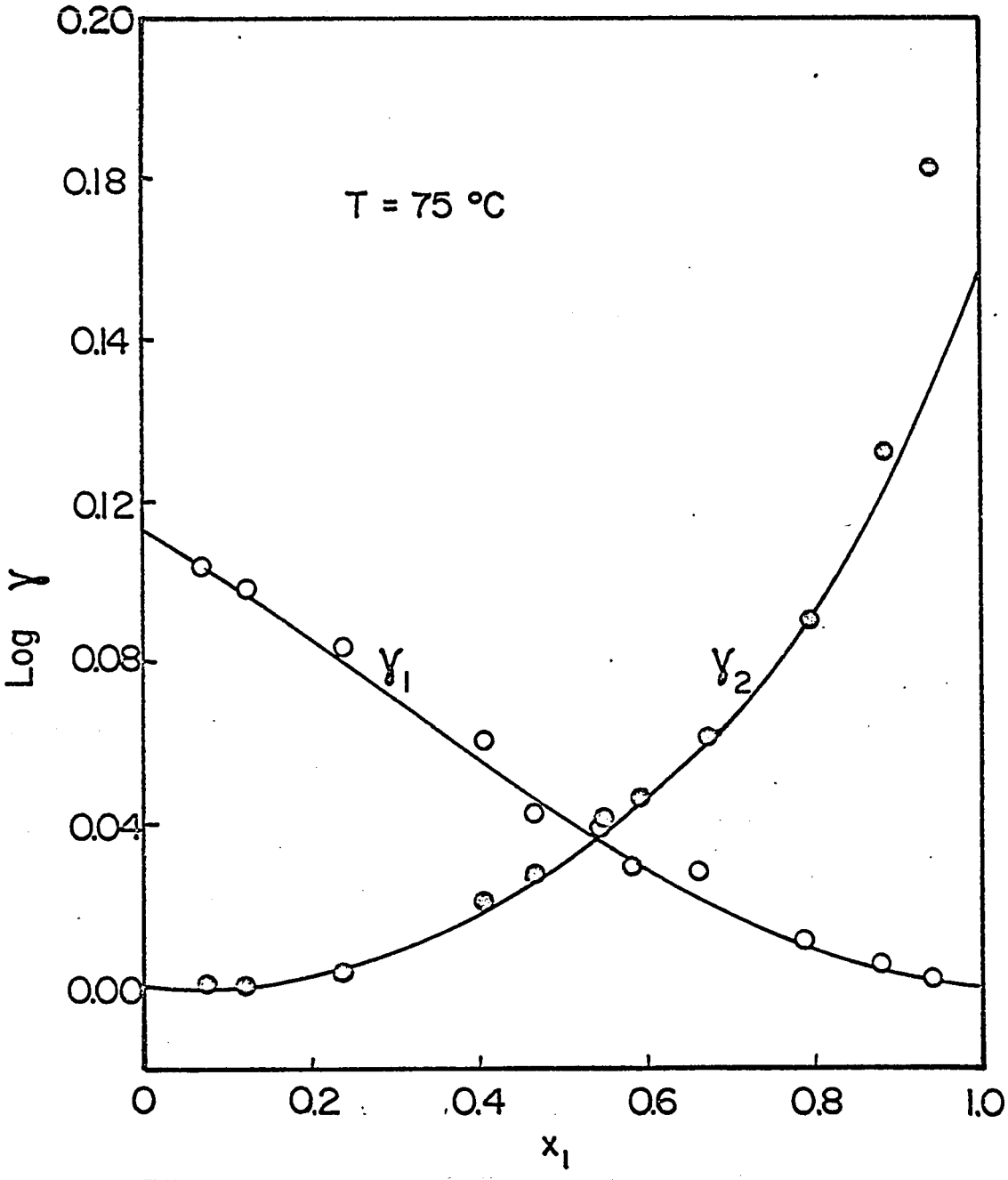


Figure 5. Activity coefficients vs. composition diagram for the benzene(1)-n-heptane(2) system at 75°C

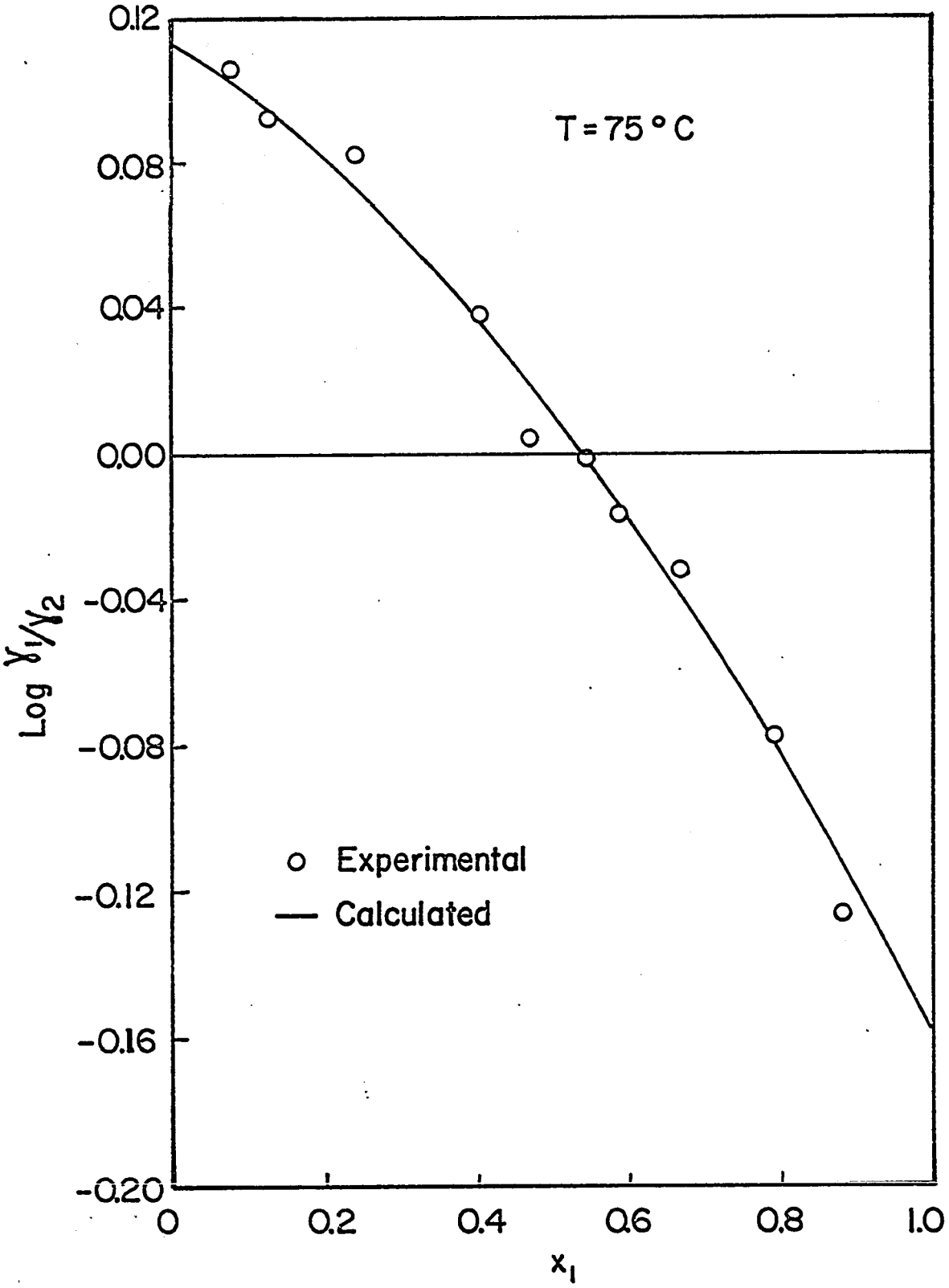


Figure 6. log γ_1/γ_2 vs. composition diagram for the benzene(1)-n-heptane(2) system at 75°C

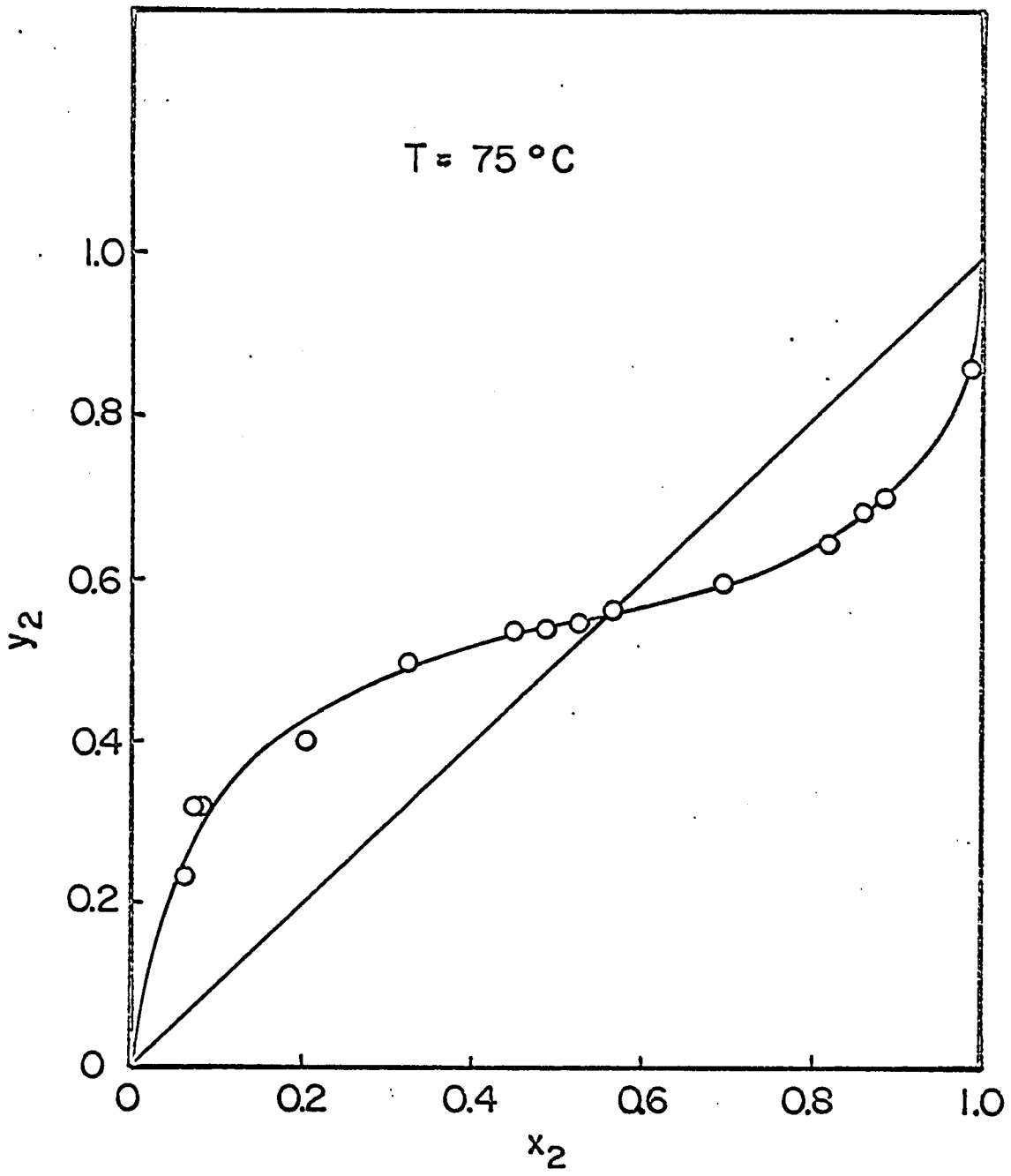


Figure 7. Binary x-y plot for the n-heptane(2)-n-propyl alcohol(3) system at 75°C

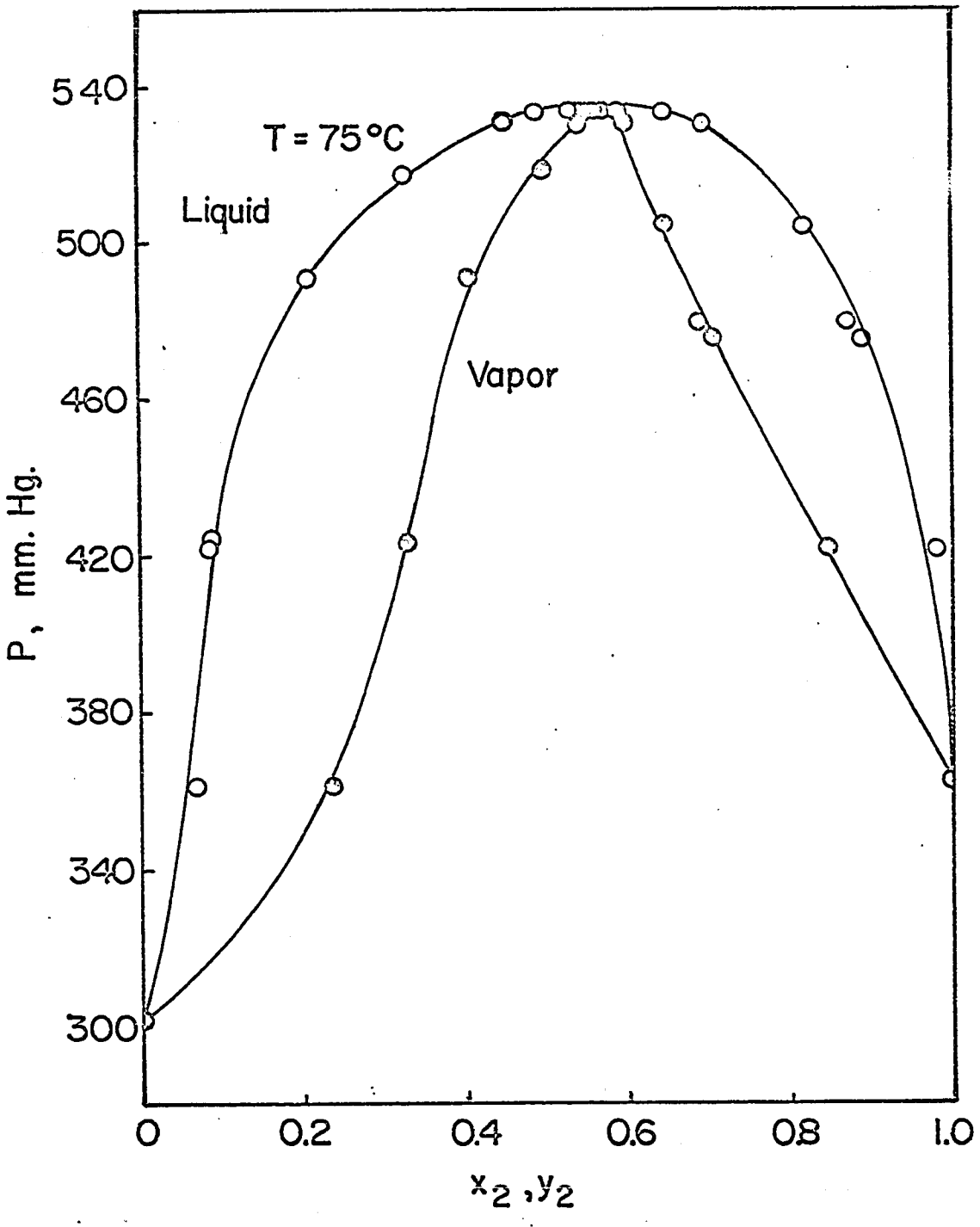


Figure 8. Total pressure vs. composition diagram for the n-heptane(2)-n-propyl alcohol(3) system at 75°C

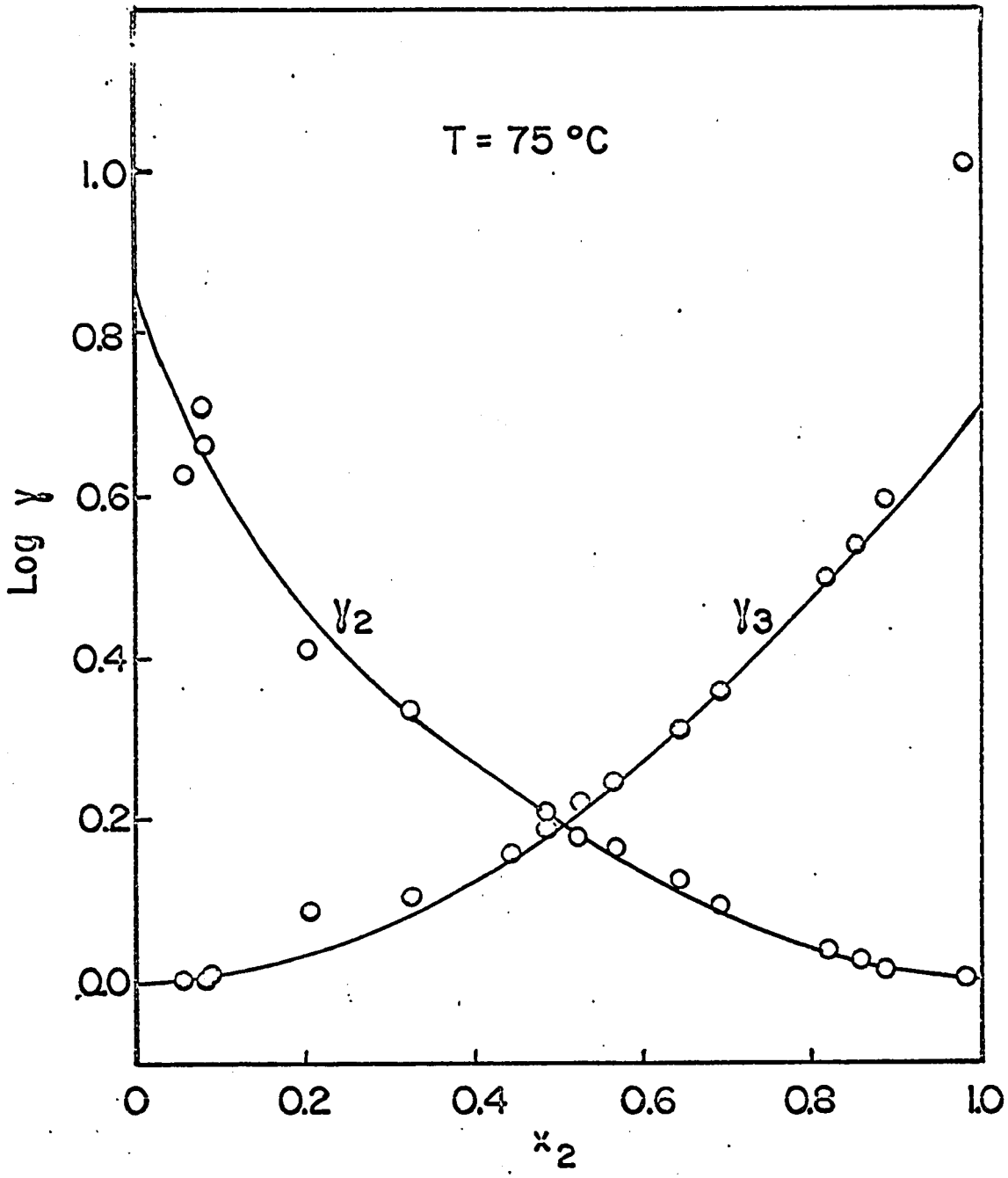


Figure 9. Activity coefficients vs. composition diagram for the n-heptane(2)-n-propyl alcohol(3) system at 75°C

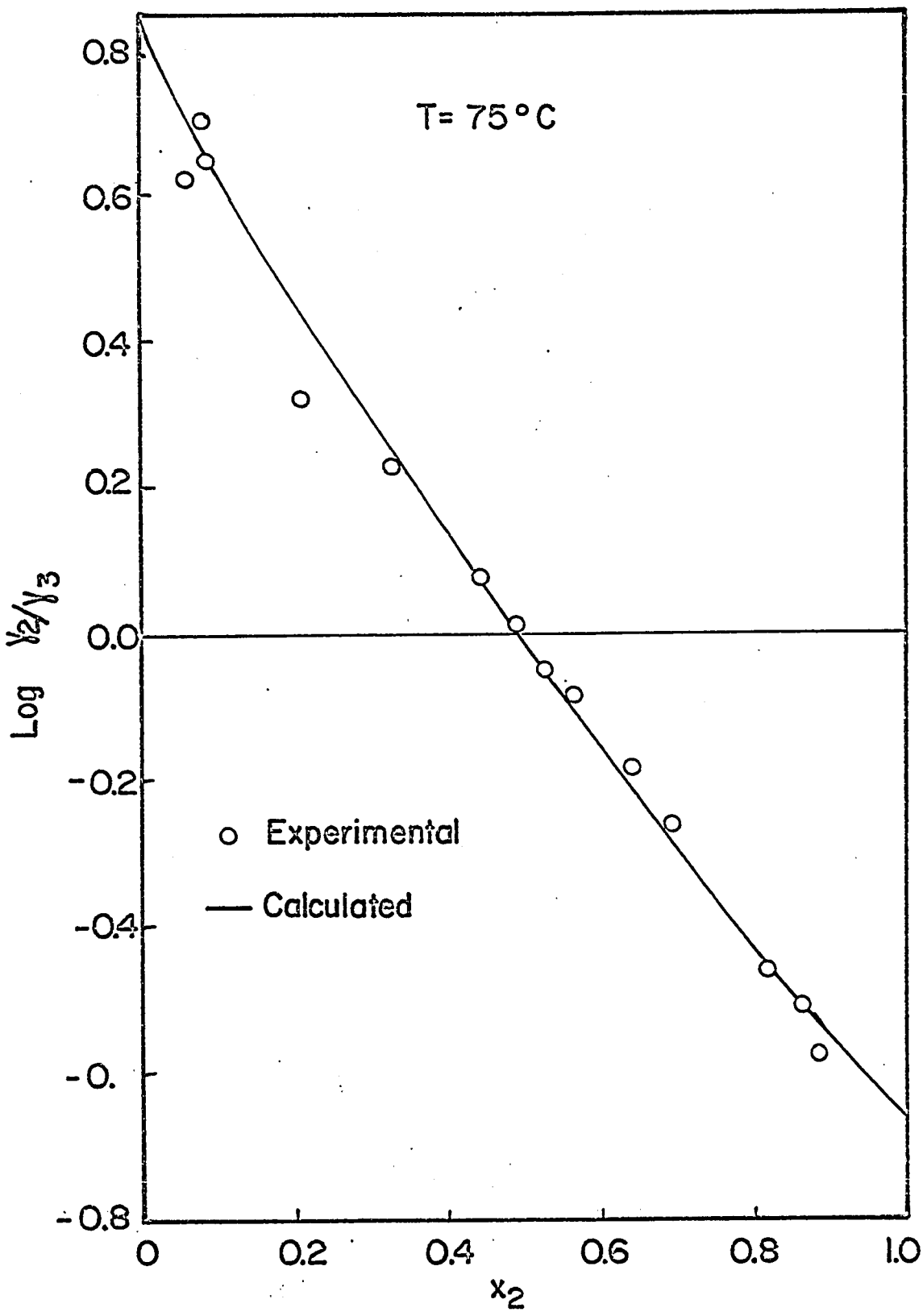


Figure 10. log γ_2/γ_3 vs. composition diagram for the n-heptane(2)-n-propyl alcohol(3) system at 75°C.

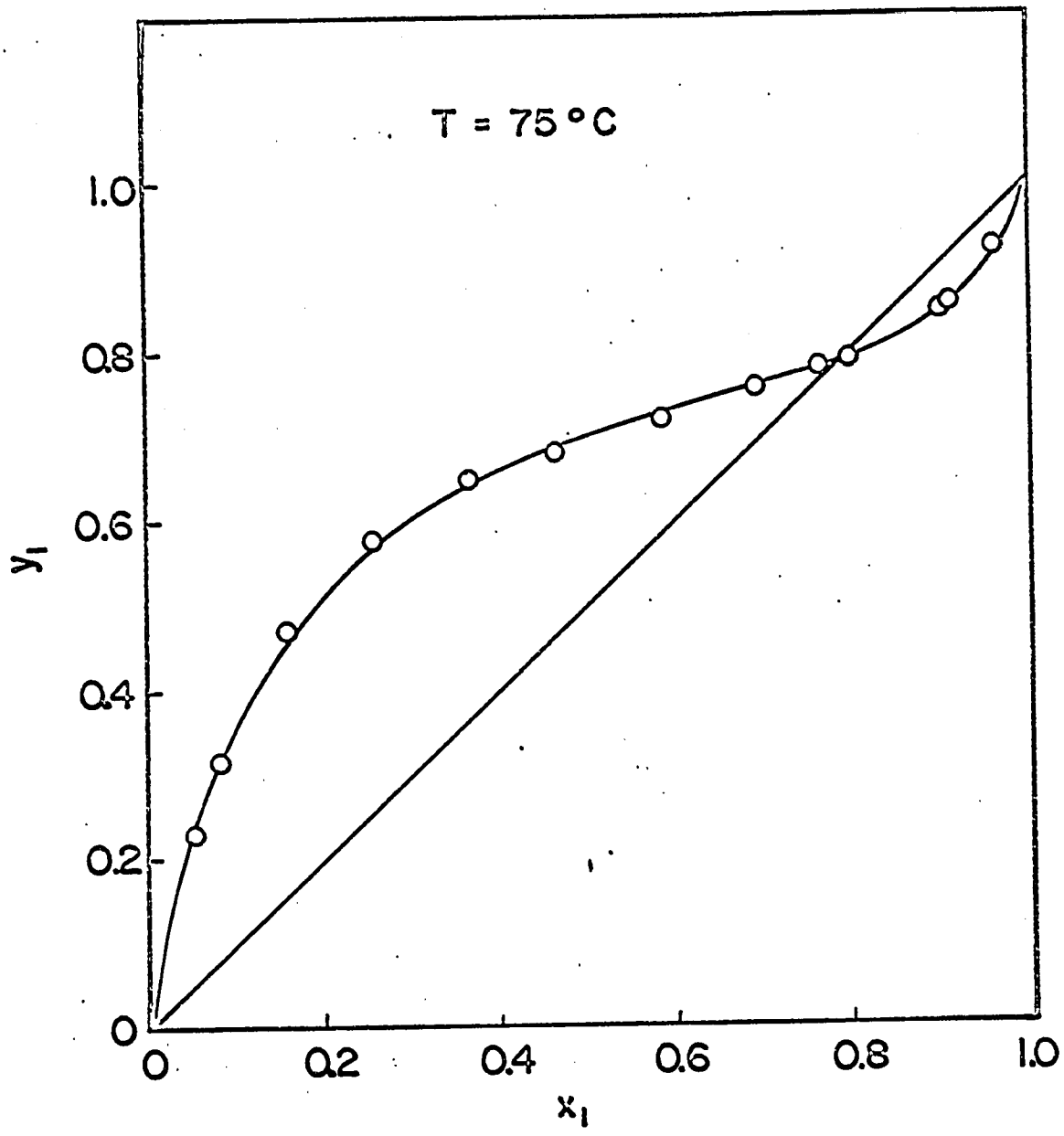


Figure 11. Binary x-y curve for the n-propyl alcohol (3)-benzene(1) system at 75°C

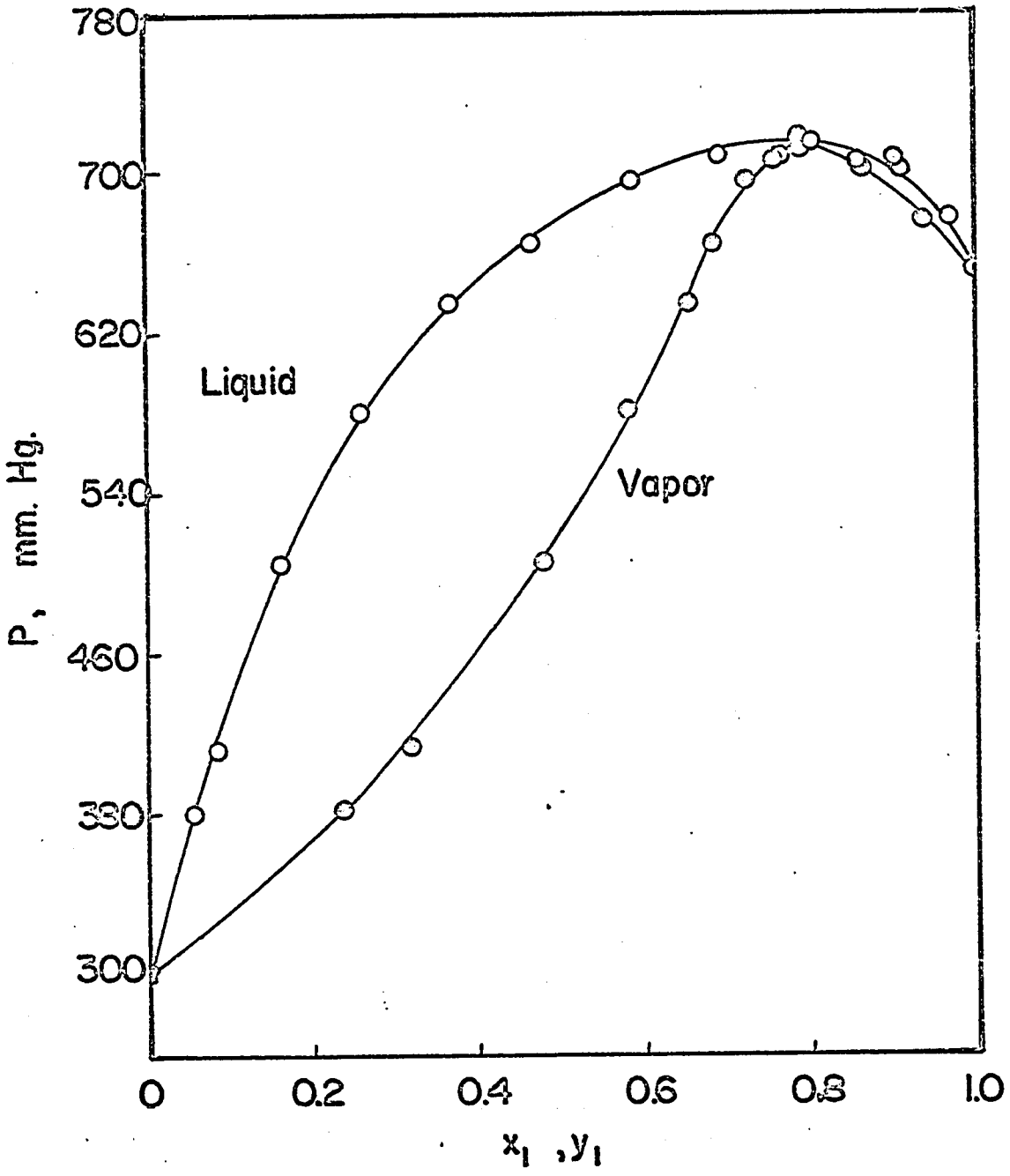


Figure 12. Total pressure vs. composition diagram for the n-propyl alcohol(3)-benzene(1) system at 75°C

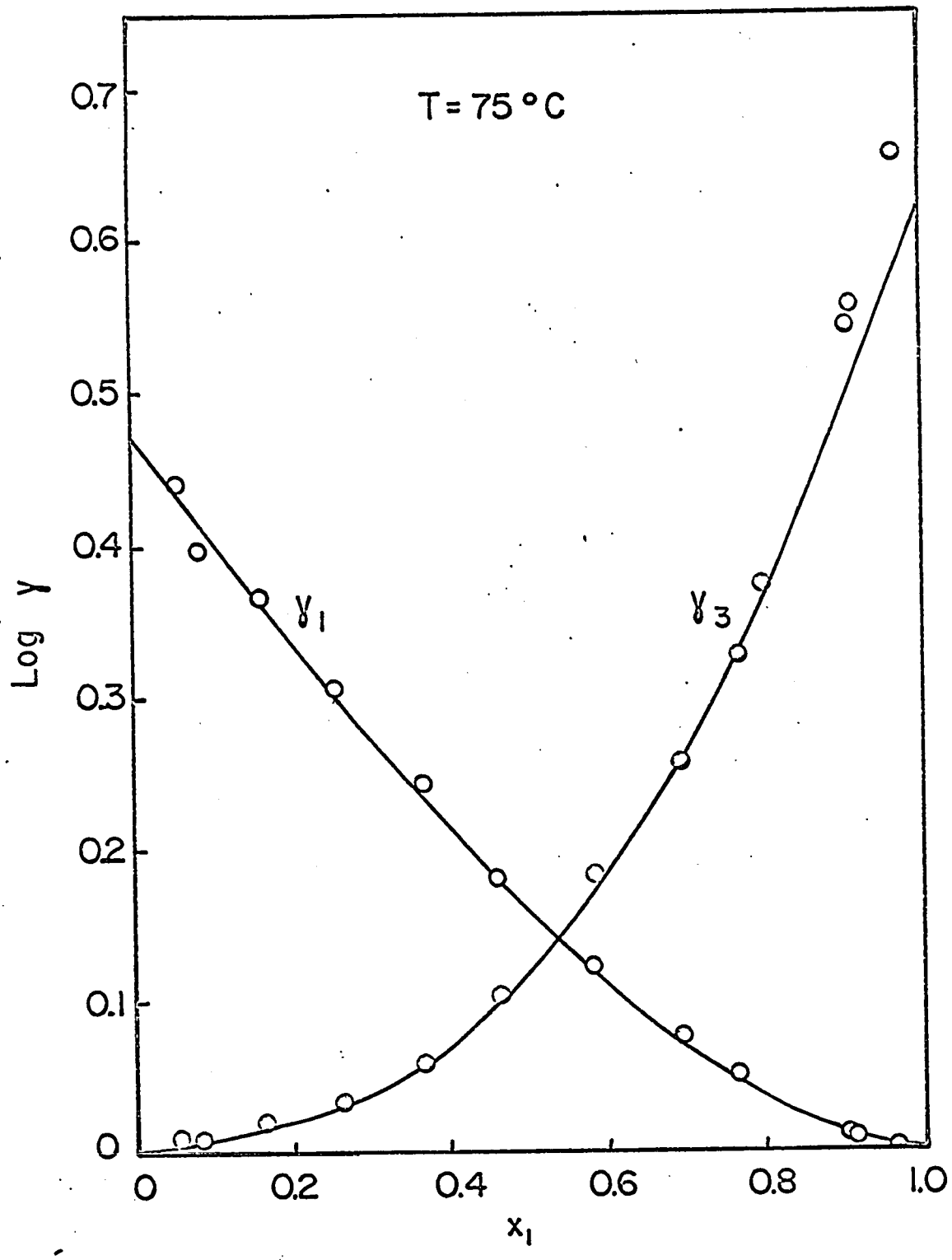


Figure 13. Activity coefficients vs. composition diagram for the n-propyl alcohol(3)-benzene(1) system at 75°C

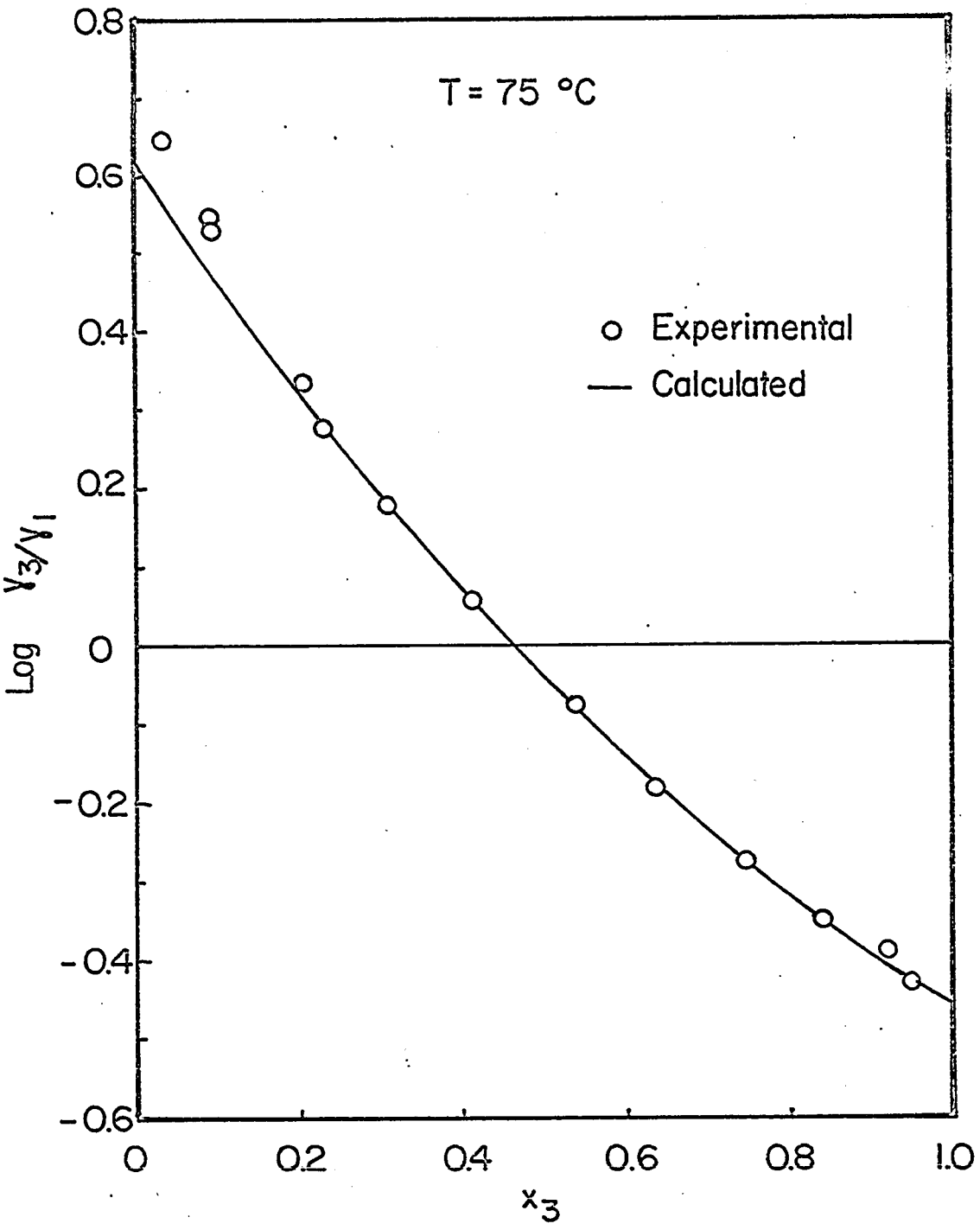


Figure 14. log γ_3/γ_1 vs. composition diagram for the n-propyl alcohol(3)-benzene(1) system at 75°C

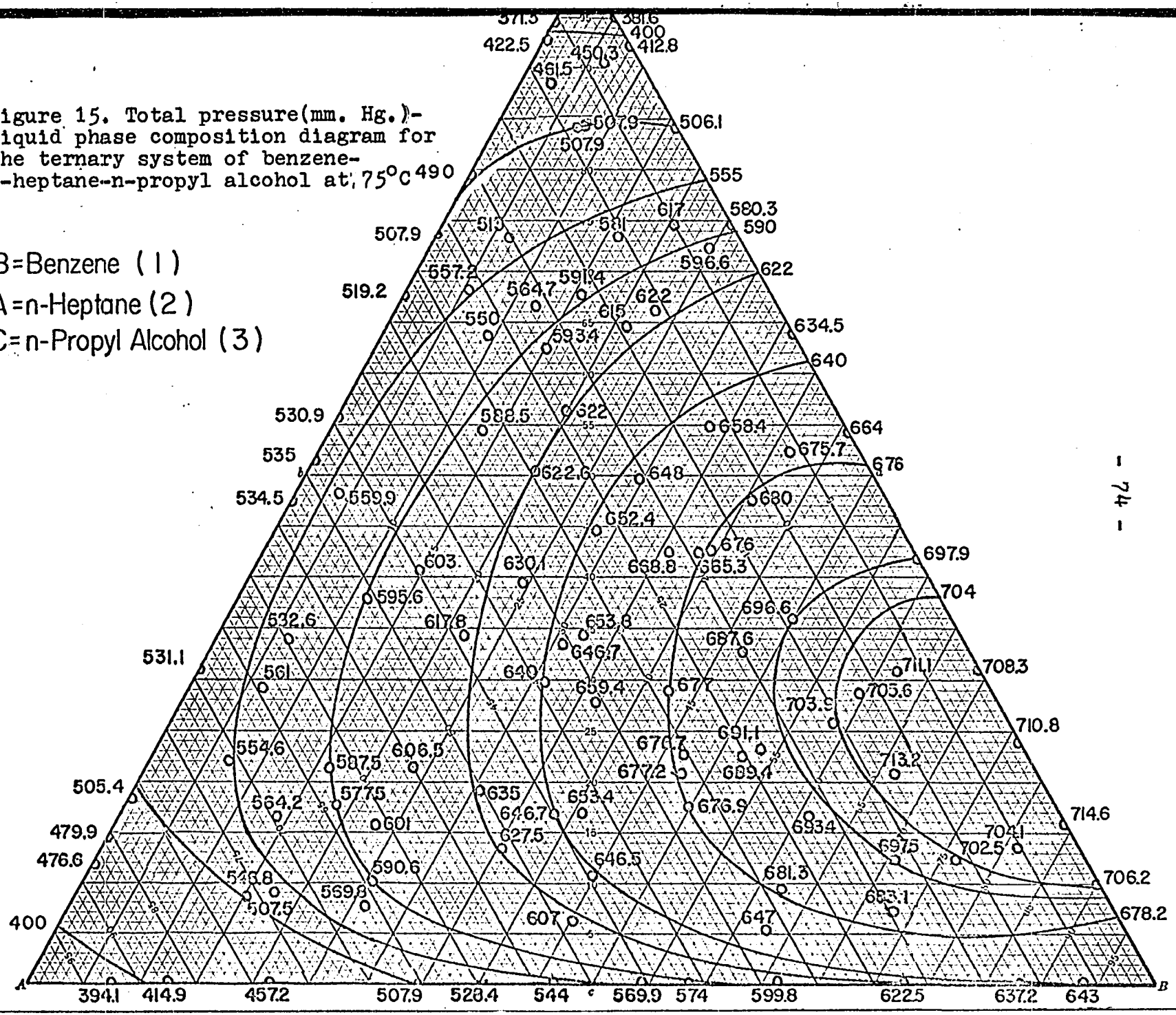
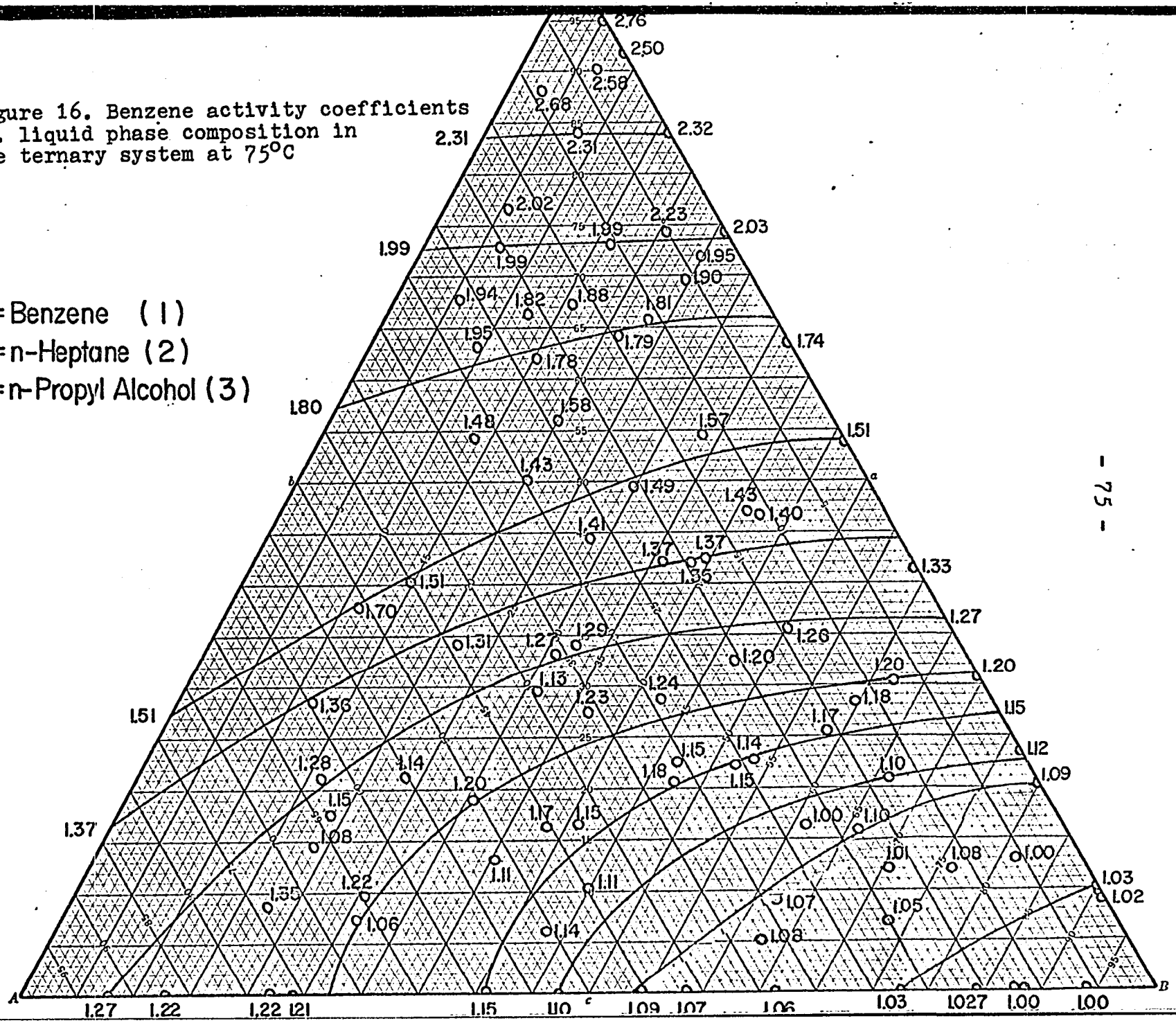


Figure 15. Total pressure(mm. Hg.)-liquid phase composition diagram for the ternary system of benzene-n-heptane-n-propyl alcohol at 75°C

Figure 16. Benzene activity coefficients vs. liquid phase composition in the ternary system at 75°C



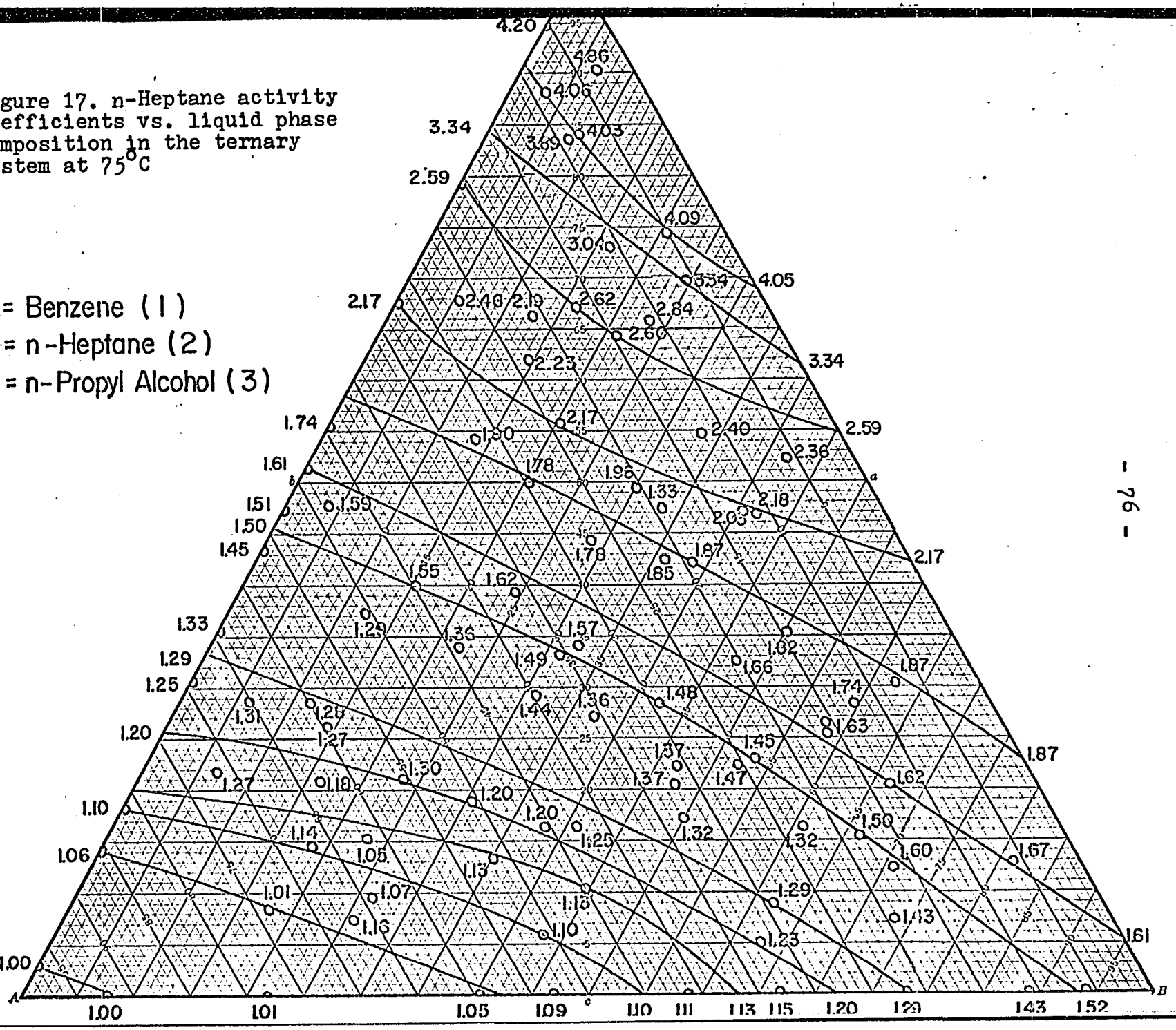
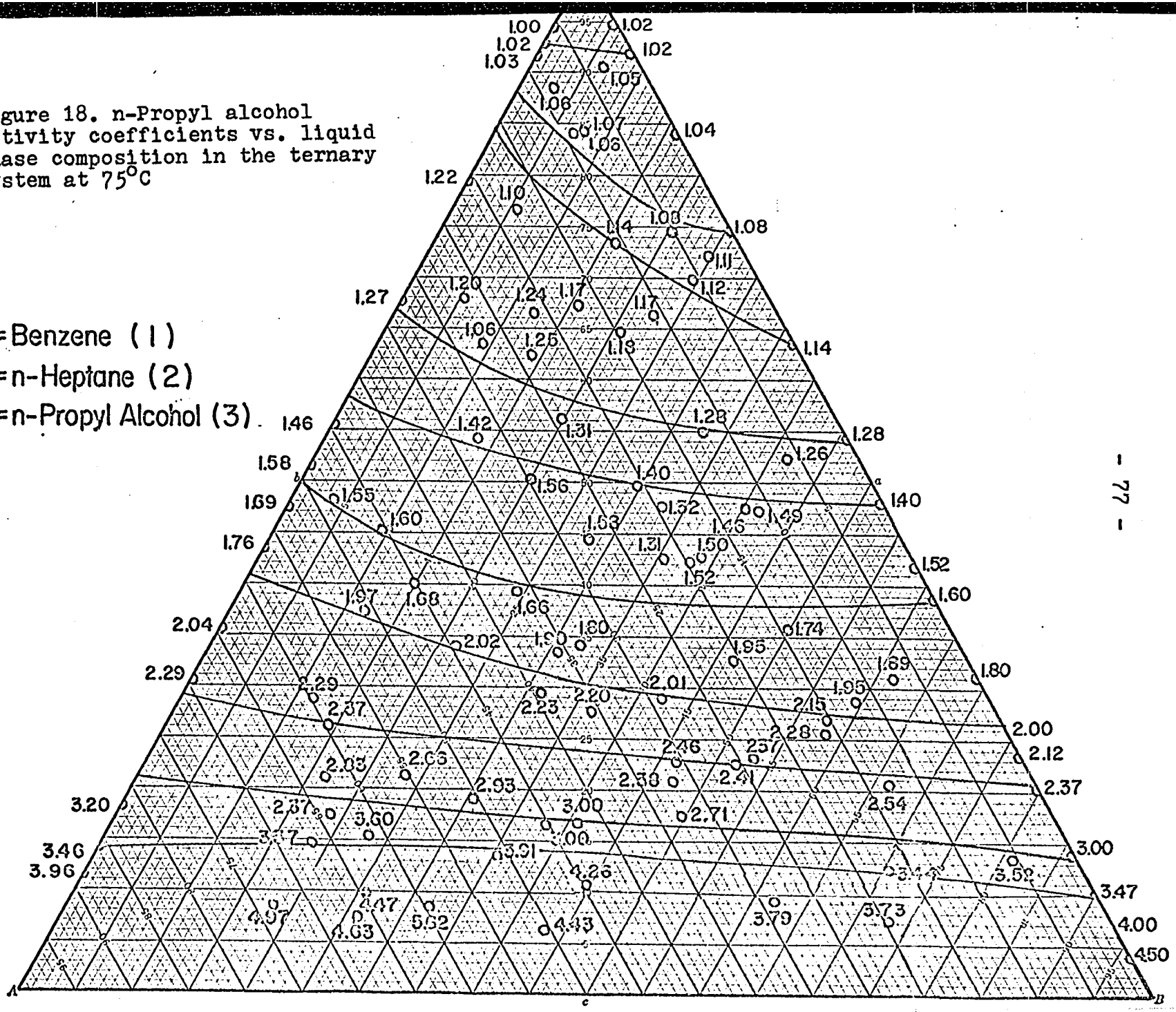


Figure 17. n-Heptane activity coefficients vs. liquid phase composition in the ternary system at 75°C

Figure 18. n-Propyl alcohol activity coefficients vs. liquid phase composition in the ternary system at 75°C



VI. CORRELATION OF RESULTS

In this investigation, Redlich-Kister equations (41) were applied to correlate the vapor-liquid equilibrium data of the ternary and also the three binaries.

Redlich-Kister's free energy function for the ternary system is represented by the following equation:

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3 \left[C_{123} + D_3 (x_1-x_2) + D_1 (x_2-x_3) + D_2 (x_3-x_1) + \cdots \right] \quad (34)$$

where $$Q_{123} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3. \quad (35)$$

In Equations 34 and 35, x_1, x_2 and x_3 are experimentally determined ternary liquid mole fractions and $\log \gamma_1$, $\log \gamma_2$ and $\log \gamma_3$ are their corresponding liquid phase activity coefficients. Q_{12}, Q_{23} and Q_{31} are the excess free energies of the binary systems and can be evaluated as follows:

$$Q_{12} = x_1x_2 \left[B_{12} + C_{12} (x_1-x_2) + D_{12} (x_1-x_2)^2 \right] \quad (36)$$

$$Q_{23} = x_2x_3 \left[B_{23} + C_{23} (x_2-x_3) + D_{23} (x_2-x_3)^2 \right] \quad (37)$$

$$Q_{31} = x_3x_1 \left[B_{31} + C_{31} (x_3-x_1) + D_{31} (x_3-x_1)^2 \right] \quad (38)$$

The Redlich-Kister constants for the binary systems are determined from the characteristic points on the log γ_1/γ_j vs. x_1 plot as suggested by Redlich and Kister (41) in the system of components i and j. Values of those characteristic points are listed in Table 15. The values of these constants, B_{12}, C_{12} and D_{12} for the system of benzene(1)-n-heptane(2), B_{23}, C_{23} and D_{23} for the n-heptane(2)-n-propyl alcohol(3) system and B_{31}, C_{31} and D_{31} for the system of n-propyl alcohol(3)-benzene(1), are listed in Table 16.

Rearranging Equation 34, Equation 39 is obtained as follows:

$$C_{123} + D_3 (x_1-x_2) + D_1 (x_2-x_3) + D_2 (x_3-x_1) =$$

$$(Q_{123}-Q_{12}-Q_{23}-Q_{31})/x_1x_2x_3 \qquad (39)$$

Employing the least squares fitting, sixty two sets reliable experimental values were used in determining the constants in Equation 39. The constants thus determined are as follows:

$C_{123} = 1.0487$

$D_1 = -2.7358$

$D_2 = -2.2500$

$D_3 = -2.5950$

The reliability of the ternary constants was checked by calculating the term Q_{123} . The calculated Q_{123} values for the ternary system are compared with the experimental values as shown in Table 13.

VII. DISCUSSION

1. The vapor pressure data for pure components at 75°C were calculated from the Antoine equation

$$\log p = A - \frac{B}{C + t} .$$

For benzene, n-heptane and n-propyl alcohol, these constants were taken from literature (1, 14). The second virial coefficient for n-propyl alcohol was calculated from the equation of Keyes, Smith and Gerry (30) using the critical constants T_c=536.9°K and P_c=50.15 atm. (48) and those for benzene and n-heptane were obtained from interpolating the available literature values given by Brown (5). The liquid molar volumes of benzene, n-heptane and n-propyl alcohol were taken from Timmermans (48). Both the second virial coefficients and liquid molar volumes used for this study are listed in Table 14.

2. Reliability of the experimental results.

(a). For the system of benzene(1)-n-heptane(2), the net area of the $\log \gamma_1/\gamma_2$ vs. x_1 plot is 0.000015 at 75°C. The binary Redlich-Kister constants evaluated from the plot fit the experimental data reasonably well as illustrated in Figure 6. It is therefore believed that the experimental data are consistent.

(b). For the system of n-heptane(2)-n-propyl alcohol(3), the net area of the log γ_2/γ_3 vs. x_2 plot is 0.00125. The Redlich-Kister constants fit the experimental data adequately as indicated in Figure 10. Hence, it may be concluded that the experimental data are thermodynamically consistent.

(c). For the system of n-propyl alcohol(3)-benzene(1), the net area of the log γ_3/γ_1 vs. x_3 diagram is 0.001675. The binary Redlich-Kister constants of this system also fit the experimental data properly as shown in Figure 14. Thus, it is claimed that the data are consistent.

(d). For the ternary system, the consistency of the data was checked by the method of Li and Lu (31) and that of McDermott and Ellis (35). Li and Lu's method was used to test the consistency of a set of data, while the method of McDermott and Ellis was employed to check the consistency of a single experimental point. If one set of data proved by Li and Lu's method (31) was much in error, points in this set would be examined one by one by the method of McDermott and Ellis (35), and therefore the inconsistent one could be singled out. The total deviation (31) for runs 23, 15, 19, 6, 3, 10, 9 and 12 was observed to be 22%. From the consistency test suggested by McDermott and Ellis (35), runs 15, 19 and 9 were considered to be inconsistent. Consequently,

these points were excluded when the consistency test method proposed by Li and Lu was employed. The deviation was then decreased to 0.27% from 22%. Following this procedure, it may be stated that runs 1, 9, 15,16, 19, 20, 26, 27, 38, 56, 59, 64, 69, 74, 75, 76 and 78 are considered to be less reliable as indicated by the test (35).

The results of the consistency test are summarized and shown in Figure 26. It appears that most of the data determined for the ternary system are consistent. However, the data in the region of very high concentration of any component are less consistent. The fact is that the uncertainty of the analytical technique increases when one component is in much high concentration than others. This shows why the experimental determination of terminal activity coefficients is difficult. In conclusion, the data at 75°C are considered to be consistent.

3. Azeotrope determination

(a). To determine the conditions for azeotrope formation for the system of benzene-n-heptane, P-x and x-y diagrams were drawn. No azeotrope was found in this system as shown in Figures 3 and 4. Previously, Brown and Ewald (6) suggested that an azeotrope might be found at a high benzene concentration at a temperature below 38°C. The result of this investigation seems to confirm their sugges-

tion.

(b). For the system n-heptane(2)-n-propyl alcohol (3), the P-x diagram is rather flat on either side of the azeotrope as shown in Figure 8. This condition makes it difficult to select precisely the true azeotropic point. When the x-y diagram (Figure 7) is drawn, the azeotrope may be found graphically without difficulty. The pressure assigned to the azeotrope was the maximum of the P-x diagram. In most cases, the final point was very close to the previously selected one. At 75°C, the azeotrope found for this system from the x-y plot was at x_2=0.56.

(c). An x-y diagram (Figure 11) was also drawn to determine the azeotrope for the system of n-propyl alcohol (3)-benzene(1) because the P-x diagram (Figure 12) is also rather flat on either side of the azeotrope. The azeotrope observed in this investigation from Figure 11 was at x_1=0.785.

(d). No azeotrope was found in this ternary system directly from the experiment. However, it is interesting to mention that an azeotrope trough (43) joining binary azeotropes of the systems of n-heptane(2)-n-propyl alcohol(3) and n-propyl alcohol(3)-benzene(1) was noticed. It is obvious that most of the vapor compositions tend to converge along a path which connects the azeotropes of the two binaries as shown in Figure 27.

4. Isotherm Interpolation. The three binary and ternary isotherms were used to interpolate the complete isothermal ternary data in a triangular diagram. It is noted that the benzene vapor isoforms are nearly regularly spaced as the mole fraction of benzene in the vapor phase is lower than 0.65. The experimental ternary points on each isotherm permit the complete isoforms to be sketched in with confidence as to their reliability (Figure 28).

5. The ternary as well as the binary experimental vapor-liquid equilibrium data have been correlated satisfactorily with the Redlich-Kister equations. The calculated activity coefficients deviates from the experimental values within 5% for the binary systems, and within 13% for the ternary system.

VIII. CONCLUSIONS

1. Vapor-liquid equilibrium data obtained for the binary and ternary systems in this investigation are considered to be thermodynamically consistent.

2. The results indicate that the modified Gillespie equilibrium still can be used to produce without difficulty good equilibrium data and the technique of analysis for the binary and ternary systems proves to be adequate.

3. The binary Redlich-Kister constants at 75°C determined from experimental results are as follows:

(a). Benzene(1)-n-Heptane(2) System

$B_{12} = 0.1386$

$C_{12} = 0.0240$

$D_{12} = -0.0016$

(b). n-Heptane(2)-n-Propyl Alcohol(3) System

$B_{23} = 0.7467$

$C_{23} = 0.0120$

$D_{23} = 0.0893$

(c). n-Propyl Alcohol(3)-Benzene(1) System

$B_{31} = 0.5415$

$C_{31} = -0.0856$

$D_{31} = 0.0020$

4. The ternary Redlich-Kister constants at 75°C evaluated by the IBM 1620 computer are listed below:

$$C_{123} = 1.0487$$
$$D_1 = -2.7385$$
$$D_2 = -2.2500$$
$$D_3 = -2.2595$$

IX. NOMENCLATURE

A, B	=	constants of van Laar equation
A, B	=	constants of Margules equation
A, B, C	=	constants of Antoine equation
a, b	=	any two points on the same curve in a triangular plot
a, b, c .... y, z	=	points on a loop in a triangular plot
B_{ii}	=	second virial coefficient of component i in the virial equation of state
B_{12}, C_{12}, D_{12} B_{23}, C_{23}, D_{23} B_{31}, C_{31}, D_{31}	=	constants of Redlich-Kister equation in the binary systems
C_{123}, D_1, D_2, D_3	=	constants of Redlich-Kister equation in the ternary system
f	=	fugacity
log	=	logarithm to base 10
N	=	number of components
P	=	total pressure
P_c	=	critical pressure
p	=	vapor pressure
Q	=	$\Delta G^E/2.303\ RT$ = excess free energy function
R	=	gas constant
T	=	absolute temperature

T_c = critical temperature

t = temperature

V = molar volume

x = mole fraction in the liquid phase

y = mole fraction in the vapor phase

$Z_i = \exp\left[\frac{(p_i - P)\,(V_i^l - B_{ii})}{RT}\right]$

α = residual molar volume

γ = activity coefficient

Γ = liquid phase activity coefficient

φ = fugacity coefficient

Superscripts

l = liquid phase

v = vapor phase

o = standard state

Subscripts

1 = component 1

2 = component 2

3 = component 3

12 = components 1 and 2

23 = components 2 and 3

31 = components 3 and 1

123 = components 1, 2 and 3

i = component i

ia = component i at point a

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XI. APPENDIX I

TABLE 6

Calibration of Temperature - Absolute Millivolts

For the Copper Constantan Thermocouple

Temperature °C	E.M.F. Absolute Millivolts
0.00	0.0005
45.82	1.8605
45.95	1.8620
50.15	2.0480
59.47	2.4535
68.95	2.8666
79.64	3.3455
89.24	3.7841
96.02	4.0937

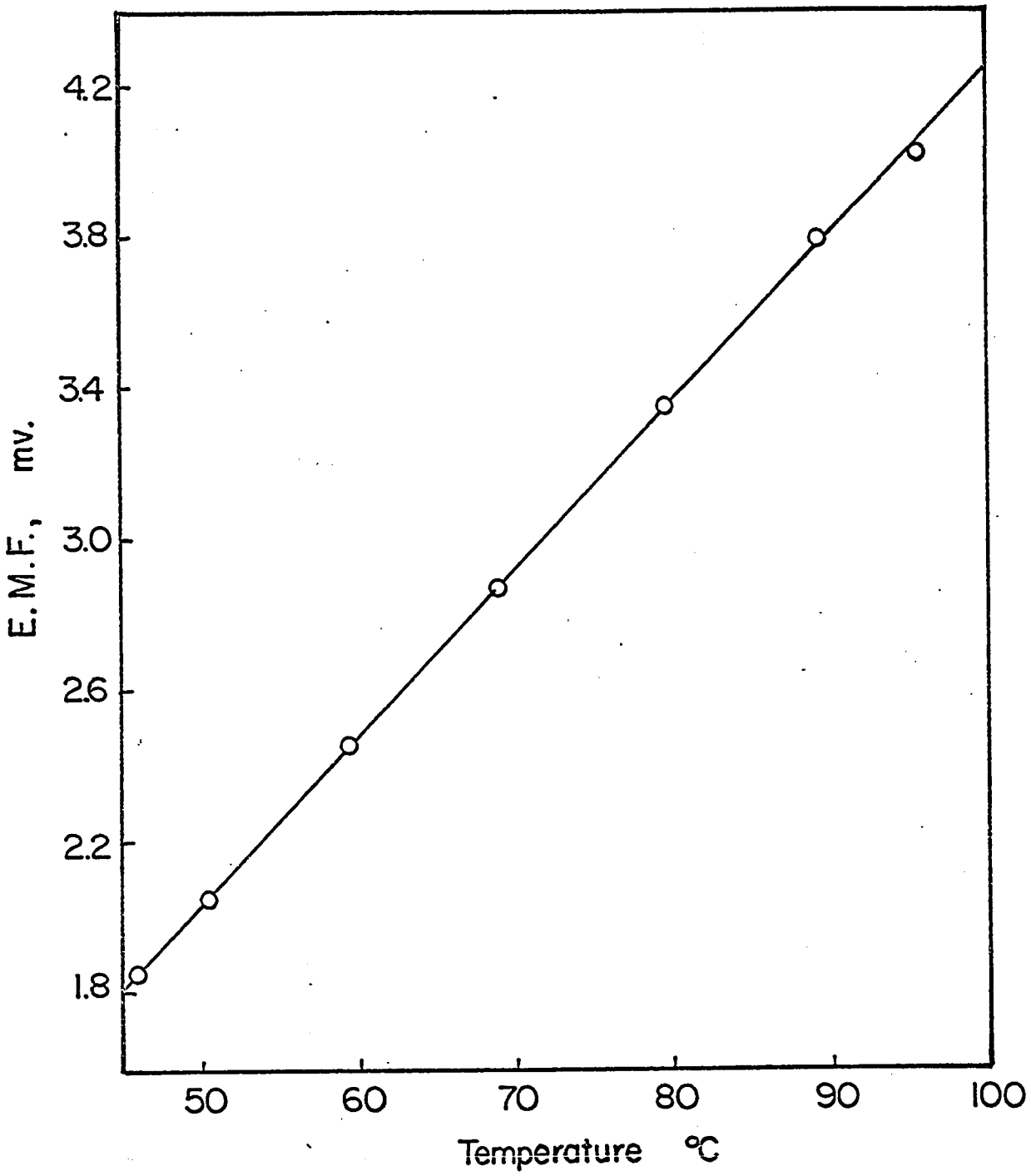


Figure 19. Calibration curve of copper constantan thermocouple

TABLE 7

Calibration of Composition - Refractive Index for the System Benzene(1) - n-Heptane (2)

Run	Mole Fraction of Benzene x_1	Refractive Index at 25°C
1	0.0000	1.3852
2	0.0703	1.3897
3	0.1370	1.3945
4	0.1945	1.3981
5	0.2953	1.4060
6	0.3799	1.4131
7	0.4901	1.4236
8	0.5846	1.4338
9	0.5941	1.4348
10	0.7048	1.4461
11	0.7079	1.4491
12	0.8803	1.4624
13	0.8832	1.4759
14	0.9001	1.4787
15	0.9095	1.4807
16	0.9236	1.4833
17	1.0000	1.4979

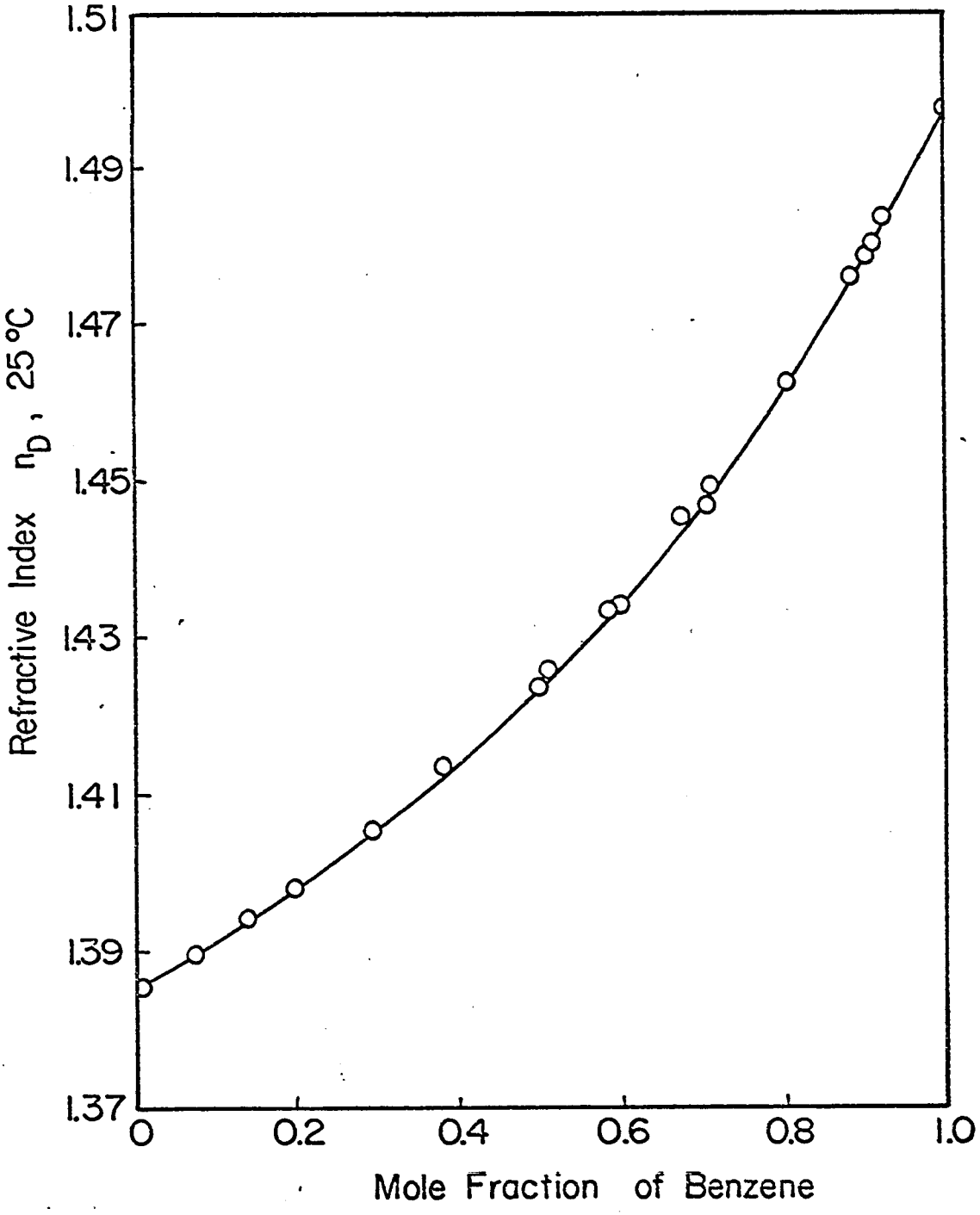


Figure 20. Calibration curve of composition-refractive index for benzene(1)-n-heptane(2) system

TABLE 8

Calibration of Composition - Refractive Index for the System n-Propyl Alcohol(3) - Benzene(1)

Run	Mole Fraction of Benzene x_1	Refractive Index at 25^0C
1	0.0000	1.3835
2	0.0663	1.3922
3	0.1170	1.3987
4	0.1235	1.3995
5	0.2097	1.4103
6	0.2459	1.4148
7	0.3050	1.4217
8	0.3354	1.4255
9	0.3642	1.4288
10	0.4014	1.4330
11	0.4746	1.4415
12	0.5580	1.4520
13	0.6910	1.4655
14	0.7569	1.4721
15	0.7630	1.4732
16	0.8771	1.4852
17	0.9367	1.4911
18	1.0000	1.4983

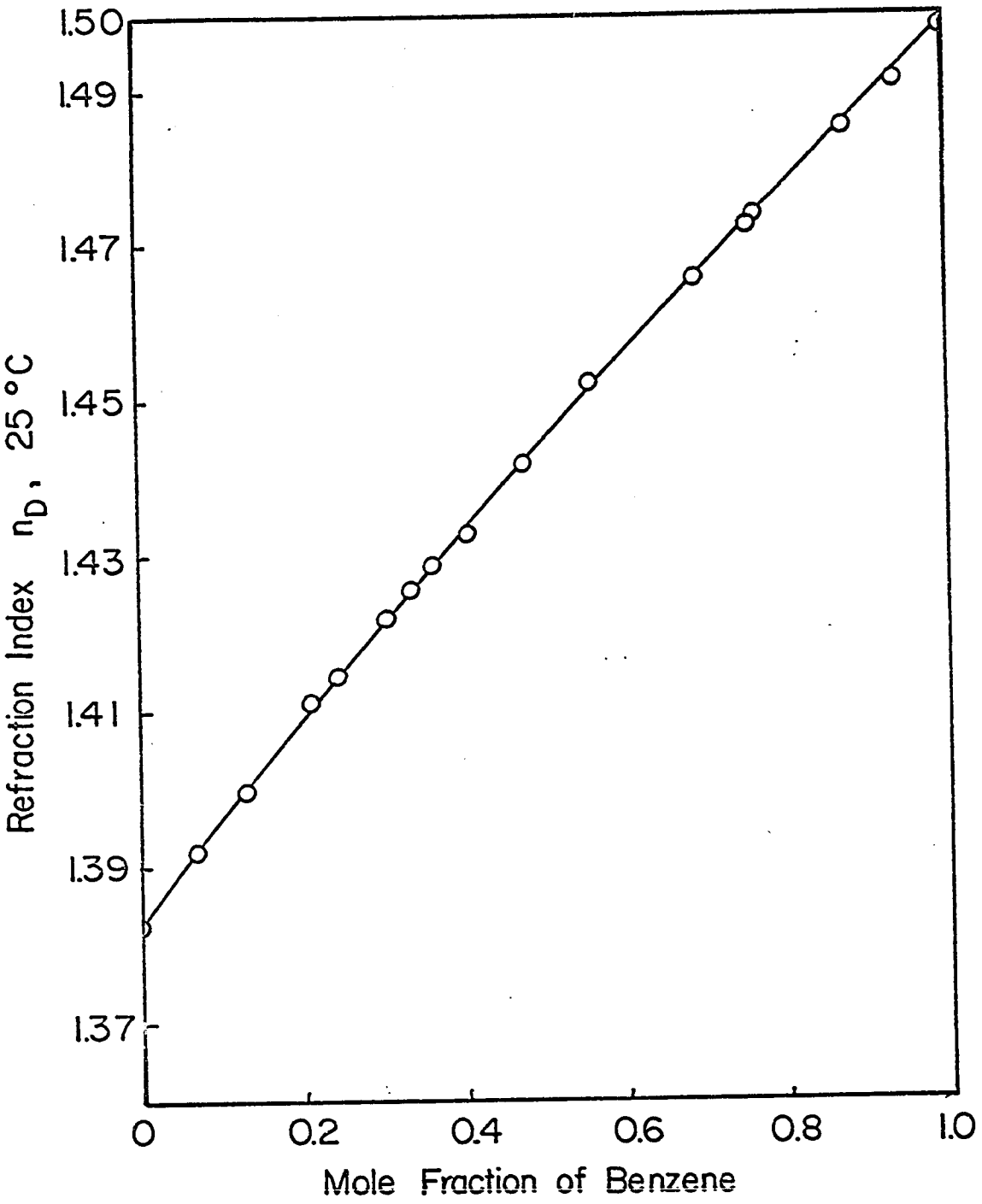


Figure 21. Calibration curve of composition - refractive index for n-propyl alcohol(3) -benzene(1) system

TABLE 9

Calibration of Mole Fraction Ratio vs. Area Ratio for the System of n-Heptane(2)-n-Propyl Alcohol(3)

Mole Fraction Ratio $\frac{\text{n-Propyl Alcohol}}{\text{n-Heptane}}$	Area Ratio $\frac{\text{n-Propyl Alcohol}}{\text{n-Heptane}}$
0.0746	0.0993
0.1392	0.1310
0.3681	0.2846
0.3877	0.2827
0.5008	0.3649
0.5266	0.4048
0.6172	0.4723
1.0271	0.7440
1.0988	0.7740
1.3063	0.9148
1.6884	1.1074
1.8068	1.1949
2.1400	1.3387
2.2551	1.3859
3.0808	1.9065
3.4592	2.0035
5.6615	2.8770
8.6597	4.0674
10.2605	4.4147
18.0965	6.5593
21.0849	7.1376

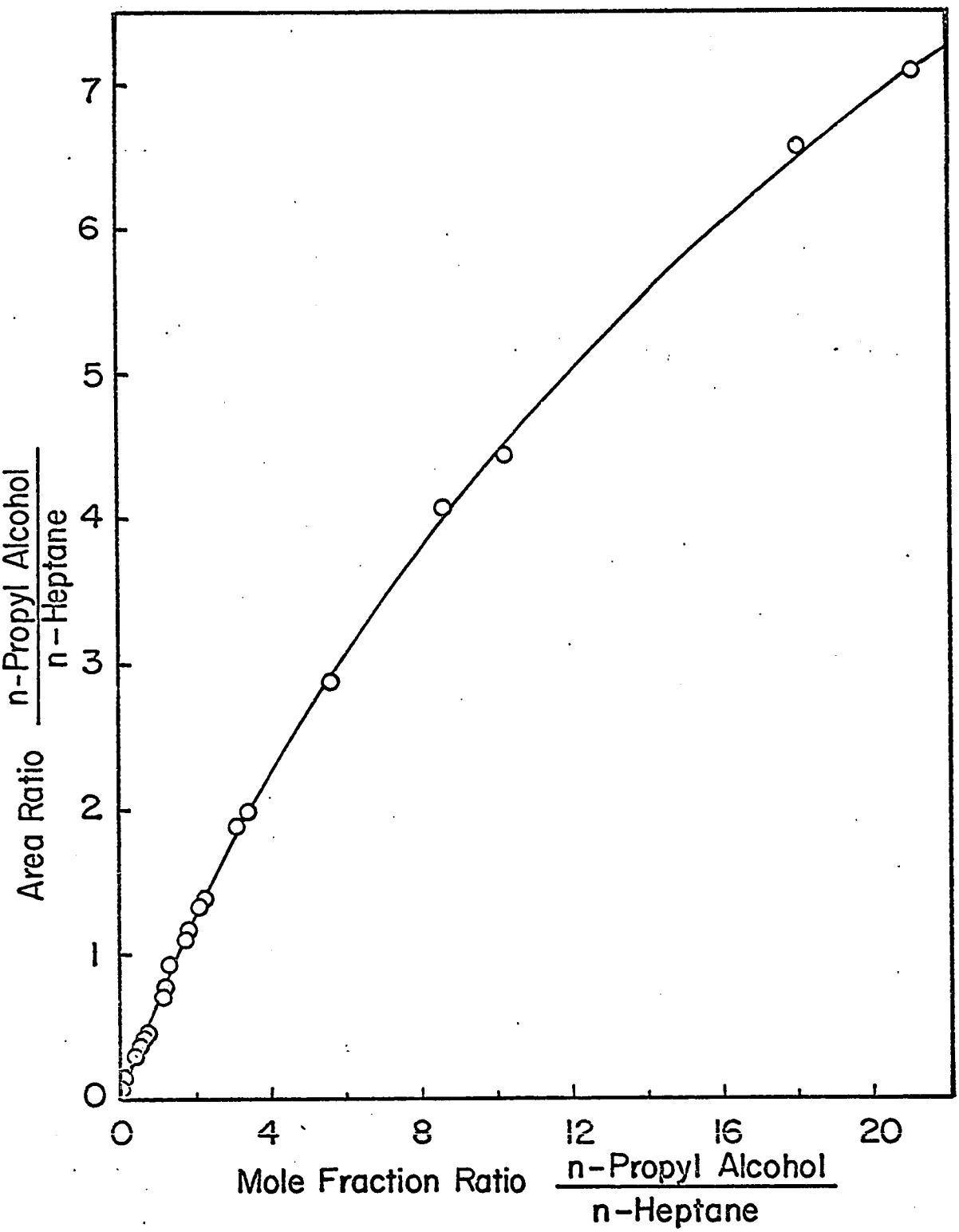


Figure 22. Calibration curve of (n-propyl alcohol/n-heptane) area vs. (n-propyl alcohol/n-heptane) mole fraction for n-heptane(2)-n-propyl alcohol(3) system

TABLE 10

Calibration of Mole Fraction Ratio vs. Area Ratio for the System

Benzene(1)-n-Heptane(2)-n-Propyl Alcohol(3)

Mole Fraction Ratio			Area Ratio		
n-Heptane / Benzene	n-Propyl Alcohol / n-Heptane	Benzene / n-Propyl Alcohol	n-Heptane / Benzene	n-Propyl Alcohol / n-Heptane	Benzene / n-Propyl Alcohol
1.2282	0.9449	0.8616	1.6449	0.6343	0.9583
0.7332	1.1849	1.1509	0.9943	0.7200	1.3968
0.5246	6.1180	0.3115	0.6891	4.1503	0.3496
0.6058	2.6887	0.6139	0.8333	1.6816	0.7135
0.4577	3.7149	0.5881	0.6013	2.4157	0.6883
0.2552	10.0970	0.3880	0.3011	7.6666	0.4331
0.7041	0.1663	8.5356	0.9552	0.0608	17.1923
0.3953	3.5934	0.7039	0.5047	2.3924	0.8280
0.6125	4.5827	0.3562	0.8510	3.0500	0.3852
0.1799	17.7696	0.3127	0.1832	16.3714	0.3333
0.1022	22.7373	0.4300	0.0819	25.7000	0.4737

.... continued

TABLE 10 (continued)

Mole Fraction Ratio			Area Ratio		
n-Heptane / Benzene	n-Propyl Alcohol / n-Heptane	Benzene / n-Propyl Alcohol	n-Heptane / Benzene	n-Propyl Alcohol / n-Heptane	Benzene / n-Propyl Alcohol
0.5094	12.4329	0.1578	0.6526	10.0967	0.1517
1.6951	0.5169	1.1412	2.4715	0.2827	1.4308
0.1887	2.3426	2.2613	0.2274	1.5000	2.9310
0.1317	2.2680	3.3455	0.1630	1.4747	4.1575
0.1833	0.9692	5.6288	0.2393	0.5890	7.0930
0.0782	1.3320	9.6038	0.0899	0.7692	14.4600
10.1916	0.7877	0.1245	24.4000	0.4508	0.0909
12.8322	0.7939	0.0098	35.4285	0.4556	0.0619
6.3462	1.1272	0.1398	11.9444	0.6628	0.1263

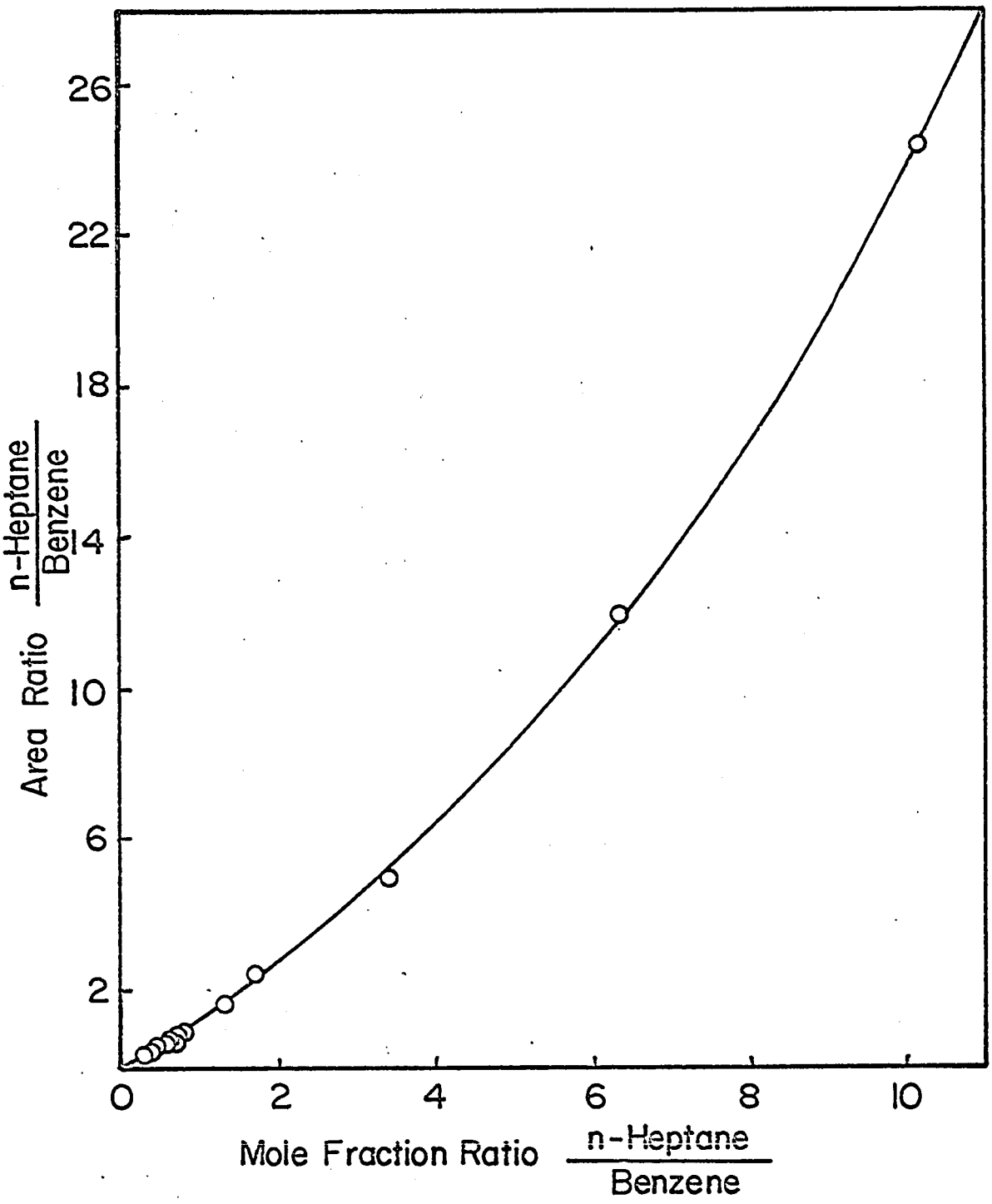


Figure 23. Calibration curve of (n-heptane/benzene) area vs. (n-heptane/benzene) mole fraction for the ternary system

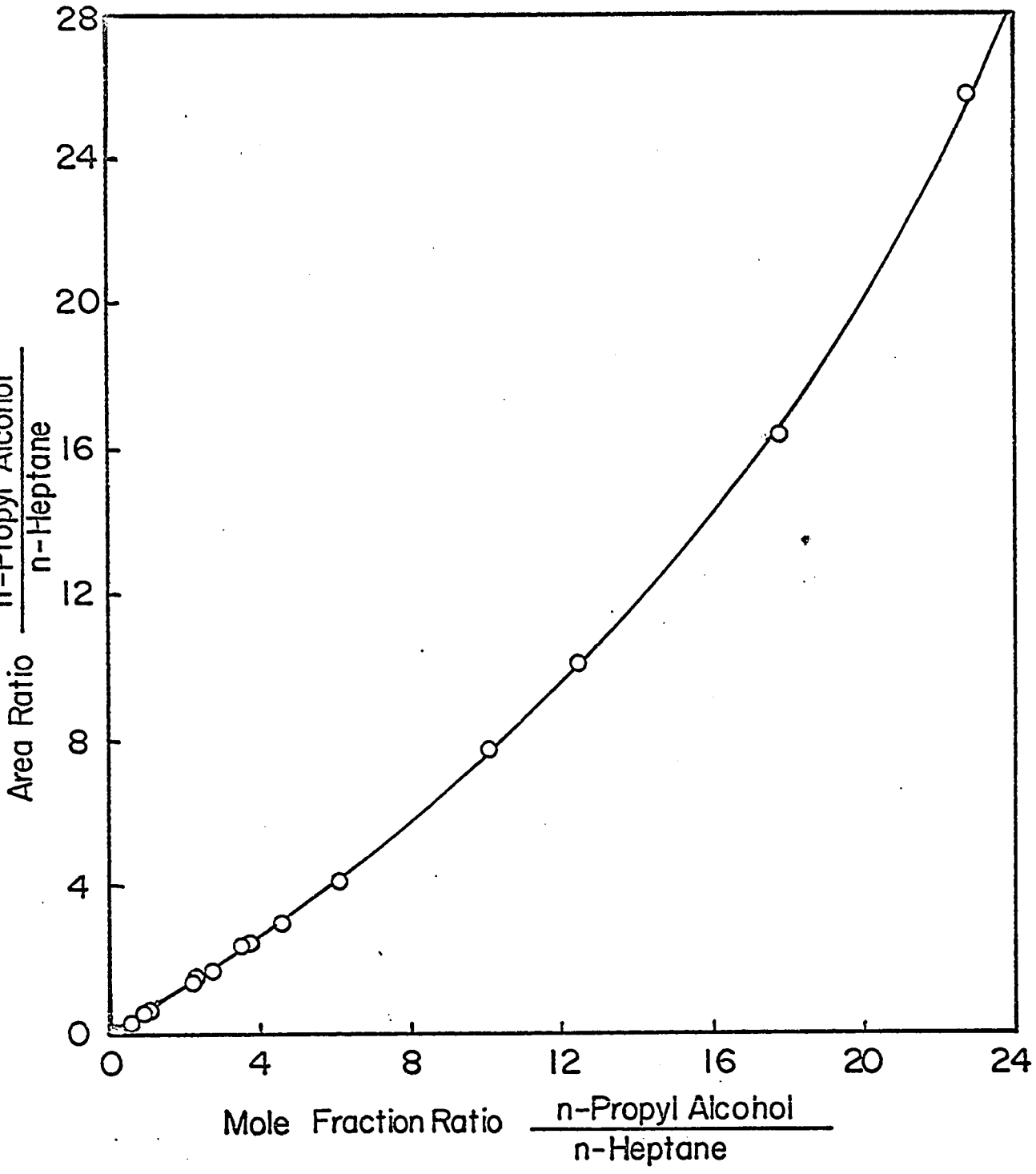


Figure 24. Calibration curve of (n-propyl alcohol/n-heptane) area vs. (n-propyl alcohol/n-heptane) mole fraction for the ternary system

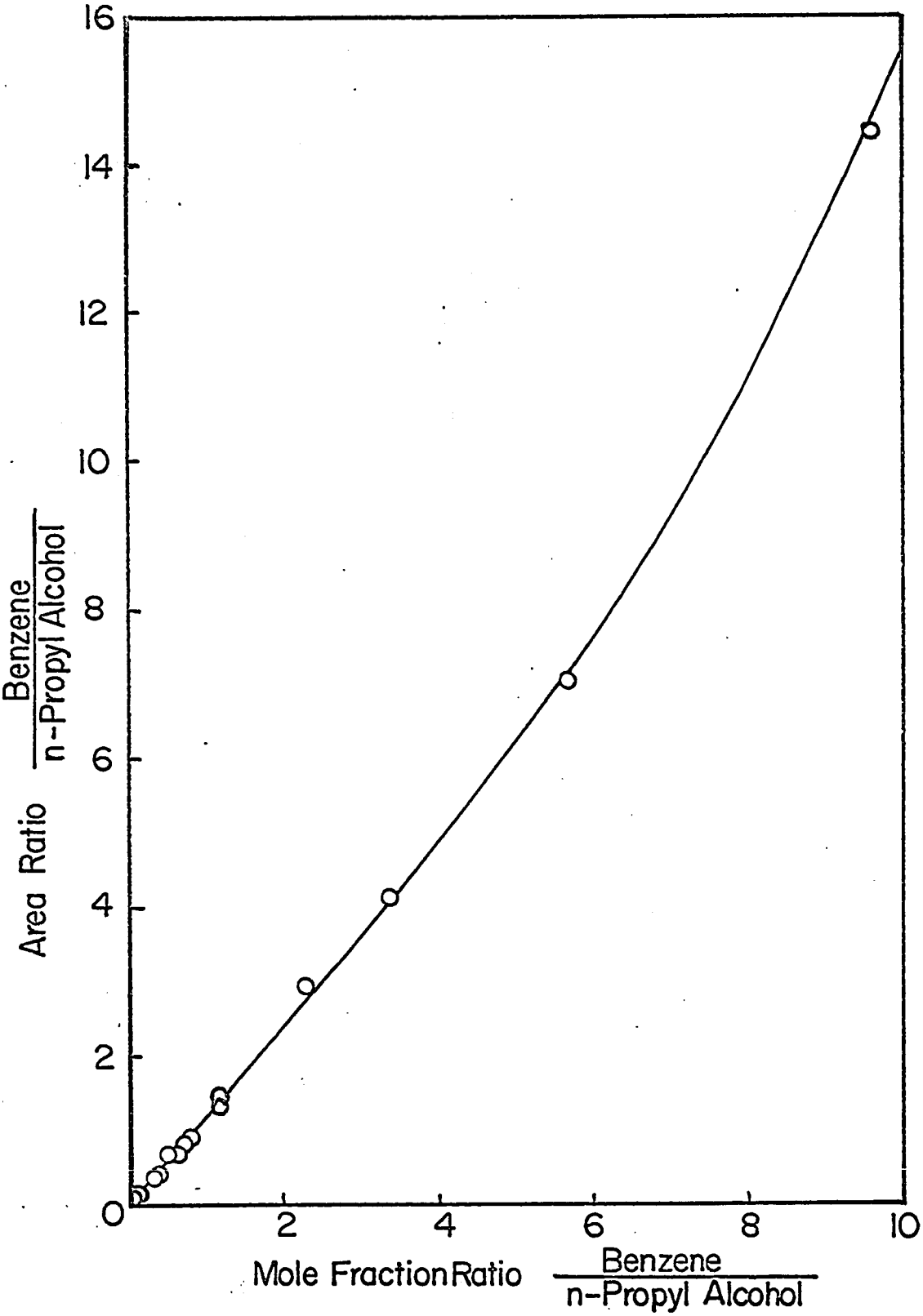


Figure 25. Calibration curve of (benzene/n-propyl alcohol) area vs. (benzene/n-propyl alcohol) mole fraction for the ternary system

TABLE 11

Operating Conditions For Gas Chromatographic Analysis

Chromatograph :	Perkin-Elmer Model 154-D
Column dimensions :	Two 4-meter x ¼-inch
Column packings :	Perkin-Elmer Type W column Calbotwax 1500 on Teffon
Carrier gas :	Helium
Flow rate :	72.9 cc/min.
Temperature :	104°C
Pressure :	27 p.s.i.g.
Sample size :	0.0045 ml. (Hamilton micro liter syringe)
Recorder :	Philips, Type PR2216A/21 Automatic Compensator

TABLE 12

Equations for Solving the Ternary Constants in the Redlich-Kister Equation

Run	$C_{123} + (x_1-x_2)\,D_3 + (x_2-x_3)\,D_1 + (x_3-x_1)\,D_2 = \frac{Q_{123}-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$
2	$C_{123} - 0.0794\,D_3 + 0.4479\,D_1 - 0.3685\,D_2 = 1.3056$
3	$C_{123} + 0.5342\,D_3 + 0.1264\,D_1 - 0.6606\,D_2 = 2.1869$
4	$C_{123} + 0.4031\,D_3 + 0.5871\,D_1 - 0.1840\,D_2 = 2.1894$
5	$C_{123} - 0.5648\,D_3 + 0.6495\,D_1 - 0.8470\,D_2 = 0.7695$
6	$C_{123} + 0.3404\,D_3 + 0.1933\,D_1 - 0.5337\,D_2 = 2.1186$
7	$C_{123} - 0.3900\,D_3 + 0.5495\,D_1 - 0.1595\,D_2 = 1.3549$
8	$C_{123} - 0.0045\,D_3 + 0.3407\,D_1 - 0.3362\,D_2 = 0.9375$
10	$C_{123} + 0.5361\,D_3 + 0.0440\,D_1 - 0.5801\,D_2 = 1.3215$
11	$C_{123} - 0.1611\,D_3 + 0.3836\,D_1 - 0.2225\,D_2 = 0.8555$
12	$C_{123} + 0.7574\,D_3 + 0.0770\,D_1 - 0.6804\,D_2 = 1.2566$
13	$C_{123} - 0.4838\,D_3 + 0.5214\,D_1 - 0.0376\,D_2 = 1.3171$
14	$C_{123} - 0.3856\,D_3 + 0.4603\,D_1 - 0.0747\,D_2 = 0.7101$
15	$C_{123} + 0.4785\,D_3 + 0.0227\,D_1 - 0.5012\,D_2 = 1.5683$
17	$C_{123} - 0.0163\,D_3 + 0.2572\,D_1 - 0.2409\,D_2 = 1.0296$
18	$C_{123} - 0.0669\,D_3 + 0.2807\,D_1 - 0.2138\,D_2 = 0.9778$
21	$C_{123} + 0.1623\,D_3 + 0.1517\,D_1 - 0.3140\,D_2 = 1.0375$
22	$C_{123} - 0.1962\,D_3 + 0.3116\,D_1 - 0.1154\,D_2 = 2.1253$
23	$C_{123} + 0.5342\,D_3 - 0.0776\,D_1 - 0.4566\,D_2 = 1.0277$

TABLE 12 (continued)

Run	$C_{123} + (x_1-x_2)\,D_3 + (x_2-x_3)\,D_1 + (x_3-x_1)\,D_2 = \frac{Q_{123}-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$
24	$C_{123} + 0.1549\,D_3 + 0.1080\,D_1 + 0.2629\,D_2 = 0.9455$
25	$C_{123} - 0.3251\,D_3 + 0.3438\,D_1 - 0.0187\,D_2 = 1.2732$
28	$C_{123} + 0.2880\,D_3 + 0.0248\,D_1 - 0.3128\,D_2 = 0.9646$
29	$C_{123} + 0.1589\,D_3 + 0.0739\,D_1 - 0.2328\,D_2 = 0.7818$
30	$C_{123} + 0.2660\,D_3 + 0.0265\,D_1 - 0.2925\,D_2 = 0.9667$
31	$C_{123} + 0.4293\,D_3 - 0.1042\,D_1 - 0.3251\,D_2 = 0.8411$
32	$C_{123} + 0.4242\,D_3 - 0.1054\,D_1 - 0.3188\,D_2 = 1.1957$
33	$C_{123} - 0.4690\,D_3 + 0.3409\,D_1 + 0.1281\,D_2 = 1.3900$
34	$C_{123} + 0.0066\,D_3 + 0.0833\,D_1 - 0.0899\,D_2 = 0.7921$
35	$C_{123} + 0.4740\,D_3 - 0.1663\,D_1 - 0.3077\,D_2 = 1.0245$
36	$C_{123} - 0.4875\,D_3 + 0.3119\,D_1 + 0.1756\,D_2 = 1.4073$
37	$C_{123} + 0.1303\,D_3 + 0.0000\,D_1 - 0.1303\,D_2 = 0.8413$
39	$C_{123} - 0.0847\,D_3 + 0.0943\,D_1 - 0.0096\,D_2 = 0.8157$
40	$C_{123} + 0.5431\,D_3 - 0.2349\,D_1 - 0.3082\,D_2 = 1.5046$
41	$C_{123} + 0.2666\,D_3 - 0.1256\,D_1 - 0.1410\,D_2 = 0.9120$
42	$C_{123} - 0.0469\,D_3 + 0.0235\,D_1 + 0.0234\,D_2 = 0.7547$
43	$C_{123} - 0.0135\,D_3 - 0.0037\,D_1 + 0.0172\,D_2 = 0.7839$
44	$C_{123} - 0.2220\,D_3 + 0.0992\,D_1 + 0.1228\,D_2 = 1.4106$

TABLE-12 (continued)

Run	$C_{123} + (x_1-x_2)\,D_3 + (x_2-x_3)\,D_1 + (x_3-x_1)\,D_2 = \frac{Q_{123}- Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$
45	$C_{123} + 0.3568\,D_3 - 0.2163\,D_1 - 0.1405\,D_2 = 1.0114$
46	$C_{123} - 0.3967\,D_3 + 0.1327\,D_1 + 0.2640\,D_2 = 1.1153$
47	$C_{123} - 0.1180\,D_3 - 0.0290\,D_1 + 0.1470\,D_2 = 0.7172$
48	$C_{123} - 0.3020\,D_3 + 0.0450\,D_1 + 0.2570\,D_2 = 0.9750$
49	$C_{123} + 0.1852\,D_3 - 0.2250\,D_1 + 0.0398\,D_2 = 0.6005$
50	$C_{123} + 0.1192\,D_3 - 0.1956\,D_1 + 0.0764\,D_2 = 0.8988$
51	$C_{123} + 0.2145\,D_3 - 0.2488\,D_1 + 0.3430\,D_2 = 0.8011$
52	$C_{123} + 0.0084\,D_3 - 0.1765\,D_1 + 0.1681\,D_2 = 0.9012$
53	$C_{123} - 0.3545\,D_3 + 0.00000D_1 + 0.3545\,D_2 = 1.3355$
54	$C_{123} + 0.3086\,D_3 - 0.3578\,D_1 + 0.0492\,D_2 = 1.2179$
55	$C_{123} + 0.1317\,D_3 - 0.2803\,D_1 + 0.1486\,D_2 = 0.3981$
57	$C_{123} + 0.0872\,D_3 - 0.2903\,D_1 + 0.2031\,D_2 = 0.6584$
58	$C_{123} - 0.0927\,D_3 - 0.2056\,D_1 + 0.2983\,D_2 = 1.0179$
60	$C_{123} - 0.1887\,D_3 - 0.2224\,D_1 + 0.4111\,D_2 = 0.6266$
61	$C_{123} + 0.2094\,D_3 - 0.4294\,D_1 + 0.2200\,D_2 = 0.8181$
62	$C_{123} - 0.0387\,D_3 - 0.3208\,D_1 + 0.3595\,D_2 = 0.7472$
63	$C_{123} - 0.0987\,D_3 - 0.3844\,D_1 + 0.4831\,D_2 = 0.8153$
65	$C_{123} + 0.0650\,D_3 - 0.5006\,D_1 + 0.4356\,D_2 = 0.7893$

TABLE 12 (continued)

Run	$C_{123} + (x_1-x_2)\,D_3 + (x_2-x_3)\,D_1 + (x_3-x_1)\,D_2 = \frac{Q_{123}-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$
66	$C_{123} + 0.1180\,D_3 - 0.5490\,D_1 + 0.4310\,D_2 = 1.0548$
67	$C_{123} - 0.0961\,D_3 - 0.4562\,D_1 + 0.5523\,D_2 = 0.9285$
68	$C_{123} - 0.0167\,D_3 - 0.5103\,D_1 + 0.5270\,D_2 = 0.8781$
70	$C_{123} + 0.1810\,D_3 - 0.6387\,D_1 + 0.4577\,D_2 = 1.5255$
71	$C_{123} - 0.0453\,D_3 - 0.1681\,D_1 + 0.2134\,D_2 = -1.4949$
72	$C_{123} + 0.0492\,D_3 - 0.6223\,D_1 + 0.5731\,D_2 = 1.4698$
73	$C_{123} + 0.1495\,D_3 - 0.6945\,D_1 + 0.5450\,D_2 = 2.5577$
77	$C_{123} - 0.0602\,D_3 - 0.7971\,D_1 + 0.8573\,D_2 = 5.3417$

TABLE 13

Comparison of Experimental and Calculated Q_{123}

Run	$\frac{Q_{123}(expt)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	$\frac{Q_{123}(calcd)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	Q_{123} (expt)	Q_{123} (calcd)
2	1.3056	0.8319	0.0861	0.0798
3	2.1869	0.9822	0.0858	0.0735
4	2.1894	0.7673	0.1011	0.0824
5	0.7695	0.7385	0.0839	0.0835
6	2.1186	0.9515	0.1130	0.0942
7	1.3549	0.7855	0.1051	0.0959
8	0.9375	0.8832	0.1113	0.1101
10	1.3215	1.0222	0.1060	0.1015
11	0.8555	0.8639	0.1221	0.1223
12	1.2566	1.0789	0.0844	0.0834
13	1.3171	0.8000	0.1294	0.1201
14	0.7101	0.8288	0.1258	0.1284
15	1.5683	1.0331	0.1305	0.1203

.... continued

TABLE 13 (continued)

Run	$\frac{Q_{123}(expt)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	$\frac{Q_{123}(calcd)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	Q_{123} (expt)	Q_{123} (calcd)
17	1.0296	0.9239	0.1454	0.1424
18	0.9778	0.9130	0.1447	0.1428
21	1.0375	0.9734	0.1468	0.1450
22	-2.1253	0.8992	0.0625	0.1515
23	1.0277	1.0813	0.1311	0.1320
24	0.9455	0.9947	0.1568	0.1583
25	1.2732	0.8848	0.1673	0.1567
28	0.9646	1.0339	0.1544	0.1564
29	0.7818	1.0113	0.1585	0.1660
30	0.9667	1.0333	0.1578	0.1598
31	0.8412	1.0952	0.1501	0.1561
32	1.1957	1.0958	0.1596	0.1572
33	1.3900	0.8875	0.1777	0.1671

.... continued

TABLE 13 (continued)

Run	$\frac{Q_{123}(expt)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	$\frac{Q_{123}(calcd)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	Q_{123} (expt)	Q_{123} (calcd)
34	0.7921	1.0082	0.1760	0.1838
35	1.0245	1.1250	0.1539	0.1559
36	1.4073	0.9018	0.1826	0.1728
37	0.8413	1.0474	0.1771	0.1843
39	0.8156	1.0036	0.1836	0.1904
40	1.5046	1.1576	0.1537	0.1488
41	0.9120	1.1072	0.1773	0.1834
42	0.7547	1.0377	0.1875	0.1979
43	0.7839	1.0506	0.1890	0.1988
44	1.4106	1.0026	0.2108	0.1974
45	1.0114	1.1504	0.1737	0.1773
46	1.1153	0.9880	0.1974	0.1946
47	0.7172	1.0639	0.1942	0.2063

.... continued

TABLE 13 (continued)

Run	$\frac{Q_{123}(\text{expt})-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	$\frac{Q_{123}(\text{calcd})-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	Q_{123} (expt)	Q_{123} (calcd)
48	0.9750	1.0297	0.2009	0.2024
49	0.6005	1.1562	0.1788	0.1964
50	0.8988	1.1426	0.1932	0.2014
51	0.8012	1.1675	0.1826	0.1937
52	0.9012	1.1343	0.1990	0.2070
53	1.3355	1.0521	0.2067	0.2011
54	1.2179	1.2196	0.1790	0.1791
55	0.3981	1.1836	0.1745	0.1985
57	0.6584	1.1889	0.1838	0.1999
58	1.0179	1.1494	0.2030	0.2069
60	0.6266	1.1585	0.1894	0.2019
61	0.8181	1.2553	0.1692	0.1788
62	0.7472	1.2049	0.1859	0.1982

.... continued

TABLE 13 (continued)

Run	$\frac{Q_{123}(expt)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	$\frac{Q_{123}(calcd)-Q_{12}-Q_{23}-Q_{31}}{x_1x_2x_3}$	Q_{123} (expt)	Q_{123}(calcd)
63	0.8153	1.2363	0.1781	0.1868
65	0.7892	1.2912	0.1605	0.1703
66	1.0548	1.3142	0.1548	0.1591
67	0.9285	1.2712	0.1678	0.1736
68	0.8781	1.2967	0.1592	0.1665
70	1.5255	1.3572	0.1354	0.1337
71	-1.4949	1.1308	0.1209	0.2083
72	1.4698	1.3505	0.1416	0.1401
73	2.5577	1.3846	0.1270	0.1178
77	5.3417	1.4365	0.0862	0.0779

TABLE 14

Second Virial Coefficients and Molar Volumes at 75°C

	B_{ii}(liter/mole)	V_i^l(liter/mole)
Benzene(1)	-0.993	0.0954
n-Heptane(2)	-1.565	0.1576
n-Propyl Alcohol(3)	-1.053	0.0794

TABLE 15

Characteristic Points on the $\log \gamma_1/\gamma_2$ vs. x_1 Plot

x_1	0.0000	0.1464	0.2113
$\log \gamma_1/\gamma_2$	$B_{12}-C_{12}+D_{12}$	$0.7071B_{12}-1/4C_{12}$	$0.5773\ (B_{12}-1/3C_{12})$

x_1	0.2959	0.5000
$\log \gamma_1/\gamma_2$	$0.4082\ (B_{12}-2/3D_{12}) + 1/4C_{12}$	$0.5C_{12}$

x_1	0.7041	0.7887
$\log \gamma_1/\gamma_2$	$-0.4082\ (B_{12}-2/3D_{12}) + 1/4C_{12}$	$-0.5773\ (B_{12}-1/3C_{12})$

x_1	0.8536	1.0000
$\log \gamma_1/\gamma_2$	$-0.7071B_{12}-1/4C_{12}$	$-B_{12}-C_{12}-D_{12}$

TABLE 16

Redlich-Kister Constants for the Binary Systems of Benzene-n-Heptane, n-Heptane-n-Propyl Alcohol and n-Propyl Alcohol-Benzene at 75°C.

System Benzene(1)-n-Heptane(2)

$B_{12} = 0.1386$

$C_{12} = 0.0240$

$D_{12} = -0.0016$

System n-Heptane(2)-n-Propyl Alcohol(3)

$B_{23} = 0.7467$

$C_{23} = 0.0120$

$D_{23} = 0.0893$

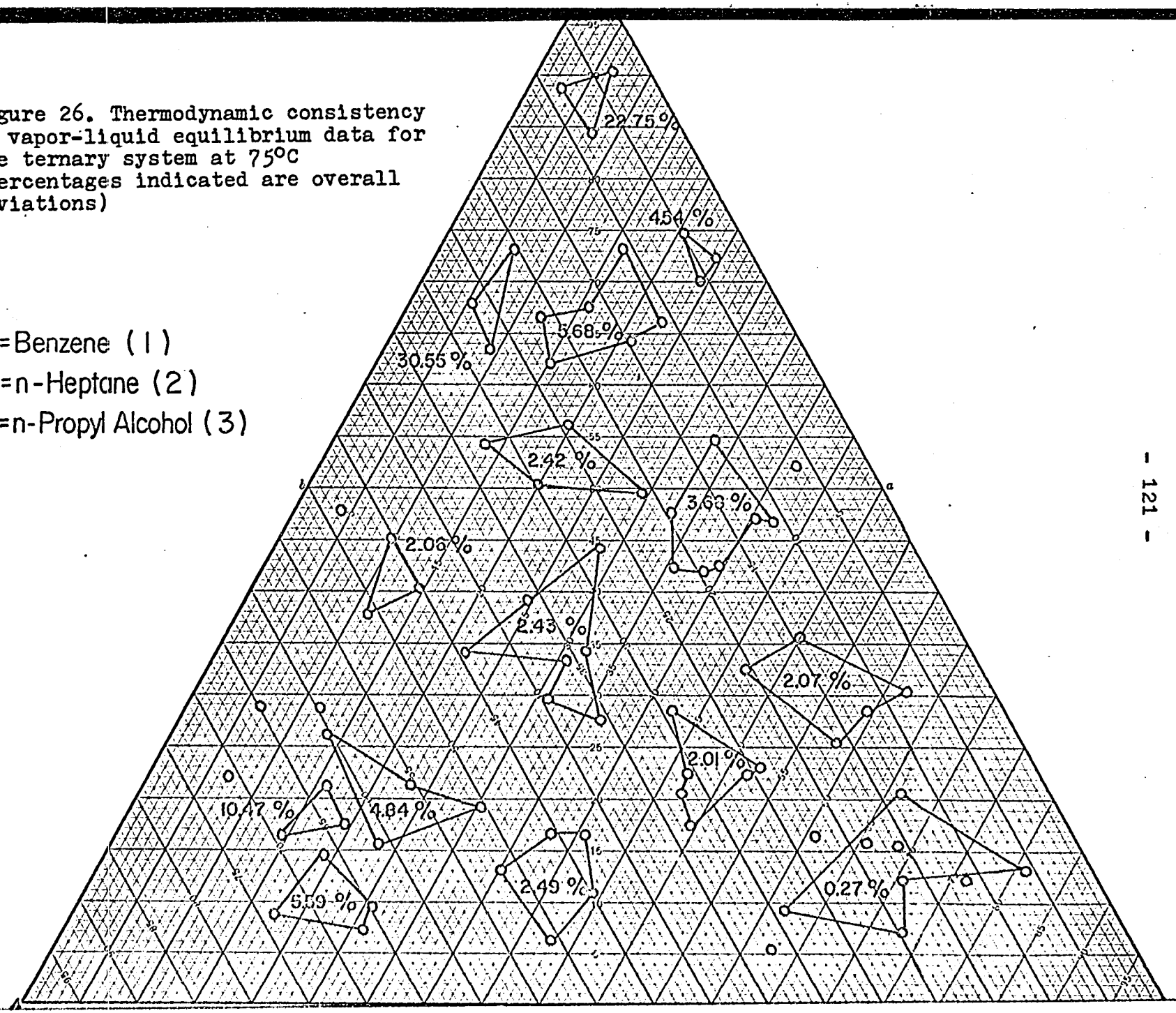
System n-Propyl Alcohol(3)-Benzene(1)

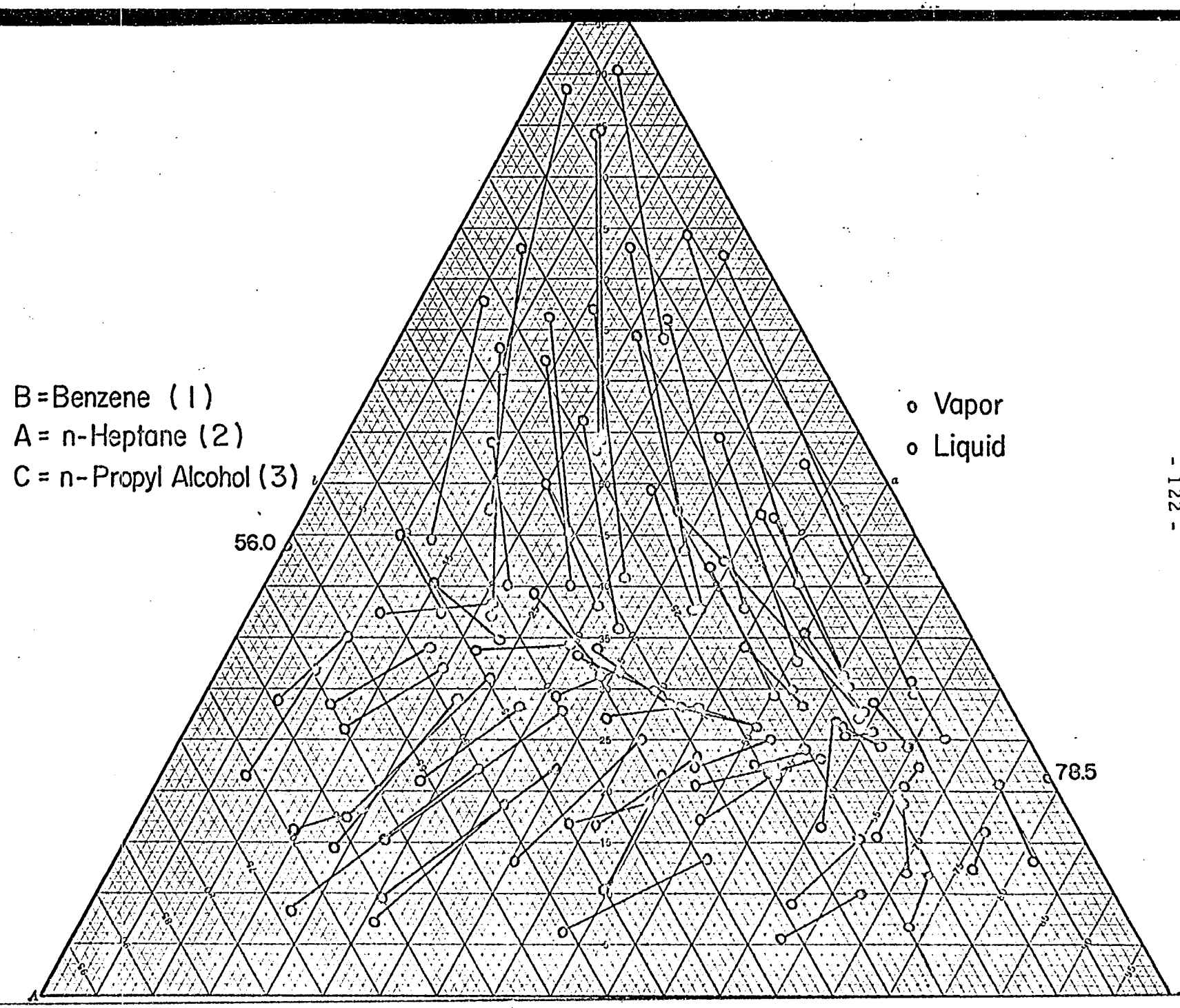
$B_{31} = 0.5415$

$C_{31} = -0.0856$

$D_{31} = 0.0020$

Figure 26. Thermodynamic consistency of vapor-liquid equilibrium data for the ternary system at 75°C (percentages indicated are overall deviations)




B = Benzene (1)
A = n-Heptane (2)
C = n-Propyl Alcohol (3)
o Vapor
o Liquid
56.0
78.5

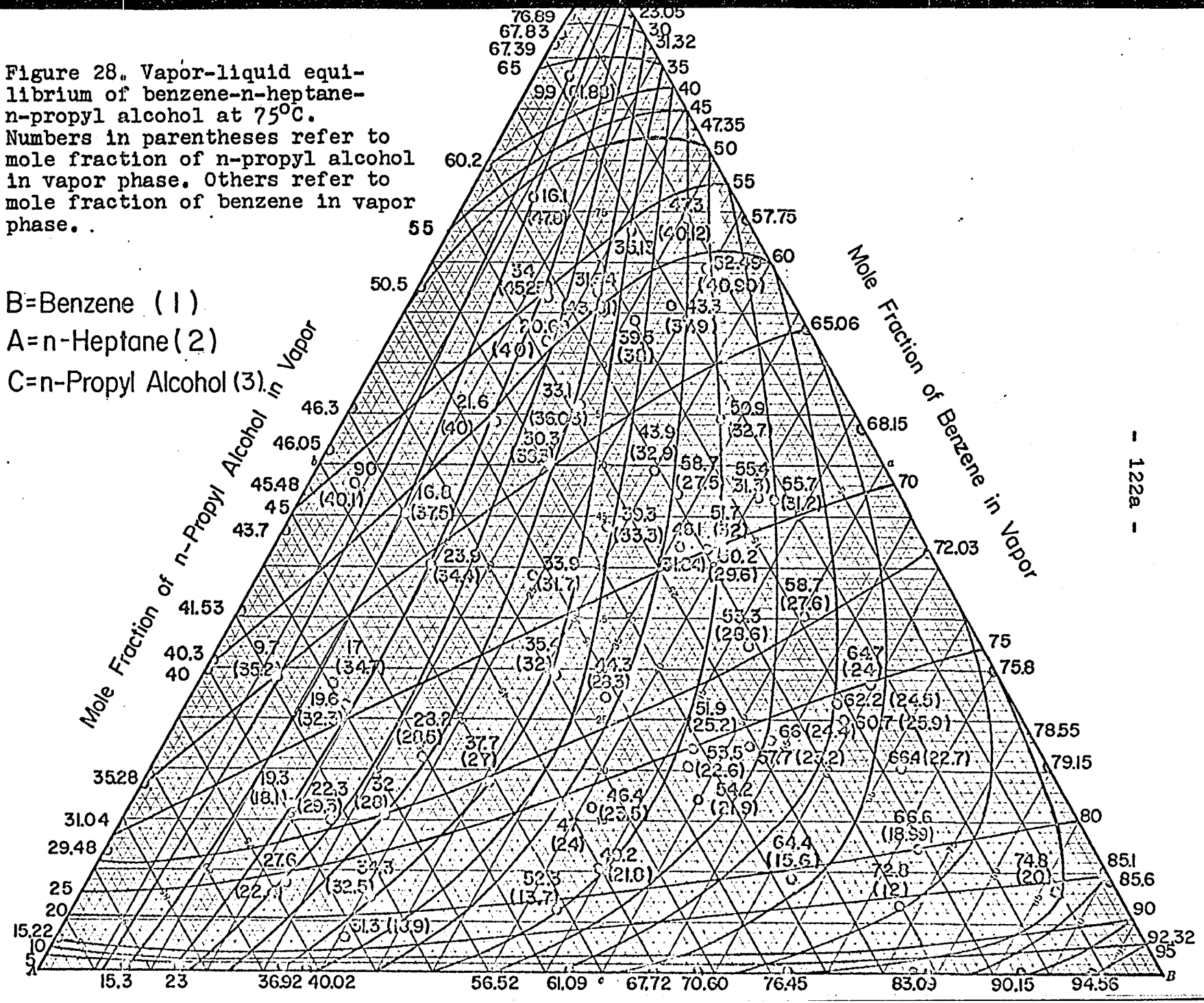


Figure 28. Vapor-liquid equilibrium of benzene-n-heptane-n-propyl alcohol at 75°C. Numbers in parentheses refer to mole fraction of n-propyl alcohol in vapor phase. Others refer to mole fraction of benzene in vapor phase. .

XII. APPENDIX II

SAMPLE CALCULATIONS

1. Calculation of mole fractions, mole fraction ratios and area ratios for calibration.

Using Table 10, run 1 as an example.

(a). Calculation of mole fractions:

From the experiment, a sample has the following composition by weighing:

benzene(1) = 1.9408 gms.

n-heptane(2) = 3.0571 gms.

n-propyl alcohol(3) = 1.7331 gms.

Therefore,

$x_1 = 0.2952$

$x_2 = 0.3624$

$x_3 = 0.3434$

(b). Calculation of the mole fraction ratios:

$$\frac{\text{Mole fraction of n-heptane}}{\text{Mole fraction of benzene}} = \frac{0.3624}{0.2952} = 1.2282$$

$$\frac{\text{Mole fraction of n-propyl alcohol}}{\text{Mole fraction of n-heptane}} = \frac{0.3434}{0.3624} = 0.9494$$

$$\frac{\text{Mole fraction of benzene}}{\text{Mole fraction of n-propyl alcohol}} = \frac{0.2952}{0.3434} = 0.8616$$

(c). Evaluation of the area ratios:

From the experimental results, the peak areas of benzene, n-heptane and n-propyl alcohol are as follows:

benzene(1) = 113.5

n-heptane(2) = 69

n-propyl alcohol(3) = 72

Therefore,

$$\frac{\text{Peak area of n-heptane}}{\text{Peak area of benzene}} = \frac{69}{113.5} = 1.6449$$

$$\frac{\text{Peak area of n-propyl alcohol}}{\text{Peak area of n-heptane}} = \frac{72}{69} = 0.6363$$

$$\frac{\text{Peak area of benzene}}{\text{Peak area of n-propyl alcohol}} = \frac{113.5}{72} = 0.9583$$

2. Calculation of mole fraction of unknown.

Using Table 5, run 62 of liquid sample as an example.

From experimental determinations, the area ratios were obtained as follows:

$$\frac{\text{Peak area of n-heptane(2)}}{\text{Peak area of benzene(1)}} = 1.6113$$

$$\frac{\text{Peak area of n-propyl alcohol(3)}}{\text{Peak area of n-heptane(2)}} = 1.5176$$

$$\frac{\text{Peak area of benzene(1)}}{\text{Peak area of n-propyl alcohol(3)}} = 0.4088$$

From Figures 23, 24 and 25,

$$\frac{x_2}{x_1} = 1.183$$

$$\frac{x_3}{x_2} = 2.340$$

$$\frac{x_1}{x_3} = 0.358$$

Since $x_1 + x_2 + x_3 = 1$

and $x_2/x_1 = 1.183, \quad x_1/x_3 = 0.358$

therefore $x_1 + 1.183\, x_1 + 1/0.358\, x_1 = 1$

$$x_1 = \frac{1}{3.9293} = 0.2006$$

and $x_2 = 1.183\ (0.2006) = 0.2393$

so that $x_3 = 0.5601$

3. Evaluation of Z values.

Using Table 5, run 43 as an example.

Since $Z_2 = \exp\left[(p_2-P)\ (V_2^1-B_{22})/RT\right]$

and $p_2 = 361.5$ mm. Hg.

therefore $Z_2 = \exp\left[(-292.3)\ (1.7226)/(760)\ (0.082)\ (348.18)\right]$

$= 0.9773.$

By a procedure similar to that above,

at $p_1 = 647.8$ mm. Hg.

$Z_1 = 0.9997$

and at $p_3 = 301.9$ mm. Hg.

$Z_3 = 0.9818$

4. Evaluation of liquid phase activity coefficients.

Using Table 5, run 29 as an example.

Since $$\gamma_1 = \frac{Z_1 \, P \, y_1}{p_1 \, x_1}$$

Therefore,

$$\gamma_1 = \frac{0.9986 \times 676.4 \times 0.5192}{647.8 \times 0.4693}$$

In the same manner,

at $p_2 = 361.5$ mm. Hg.

$\gamma_2 = 1.3666$

and at $p_3 = 301.9$ mm. Hg.

$\gamma_3 = 2.4643$

5. Determination of binary Redlich-Kister constants.

The determination of B_{12}, C_{12} and D_{12} may be shown here as an example.

From Figure 6, the following values of log (γ_1/γ_2) are obtained in corresponding with those characteristic points.

x_1	0.1464	0.2113	0.2959	0.5000
$\log \gamma_1/\gamma_2$	0.092	0.081	0.064	0.012

The method proposed by Redlich and Kister (41) is employed and from Table 15, the following relation is obtained.

(a). $0.5\ C_{12} = 0.012$

$C_{12} = 0.0240$

(b). $0.7071\ B_{12} - 0.25\ C_{12} = 0.092$

$0.7071\ B_{12} - (0.25)\ (0.0240) = 0.092$

$B_{12} = 0.1386$

(c). $0.4082\ (B_{12}-1/3D_{12}) + 1/4\ C_{12} = 0.063$

$0.4082\ (0.1386-1/3D_{12}) +(1/4)\ (0.0240) = 0.063$

$D_{12} = -0.0016$

6. Evaluation of the right hand values of the equations in Table 12.

Using run 42 as an example.

Since $C_{123} + (x_1-x_2)\ D_3 + (x_2- x_3)\ D_1 + (x_3-x_1)\ D_2 = \dfrac{Q_{123} - Q_{12} - Q_{23} - Q_{31}}{x_1\ x_2\ x_3}$

where $Q_{123} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3$

$= (0.3099)(0.1046) + (0.3568)(0.1732) + (0.3333)(0.2799)$

$= 0.1875$

$$Q_{12} = x_1 x_2 \left[B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 \right]$$

$$= (0.3099)(0.3568) \left[(0.1386 + (0.0240) \right.$$

$$\left. (0.3099 - 0.3568) + (-0.0016)(0.3099 - 0.3568)^2 \right]$$

$$= 0.01520$$

$$Q_{23} = x_2 x_3 \left[B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2 \right]$$

$$= (0.3568)(0.3333) \left[0.7467 + (-0.0120) \right.$$

$$\left. (0.3568 - 0.3333) + (0.0893)(0.3568 - 0.3333)^2 \right]$$

$$= 0.0888$$

$$Q_{31} = x_3 x_1 \left[B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2 \right]$$

$$= (0.3333)(0.3099) \left[0.5415 + (-0.0856) \right.$$

$$\left. (0.3333 - 0.3099) + (0.0020)(0.3333 - 0.3099)^2 \right]$$

$$= 0.0557$$

Finally

$$\frac{Q_{123} - Q_{12} - Q_{23} - Q_{31}}{x_1 \, x_2 \, x_3}$$

$$= \frac{0.1875 - 0.0152 - 0.0888 - 0.0577}{(0.3099)\,(0.3568)\,(0.3333)}$$

$$= 0.8156$$

7. Consistency Test

(a). McDermott and Ellis' Method

Using Table 5, runs 66 and 72 as example.

$$(x_1)_{66} + (x_1)_{72} = 0.2290 + 0.1587 = 0.3877$$

$$(x_2)_{66} + (x_2)_{72} = 0.1110 + 0.1095 = 0.2205$$

$$(x_3)_{66} + (x_3)_{72} = 0.6600 + 0.7318 = 1.3918$$

$$(\log \gamma_1)_{72} - (\log \gamma_1)_{66} = 0.2991 - 0.2595 = 0.0396$$

$$(\log \gamma_2)_{72} - (\log \gamma_2)_{66} = 0.4839 - 0.4540 = 0.0299$$

$$(\log \gamma_3)_{72} - (\log \gamma_3)_{66} = 0.0562 - 0.0681 = -0.0119$$

Thus

$$\left[(x_1)_{66} + (x_1)_{72}\right]\left[(\log \gamma_1)_{72} - (\log \gamma_1)_{66}\right] = 0.0154$$

$$\left[(x_2)_{66} + (x_2)_{72}\right]\left[(\log \gamma_2)_{72} - (\log \gamma_2)_{66}\right] = 0.0066$$

$$\left[(x_3)_{66} + (x_3)_{72}\right]\left[(\log \gamma_3)_{72} - (\log \gamma_3)_{66}\right] = -0.0166$$

and so Deviation = 0.0154 + 0.0066 + (-0.0166)

= -0.0054

(b). Li and Lu's Method

Using Table 5, runs 37, 29, 24, 21, 28 and 30 as an example.

The following table is obtained from experimental data.

Consistency Test Table (Li and Lu's method)

Run	x_1	$\log \gamma_1$	$x_1(\log \gamma_{1p} - \log \gamma_{1f})$	x_2	$\log \gamma_2$	$x_2(\log \gamma_{2p} - \log \gamma_{2f})$	x_3	$\log \gamma_3$	$x(\log \gamma_{3p} - \log \gamma_{3f})$
37	0.4202	0.0942	-0.00269	0.2899	0.1707	0.00884	0.2899	0.3035	-0.00270
29	0.4693	0.0619	0.01014	0.3050	0.1356	0.01034	0.2257	0.3918	-0.01657
24	0.4726	0.0726	0.00076	0.3177	0.1368	0.00470	0.2098	0.3769	-0.00885
21	0.4921	0.0603	0.00561	0.3298	0.1208	-0.00755	0.1781	0.4340	0.00055
28	0.5336	0.0612	0.00256	0.2456	0.1597	-0.01113	0.2208	0.3738	0.01137
30	0.5195	0.0555	-0.01714	0.2535	0.1661	-0.00279	0.2270	0.3825	0.01596

$$\sum + = 0.07083$$

$$\sum - = 0.06942$$

$$\% \text{ Deviation} = \frac{0.07083 - 0.06942}{\frac{0.07083 + 0.06942}{2}} \times 100$$

$$= 2.01\%$$